

# A Fiber-Optic Fluorescence Sensor for Lithium Ion in Acetonitrile

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**A novel fiber-optic fluorescence sensor based on a controlled-release reagent for the determination of lithium ion in organic solvents is proposed. The fluorogenic indicator 2-(2-hydroxyphenyl)benzoxazole is contained in a mini-polyethylene tube as the reagent reservoir and is brought into contact with the analyte solution by diffusion across a poly(vinyl chloride) (PVC) membrane to form a strongly fluorescent complex at the membrane/solution interface. The fluorescence signals produced are measured via two joined optical fibers positioned closely to the backside of the PVC membrane for light illumination and collection. The sensor is useful for measuring  $\text{Li}^+$  at concentrations in acetonitrile ranging from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-2}$  M with a detection limit of  $3.0 \times 10^{-7}$  M. The steady-state response can be reached within seconds, and the signal changes are fully reversible. The sensor shows minimal interference effects from other alkali metal and alkaline earth metal cations and has good stability and durability when stored in acetonitrile solutions.**

Processes taking place in nonaqueous, mixed, and partially aqueous media are far more complex than those occurring in water. Studies of processes in these media using ion sensors have opened up new possibilities for further developments in this field. Valuable data on the analytical, thermodynamic, and kinetic properties obtained by ion sensors make possible a thorough examination of acid–base and complex equilibria, and of the mechanisms and kinetics of different chemical reactions, as well as investigations of ion transport processes in solvent mixtures.<sup>1,2</sup> The obvious requirement for sensing in nonaqueous solvents is that the sensor material should have negligible solubility in the analyte solution and should not react with it. Due to this limitation, only a few types of potentiometric sensors have been used in nonaqueous solvents, such as traditional solid-state membrane electrodes with glass<sup>3,4</sup> or crystalline-sensing<sup>5</sup> elements and nonplasticized polymer electrodes coupled with neutral carriers<sup>6–8</sup> or metal phthalocyanine complexes.<sup>9,10</sup> However, these ion-selective electrodes often suffer from problems of low sensitivity,

long response times, unreliable reference electrodes, and difficult calibration.

In recent years, much interest has arisen for optical transduction in the design of chemical sensors, since optical sensors coupled with fiber optics can offer advantages relative to electrochemical ones in that they are free from electrical interference, do not require a reference electrode, and are in some cases more stable with respect to calibration.<sup>11–13</sup> Many fiber-optic ion sensors have been reported, although most have been employed for aqueous analyses. These sensors typically involve a reversible reagent chemistry physically confined or chemically bound at or near the fiber end face, which interacts with analyte to produce an optically detectable signal. Problems associated with such reagent-based fiber-optic ion sensors include photodegradation of the indicator ligand, leaching of the ligand from the immobilization substrate or the confinement membrane, and most importantly, irreversible complex formation between the target ion and the ligand.<sup>11–13</sup> To solve these problems, continuously sensing reservoir sensors have been developed, in which the indicator is contained in a reservoir situated close to the fiber tip, which is brought into contact with the analyte solution in a volume viewed by the fiber in a controlled manner. Polymeric delivery systems have been described for controlled release of reagent, where the ligand is incorporated into a polymer matrix and is released slowly upon contact with aqueous solution.<sup>14,15</sup> However, a limitation of this type of sensor is a long response time. Controlled reagent delivery can also be accomplished through the use of capillary tubing<sup>16</sup> or an ultrafiltration membrane<sup>17</sup> using a high-precision pressure system. But such a sensor assembly is relatively complex.

The purpose of this work is to develop a new type of fiber-optic ion sensor for use in nonaqueous solutions. Since solutions of alkali metal ion salts in aprotic solvents are of great interest

