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Specific fluorescence determination of lithium ion based on 2-(2-hydroxyphenyl)benzoxazole

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A fluorimetric method for the determination of lithium ion is described in this paper, based on the coordination reaction between 2-(2-hydroxyphenyl)benzoxazole (HPBO) and lithium ion under basic conditions in acetonitrile. The fluorescence intensity is drastically enhanced compared with that of free HPBO upon the addition of lithium ion in the range of 1.0×10^{-7} to 1.0×10^{-4} M, but not for other alkali-metal and alkaline earth metal cations such as Na^+, K^+, Ca^{2+} and Mg^{2+}

1 Introduction

The monitoring of lithium ion is of great importance not only in medical and clinical fields, but also for high energy density battery systems. A major challenge for lithium analysis is the required selectivity against Na^+ and K^+, which typically coexist with Li^+ at relatively high concentrations. Nowadays, considerable efforts have been made to develop selective ionophores for use in Li^+-selective electrodes, such as diamides, crown ethers, derivatives of natural polyether antibiotics, heteroaromatic compounds and polypropoxylates.[1] In recent work, we have explored optical alternatives to ion-selective electrodes to measure metal concentrations in electrochemical power sources such as lithium-ion batteries. This has lead to an investigation of optical ionophores for Li^+.

Fluorescence spectroscopy with high sensitivity and excellent selectivity is a firmly established and widely employed technique in analytical chemistry. However, it is unfortunate that most lithium ionophores do not have convenient visible absorption or fluorescence properties. Only a few organic compounds have been proposed for fluorescence determination of lithium. They are based on either the coordination with lithium in organic solvents or the extraction of lithium ion from an alkaline aqueous phase to an organic phase. These fluorophores include chromogenic crown ethers,[2–4] α-hydroxyanthraquinones,[5] and derivatives of 2,9-disubstituted 1,10-phenanthroline[6] and 1,3-bis(8-quinolyloxy)propane.[7] However, these methods often suffer from problems of low sensitivity, poor selectivity and tedious synthesis procedures. Recently, a novel organometallic lithium complex was synthesized from the dehydration reaction between lithium hydroxide and 2-(2-hydroxyphenyl)benzoxazole (HPBO) (Fig. 1) in ethanol.[8] NMR and optical spectroscopic analyses were performed to determine the structure of the HPBO–Li^+ complex formed.[9] This communication describes a highly sensitive and selective fluorimetric method for lithium that has been developed based on this new fluorophore.

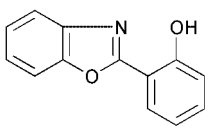

Fig. 1 Structure of 2-(2-hydroxyphenyl)benzoxazole (HPBO).

2 Experimental

2.1 Reagents

Lithium, sodium and potassium perchlorates, calcium perchlorate tetrahydrate, magnesium perchlorate hexahydrate, and HPBO were purchased from Aldrich Chemicals (Milwaukee, WI, USA). Acetonitrile, acetone, ethanol, chloroform, toluene and triethylamine were obtained from Fisher (Fair Lawn, NJ, USA). All of the chemicals were of analytical reagent grade and were used without further purification. All the solutions were prepared with acetonitrile, except for those used in the solvent effect experiments.

2.2 Fluorescence measurements

A suitable aliquot of standard metal perchlorate solution was added into a 10 mL standard flask, followed by 1.0 mL of 0.01 M triethylamine and 0.4 mL of 0.1 M HPBO, then diluted with acetonitrile to the mark and mixed well. 3.0 mL of the resulting solution was transferred into a standard 10 mm pathlength silica cell with a teflon stopper. Fluorescence spectra were recorded by a SLM-Aminco Model 8100 spectrofluorometer (Spectronic Instruments, Rochester, NY, USA) equipped with a 450 W ozone-free xenon arc lamp and an R-928 photomultiplier. The slit-width for both the excitation and emission monochromators was set to give a 2 nm spectral resolution. The fluorescence intensity was measured at the maximum emission wavelength (λ_{em}) using the corresponding maximum excitation wavelength (λ_{ex}).