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due to their utility as electrolyte systems in high energy density battery systems, lithium ion was chosen as the target ion for the present study. Lithium ion and acetonitrile are components of polymer electrolytes, and nonaqueous electrolytes are used for rechargeable lithium cells.<sup>18,19</sup> It has also been shown that insertion of lithium ion into  $V_2O_5$  thin film is influenced by acetonitrile solvent.<sup>20</sup> In this paper, a prototype fiber-optic sensor with controlled-release reagent for the determination of lithium ion in acetonitrile is reported. The sensor is based on the diffusion of the lipophilic fluorophore 2-(2-hydroxyphenyl)benzoxazole (HPBO) through a poly(vinyl chloride) (PVC) membrane into the analyte solution. Complex formation between HPBO and lithium ion occurs at the membrane/solution interface, and the fluorescence signal is measured via two optical fibers. The system is simple and has the advantage of a fast response time and simple instrument compared to other controlled-release techniques mentioned above. The system also offers several advantages over ion-selective electrodes for nonaqueous ion sensing. First, the fiber-optic sensor is not subject to the use of a reference electrode, as required in all ion-selective electrodes. This effectively eliminates problems from liquid junction potentials, which increase uncertainties in equilibrium constants and other thermodynamic data derived from potentiometry and make calibration difficult. Second, with fluorescence detection, the present sensor shows higher sensitivity, with a detection limit of  $3 \times 10^{-7}$  M.<sup>7,8</sup> Third, in the fiber-optic sensor, the fluorophore reagent diffuses from the inner solution into direct contact with the analyte solution, thus dramatically accelerating the response. Ion-selective electrodes, especially those based on nonplasticized polymer membranes,<sup>6-8</sup> need a relatively long response time for detection in nonaqueous solutions, which is due to the slow interfacial ion-exchange kinetics and diffusion-controlled equilibration of the membrane side of the phase boundary with the bulk membrane.<sup>21</sup> To the best of our knowledge, this paper reports the first fiber-optic ion sensor for use in nonaqueous media.

## EXPERIMENTAL SECTION

**Reagents.** Lithium, sodium, and potassium perchlorates, calcium perchlorate tetrahydrate, magnesium perchlorate hexahydrate, and HPBO were purchased from Aldrich Chemicals (Milwaukee, WI). Acetonitrile, tetrahydrofuran (THF), and triethylamine were obtained from Fisher (Fair Lawn, NJ). PVC was from Fluka AG (CH-9471; Buchs, Switzerland). Acetonitrile was of HPLC grade; other chemicals were of analytical reagent grade or Selectophore. All the reagents were used without further purification except for salt drying.

**Fiber-Optic Sensor Fabrication.** The PVC membrane was prepared by means of the spin-on technique.<sup>22</sup> A 0.2-mL aliquot of PVC solution in THF (0.05 g/mL) was dipped onto a rotating glass plate at a rate of  $\sim 300$  rpm, and then evaporated under THF

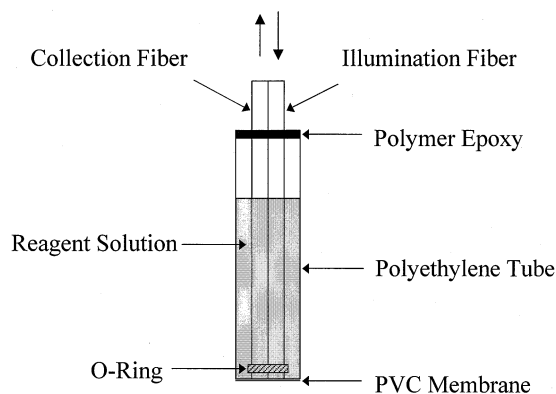


Figure 1. Schematic diagram of the fiber-optic fluorescence sensor.

atmosphere for 1 h. The transparent membrane formed had a thickness of  $\sim 20$   $\mu$ m, measured by scanning electron microscopy. In Figure 1, a schematic view of the fiber-optic sensor is shown, which is composed of two plastic optical fibers (o.d. 1 mm) and a 2-cm-long Parker Parflex polyethylene tubing ( $1/8$ -in. i.d.,  $1/4$ -in. o.d.) obtained from Technical Controls Inc. (Washington, NY). The two fibers were joined together with a rubber O-ring. A disk of 6-mm diameter was punched from the membrane and glued with THF/PVC slurry to the polyethylene tubing, which was used as a reagent reservoir holding 200  $\mu$ L of 0.1 M HPBO solution in acetonitrile. The joined fibers were inserted into the polyethylene tubing, and the ends of the fibers were placed close to the PVC membrane at a distance of 1 mm for efficient fluorescence measurement. The open end of the polyethylene tube was sealed using polymer epoxy (Devcon, Wood Dale, IL). The detected fluorescence might come from complexes that can be excited in the diffusion zone with an approximate penetration depth of 1 mm. The sensor was conditioned in 0.1 M HPBO acetonitrile solution overnight. Before measurement, the sensor was repeatedly flushed and soaked in a fresh pure acetonitrile sample for 30 min. When not in use, the sensor was stored in the conditioning solution of 0.1 M HPBO.

**Instrument.** A laboratory-built fluorometer consisting of a 150-W xenon lamp (Oriel, Stratford, CT) light source with a 0.22-m single-beam excitation monochromator (SPEX model 1681, Edison, NJ), and a 0.22 m dual-beam fluorescence monochromator (SPEX model 1680, Edison, NJ), with a photon-counting photomultiplier tube (PMT; Hamamatsu model P928P, Bridgewater, NJ), was used for all measurements. The output of the PMT was read by a photon counter (EG & G Princeton Applied Research model 1112, Princeton, NJ). The analog output of the photon counter was read by a PC using a 16-bit analog-to-digital converter (DGH model D2141) that was connected directly to the PC via an RS232 connector. The optical system consists of lenses and mirrors that focus the excitation light onto the fiber, retrieve the emission light from the fiber, and focus it onto the entrance slit of the detection system. All luminescence measurements except for reversibility tests were performed by immersing the sensor in a 10-mL beaker covered by a light-tight housing to avoid influence from surrounding lights. Sensor reversibility was checked by pumping blank and sample solutions in to and out of a flow cell (200  $\mu$ L) at a flow rate of 5 mL/min with a peristaltic pump (Pharmacia Fine Chemicals, model P-3, Sweden).

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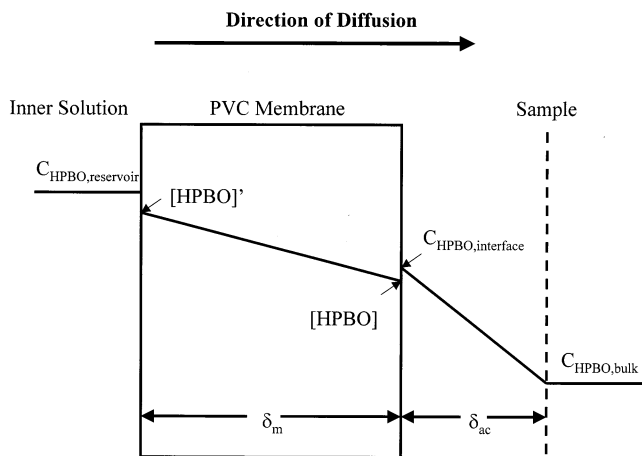


Figure 2. Schematic concentration profiles of HPBO diffusion across the PVC membrane.

**Safety Considerations.** Care has to be taken when handling HPBO and triethylamine, as they are irritants and are toxic.

## RESULTS AND DISCUSSION

**Principle of Reagent Release.** The fluorophore HPBO permeation involves the solution of HPBO at the upstream face of the PVC membrane, followed by diffusion through the membrane, and desorption from the downstream face (Figure 2).<sup>23</sup> At the solvent solution/membrane boundaries, HPBO extraction between acetonitrile phases and the membrane is quantified by the extraction constant  $K_{\text{ex}}$ :

$$K_{\text{ex}} = \frac{[\text{HPBO}]}{C_{\text{HPBO, interface}}} = \frac{[\text{HPBO}']}{C_{\text{HPBO, reservoir}}} \quad (1)$$

where  $[\text{HPBO}]$  and  $[\text{HPBO}]'$  denote the HPBO concentration in the membrane phase at the sample side and at the inner side, respectively;  $C_{\text{HPBO, interface}}$  and  $C_{\text{HPBO, reservoir}}$  represent the concentration of HPBO in the phase boundary layer on the sample side of the sample/membrane interface and in the inner reagent reservoir.