3 Results and discussion

3.1 Excitation and emission spectra

The fluorescence spectra of HPBO and the complex formed with lithium are shown in Fig. 2. It can be seen that HPBO alone has a very weak fluorescence ($\lambda_{ex}/\lambda_{em}$ = 382 nm/430 nm) and the complexation between lithium ion and HPBO results in a strongly fluorescent complex, which is consistent with the lowest excited singlet changing from n–π* to π–π* and the increase in the rigidity of the molecule.[10] The UV-Vis 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 $(3.6 \pm 0.5) \times 10^5$ M^{-2} in acetonitrile.[9] The peak of the excitation spectrum appears at 392 nm with a shoulder around 370 nm, the emission spectra exhibits a maximum at 428 nm. Fig. 2 also shows the fluorescence spectra of HPBO complexes with other alkali-metal and alkaline earth metal cations at higher concentrations, including Na^+, K^+, Ca^{2+} and Mg^{2+}. The characteristics of these complex spectra are summarized in Table 1.

3.2 Effect of HPBO concentration on fluorescence intensity

To examine the influence of HPBO concentration on the fluorescence intensity, Li^+ standards with different amounts of HPBO in the range from 0 to 1.2×10^{-2} M were tested. As shown in Fig. 3, the maximum fluorescence intensity is obtained using 4.0×10^{-3} M HPBO for 1.0×10^{-4} M Li^+. The use of lower concentrations causes a decrease in fluorescence intensity because of incomplete coordination, while the use of higher concentrations leads to reduced fluorescence because of inner filter effects. Therefore, 4.0×10^{-3} M of HPBO was selected for subsequent work.

3.3 Effect of triethylamine concentration on fluorescence intensity

Since lithium complex formation involves HPBO deprotonation of the phenolic oxygen,[9] triethylamine was used as a base. Fig. 4 illustrates the effect of triethylamine concentration on fluorescence intensity. It was found that the fluorescence intensity increased with increasing triethylamine concentration up to 1.0×10^{-3} M, and thereafter remained almost constant. Hence, 1.0×10^{-3} M of triethylamine was used as the reaction medium.

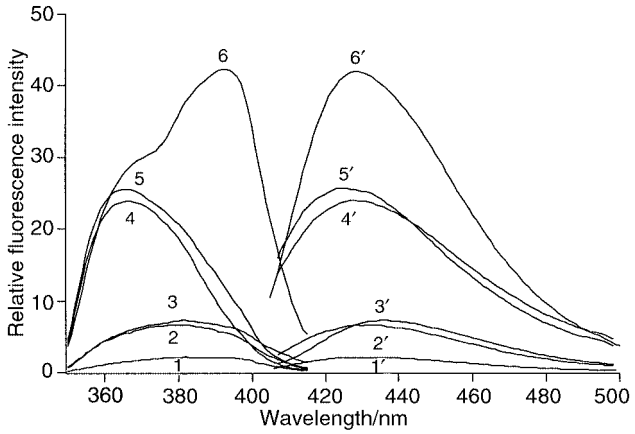

Fig. 2 Excitation and emission spectra of the blank (1 and 1′) and the complexes with 1.0×10^{-2} M K^+ (2 and 2′), 1.0×10^{-2} M Na^+ (3 and 3′), 2.0×10^{-4} M Ca^{2+} (4 and 4′), 2.0×10^{-4} M Mg^{2+} (5 and 5′), and 1.0×10^{-5} M Li^+ (6 and 6′): fluorophore, 4.0×10^{-3} M HPBO; medium, 1.0×10^{-3} M triethylamine.