As shown in Figure 2, the concentration gradient of extracted HPBO leads to a net flux of HPBO across the membrane into the sample. Upon reaching the sample/membrane interface, HPBO is continuously released into the sample, where it diffuses away into the sample bulk along a second concentration gradient. Both the transport processes are based on Fick's law. Since the diffusion in a planar membrane configuration may be formulated as one-dimensional, the concentration profiles in each of the two segments can be assumed to be linear. The analogous treatment has been described dealing with similar diffusion phenomena by Meyerhoff<sup>24</sup> and Bakker.<sup>25</sup> Hence, the HPBO fluxes within the membrane and acetonitrile diffusion layer can be expressed as

$$J_{\text{m}} = D_{\text{m}} \frac{[\text{HPBO}]' - [\text{HPBO}]}{\delta_{\text{m}}} \quad (2)$$

and

$$J_{\text{ac}} = D_{\text{ac}} \frac{C_{\text{HPBO, interface}} - C_{\text{HPBO, bulk}}}{\delta_{\text{ac}}} \quad (3)$$

where  $J_{\text{m}}$  and  $J_{\text{ac}}$  denote the flux within the membrane and acetonitrile diffusion layer;  $\delta_{\text{m}}$  and  $\delta_{\text{ac}}$  are the respective diffusion layer thicknesses, that is, the thickness of the PVC membrane and of the sample diffusion layer;  $D_{\text{m}}$  and  $D_{\text{ac}}$  are the diffusion coefficients of HPBO within the respective phase; and  $C_{\text{HPBO, bulk}}$  represents the concentration of HPBO in the bulk of the sample. At steady state, these two HPBO fluxes are equal, so the combination of eqs 2 and 3 gives

$$J_{\text{m}} = J_{\text{ac}} = D_{\text{m}} \frac{[\text{HPBO}]' - [\text{HPBO}]}{\delta_{\text{m}}} = D_{\text{ac}} \frac{C_{\text{HPBO, interface}} - C_{\text{HPBO, bulk}}}{\delta_{\text{ac}}} \quad (4)$$

Since the sample solution is prepared with pure acetonitrile, the concentration of HPBO in the sample bulk ( $C_{\text{HPBO, bulk}}$ ) equals zero. Therefore, eq 4 can be further simplified. Substitution with eq 1 into eq 4 yields

$$D_{\text{m}} K_{\text{ex}} \frac{C_{\text{HPBO, reservoir}} - C_{\text{HPBO, interface}}}{\delta_{\text{m}}} = D_{\text{ac}} \frac{C_{\text{HPBO, interface}}}{\delta_{\text{ac}}} \quad (5)$$

and after rearranging

$$C_{\text{HPBO, interface}} = \frac{C_{\text{HPBO, reservoir}}}{\frac{D_{\text{ac}} \delta_{\text{m}}}{D_{\text{m}} \delta_{\text{ac}} K_{\text{ex}}} + 1} \quad (6)$$

Equation 6 predicts that the concentration of HPBO formed at the membrane/sample interface, and therefore the fluorescence signal, will be mainly influenced by the concentration of HPBO in the reagent reservoir, the extraction constant of HPBO between acetonitrile phase and membrane phase, the ratios of the two diffusion coefficients, and the thicknesses of the two stagnant layers.

**Fluorescence Response of the Sensor as a Function of Experimental Conditions.** The fluorescence spectra of HPBO and the complex formed with lithium in acetonitrile have been studied in detail. It is found that HPBO alone has a very weak fluorescence ( $\lambda_{\text{ex}}/\lambda_{\text{em}}$  382 nm/430 nm), while the complexation between lithium ion and HPBO results in a strongly fluorescent complex, which is consistent with the lowest excited singlet state changing from  $n-\pi^*$  to  $\pi-\pi^*$  and the increase in the rigidity of the molecule. The UV-visible and fluorescence data suggest a 2:1 stoichiometry for HPBO to lithium ion, and the association constant for HPBO to lithium ion was calculated to be  $(3.6 \pm 0.5)$

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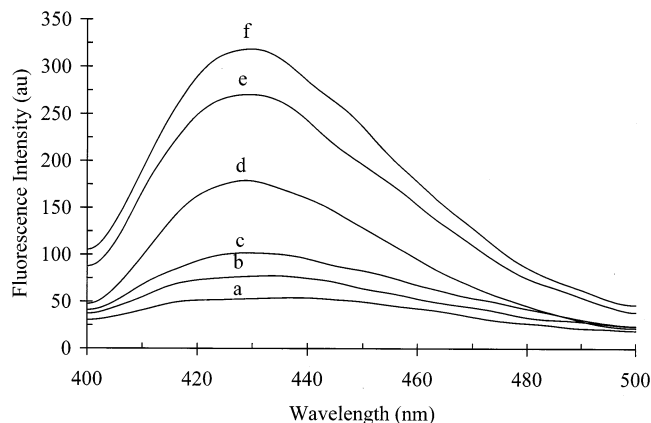


Figure 3. Emission spectra of the optical sensor with excitation at 370 nm in various concentrations of lithium ion: (a) 0 (the blank), (b)  $1.0 \times 10^{-6}$ , (c)  $1.0 \times 10^{-5}$ , (d)  $1.0 \times 10^{-4}$ , (e)  $1.0 \times 10^{-3}$ , and (f)  $1.0 \times 10^{-2}$  M; fluorophore, 0.1 M HPBO in the inner reservoir; reaction medium,  $3.0 \times 10^{-3}$  M triethylamine in the sample.

$\times 10^5 \text{ M}^{-2}$  in acetonitrile.<sup>26</sup> As a negatively charged ion, the complexed lithium is much less lipophilic than HPBO and hence the effect of its extraction into PVC membrane could be neglected. The peak of the excitation spectra appears at 392 nm with a shoulder around 370 nm. To avoid interference of scattered light from the PVC membrane, a wavelength of 370 nm was used for excitation. The fluorescence spectra obtained with the sensor are shown in Figure 3. As illustrated, the most effective wavelength range for lithium sensing is 420–440 nm. The emission spectrum reported here exhibits a maximum at 428 nm, which was used for all the measurements.

Experiments were conducted to determine the fluorescence response of the sensor to various experimental parameters. These variables either affect the reagent diffusion process including HPBO concentration in the inner reservoir and stirring in the sample solution or affect the fluorescence coordination reaction at the membrane/solution interface including triethylamine and water concentrations in the sample solution.

To examine the influence of HPBO concentration in the inner reservoir on the fluorescence intensity, various HPBO concentrations ranging from 0.001 to 0.1 M were tested. According to eq 6, the concentration of HPBO formed at the membrane/solution surface is proportional to the concentration of HPBO in the inner reservoir. Naturally, it can be predicted that increasing the HPBO concentration in the reservoir will give increasing fluorescence intensity. This situation is illustrated in Figure 4. At concentrations above 0.1 M, the HPBO solution showed a tendency to be unstable and precipitate, so 0.1 M HPBO was selected for subsequent work.

According to fundamental hydrodynamics, sample stirring can decrease the stagnant acetonitrile diffusion layer ( $\delta_{ac}$ ) and enhance HPBO mass transport from the membrane surface into the sample bulk. From eq 6, it can be suggested that sample stirring would reduce the concentration of HPBO at the membrane–sample surface, thus decreasing the fluorescence intensity. As expected, Figure 5 shows that the effect of sample stirring is very significant for the present sensor, and a sudden start of sample stirring (via a magnetic stirring bar) caused the fluorescence signal to decrease. In addition, as shown in Figure 5, large intensity

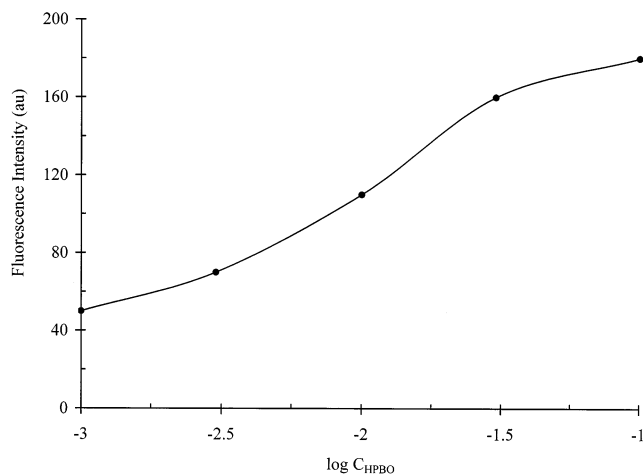


Figure 4. Effect of HPBO concentration in the reservoir on relative fluorescence intensity of  $1.0 \times 10^{-4}$  M  $\text{Li}^+$  standard.

fluctuations in the fluorescence signal were caused by sample stirring. For better sensitivity and reproducibility, all the measurements were performed without sample stirring.