Table 1 Fluorescence spectral characteristics of HPBO complexes formed with alkali-metal and alkaline earth metal cations

Metal ion	λ_{ex}/nm	λ_{em}/nm
Li^+	392	428
Na^+	382	437
K^+	382	432
Ca^{2+}	368	427
Mg^{2+}	364	424

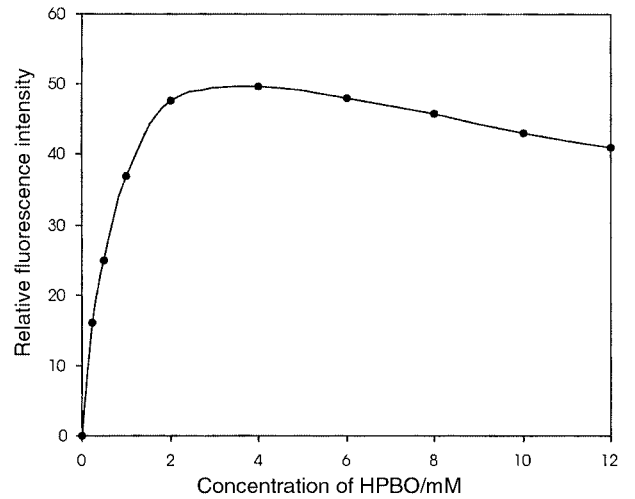

Fig. 3 Effect of HPBO concentration on relative fluorescence intensity in the presence of 1.0×10^{-4}M Li^+ standard.

3.4 Effect of solvents on fluorescence intensity

Solvent polarity and the local environment have profound effects on the emission spectra of polar fluorophores.[11] Therefore, the characteristics of several solvents including acetonitrile, acetone, ethanol, chloroform and toluene were evaluated for the present system. The results are shown in Fig. 5. It can be seen that high fluorescence intensity can be obtained when measured in polar solvents such as acetonitrile and acetone; while the fluorescence spectrum was hardly observed when nonpolar solvents such as toluene were used. The order of decreasing fluorescence intensity is acetonitrile > acetone >> chloroform > toluene, which corresponds to the order of decreasing solvent polarity. However, a relatively low intensity occurs in ethanol, which is probably due to the strong protic solvent interactions with the solute molecules.

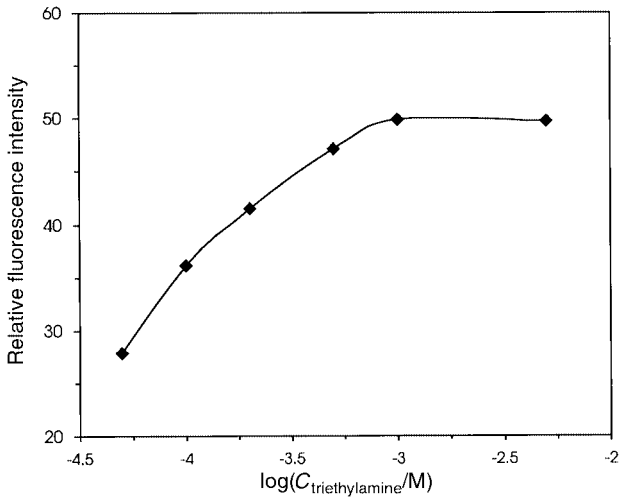

Fig. 4 Effect of triethylamine concentration on relative fluorescence intensity in the presence of 1.0×10^{-4} M Li^+ standard.