Since lithium complex formation involves HPBO deprotonation of the phenolic oxygen, triethylamine was introduced into the sample solution as a base. Figure 6 illustrates the effect of triethylamine concentration on fluorescence intensity. It was found that the fluorescence intensity increased with increasing triethylamine concentration up to  $3.0 \times 10^{-3}$  M and thereafter remained almost constant. Hence,  $3.0 \times 10^{-3}$  M triethylamine was used as the reaction medium.

The fluorescence behavior in the presence of water is of interest regarding the practical sensing of ions. The effect of water on the fluorescence intensity in the presence of lithium ion was investigated in a mixture of acetonitrile and water. As shown in Figure 7, the fluorescence intensity is dramatically affected by the presence of a small amount of water in the organic solvent; 0.2 M water would decrease the fluorescence intensity to almost the same level as that of background. Such a large water effect suggests that there is a competition between the uptake of lithium ions by HPBO and the release of lithium from HPBO caused by hydration of these ions. The hydrated lithium ion cannot form a complex with HPBO to any significant extent. Similar phenomena have also been reported for many other chromogenic ionophores, which change optical properties upon binding alkali metal ions. These ionophores are designed for use only in mixed-solvent systems, not in water since water solvates the metal ion, reducing the formation constants for these alkali metal ion–ionophore complexes.<sup>27</sup> This may be one reason few optical sensors for alkali metal ions based on chromogenic ionophores have been developed.<sup>28–30</sup> The reagent release principle presented in this paper is generally applicable to other ion chromogenic ionophores for developing optical sensors specifically responding to metal ions in organic solvents.

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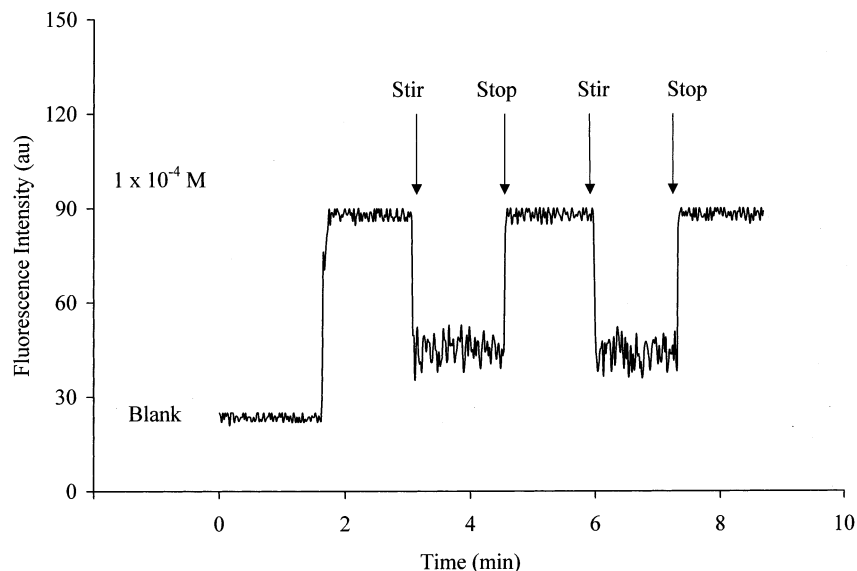


Figure 5. Effect of sample stirring on relative fluorescence intensity in the presence of  $1.0 \times 10^{-4}$  M  $\text{Li}^+$  standard.

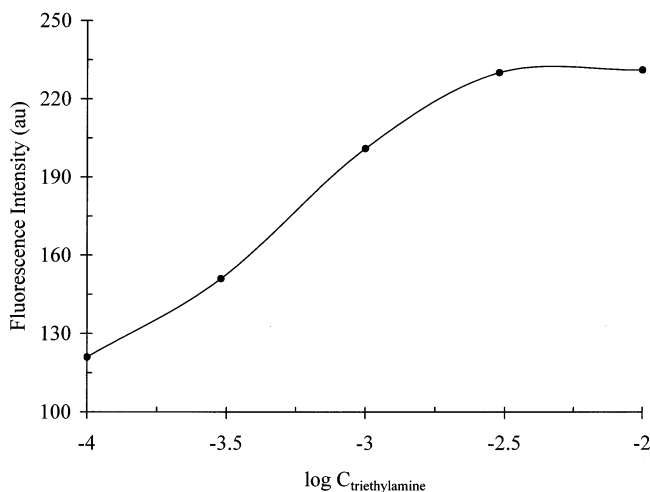


Figure 6. Effect of triethylamine concentration on relative fluorescence intensity of  $1.0 \times 10^{-4}$  M  $\text{Li}^+$  standard.

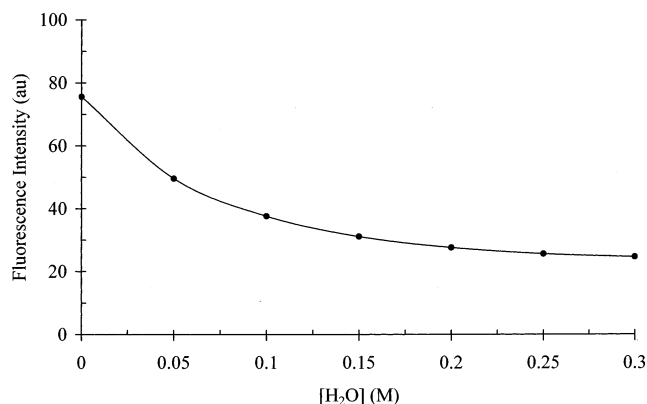


Figure 7. Effect of water concentration on relative fluorescence intensity of  $1.0 \times 10^{-4}$  M  $\text{Li}^+$  standard.

**Characteristics of the Fiber-Optic Sensor.** A typical response curve of the fiber-optic sensor showing changes in fluorescence intensity with successive addition of lithium is shown in Figure 8. In contrast to other fiber-optical sensors, which are usually subject to kinetic mass transfer through the immobilized

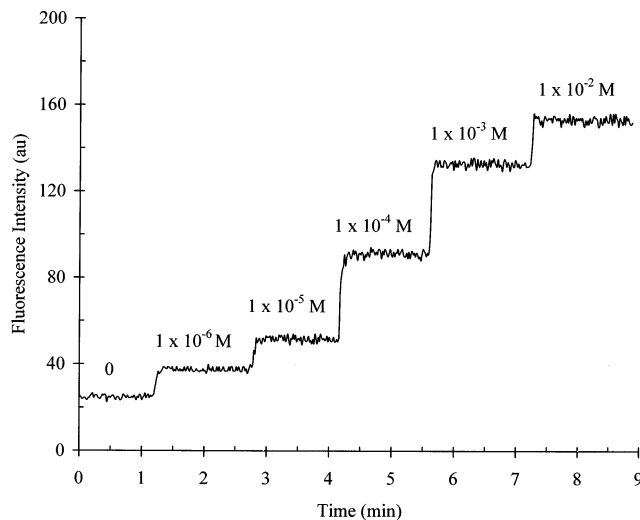


Figure 8. Time history of sensor response to successive additions of lithium ion.

reagent layers or confinement membranes, the response time of the present sensor is very fast (several seconds), which is due to fact that the indicator reagent after diffusion from the inner reservoir is in direct contact with the analyte solution. Reversibility of the sensor was evaluated by using a flow-through system. The results are shown in Figure 9. Fresh indicator reagent is continuously delivered to the reaction zone, and reaction product is readily carried away by the reagent flow so that signal changes are fully reversible.