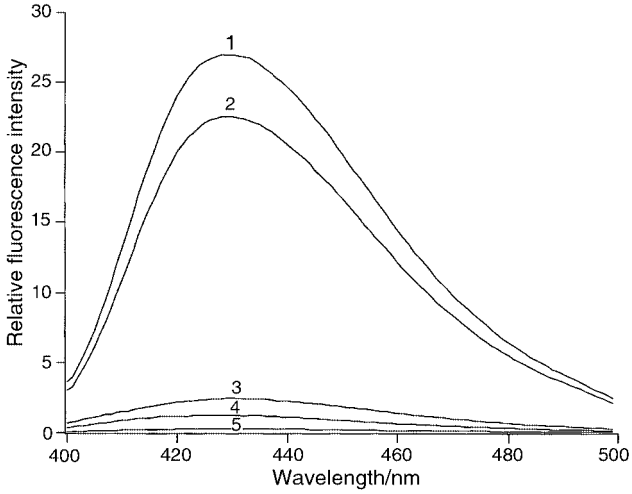

Fig. 5 Effect of solvents on relative fluorescence intensity. Solvents: 1, acetonitrile; 2, acetone; 3, ethanol; 4, chloroform; 5, toluene. Conditions: 1.0×10^{-5} M Li^+ standard; 4.0×10^{-3} HPBO; 1.0×10^{-3} M triethylamine.

3.5 Response to metal cations

Under the selected conditions described above, typical calibration curves for Li^+ and for other alkali-metal and alkaline earth metal cations including Na^+, K^+, Ca^{2+} and Mg^{2+} are shown in Fig. 6. As indicated in the figure, the present system is useful for measuring Li^+ at concentrations ranging from 1.0×10^{-7} to 1.0×10^{-4} M with a relative standard deviation of less than 5%; whereas, no response was observed up to 10^{-3} M for Na^+ or K^+, and up to 10^{-4} M for Ca^{2+} or Mg^{2+}. Thus, using the selected conditions the technique is very sensitive and has satisfactory selectivity for Li^+.

3.6 Photostability study

The photostability of the lithium complex was examined by illuminating the mixture of 4.0×10^{-3} M HPBO and 1.0×10^{-5} M Li^+ continuously using a 450 W xenon arc lamp for 1 h with the excitation bandwidth set to 2 nm. No reduction in fluorescence emission was observed after the experiment, which indicates that the photostability of the sensor is reasonably good.

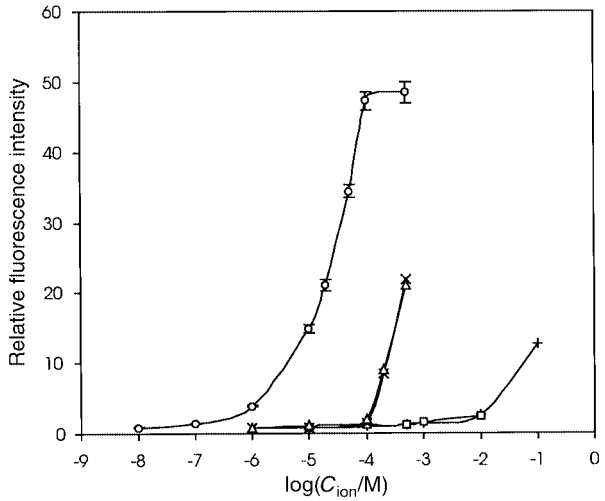

Fig. 6 Response to metal ions in the presence of 4.0×10^{-3} M HPBO and 1.0×10^{-3} M triethylamine: (○) Li^+; (+) Na^+; (□) K^+; (×) Ca^{2+}; (△) Mg^{2+}. Error bars represent one standard deviation for four measurements.

3.7 Conclusion

Compared with other fluorescence methods for the determination of lithium ion, the present system based on HPBO offers several advantages. The fluorophore shows high sensitivity and permits quantitative detection of lithium ion down to 1.0×10^{-7} M. The HPBO complex is formed efficiently only with lithium ion, exhibiting excellent selectivity against other alkali-metal and alkaline earth metal cations. The fluorescence intensity developed immediately upon addition of Li^+ with good photostability and each measurement was completed within one minute. In addition, HPBO is commercially available and there is no need for tedious synthesis procedures. The unique characteristics of this fluorophore have lead us to develop a new fluorescence-based fiber optic sensor for lithium ion. This work is now in progress in our laboratory.

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