Typical calibration curves for  $\text{Li}^+$  and for other alkali-metal and alkaline earth metal cations including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  under the selected conditions described above are shown in Figure 10. As indicated in the figure, the present system is useful for measuring  $\text{Li}^+$  at concentrations ranging from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-2}$  M. The detection limit is  $3.0 \times 10^{-7}$  M, which gives a signal equal to the blank signal plus three times the standard deviation of the blank measurement. The sigmoidal relationship shown in Figure 10 might be attributed to the formation of the

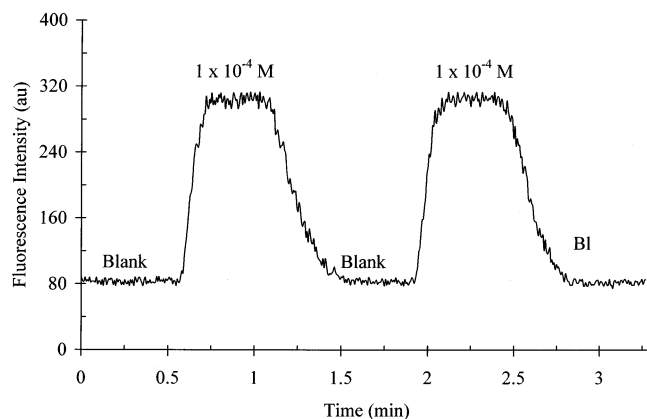


Figure 9. Recycle response profiles for the blank and  $1.0 \times 10^{-4}$  M lithium ion solutions.

2:1 complex of HPBO with lithium ion.<sup>31</sup> No response was observed up to  $10^{-3}$  M for  $\text{Na}^+$  or  $\text{K}^+$  and up to  $10^{-4}$  M for  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ . Thus, using the selected conditions, the sensor is very sensitive and has satisfactory selectivity for  $\text{Li}^+$ .

Sensor stability was evaluated by monitoring the fluorescence emission signal from a  $1.0 \times 10^{-4}$  M lithium ion solution. The results showed that, over a 30-min period, fluorescence measurements taken every 1 min showed a relative standard deviation about the mean signal of 3.5%. Some indication of the durability of the fiber-optic PVC membrane sensor in nonaqueous solvents was obtained by measuring the response to lithium ion after storage in acetonitrile containing 0.1 M HPBO for two weeks. No loss of response or selectivity was observed after this time.

## CONCLUSIONS

This paper reports the first fiber-optic ion sensor for use in nonaqueous media. With the combination of a novel reagent controlled-release method and fluorescence detection technique,

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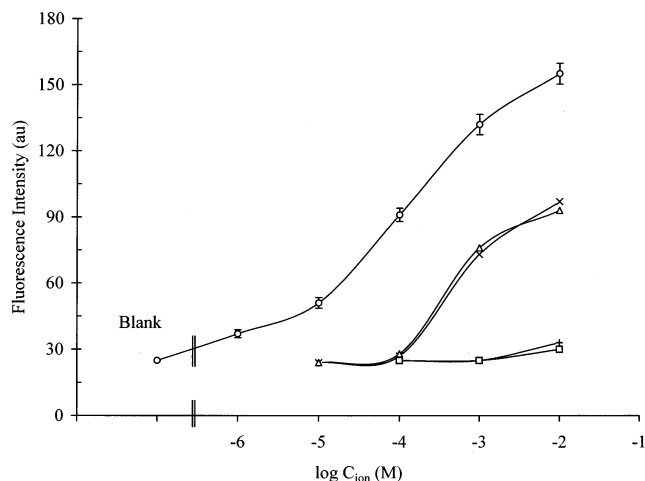


Figure 10. Sensor response curves for metal ions: (O)  $\text{Li}^+$ ; (+)  $\text{Na}^+$ ; ( $\square$ )  $\text{K}^+$ ; ( $\Delta$ )  $\text{Ca}^{2+}$ ; ( $\Delta$ )  $\text{Mg}^{2+}$ . Error bars represent one standard deviation for seven intensity measurements.

the sensor shows considerable advantages of high sensitivity, good reliability, rapidity, and simplicity for ion determination in nonaqueous solvents as compared to ion-selective electrodes. This type of fiber-optic PVC membrane sensor based on indicator reagent diffusion can be extended to other fiber-optic sensors for ions in organic solvents. However, it should be noted that there are some inherent drawbacks of this method in that the response range is limited and cannot be easily tuned, the sample pH and convection should be controlled, and water might be a significant interferent.

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