



Novel selective optode membrane for terbium ion based on fluorescence quenching of the 2-(5-(dimethylamino) naphthalen-1-ylsulfonyl)-N-phenylhydrazinecarbothioamid

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ABSTRACT

For the first time, a highly sensitive and selective fluorimetric optode membrane sensor for determination of trace amounts of Tb(III) ions was prepared. The Tb(III) sensing system was prepared by incorporating 2-(5-(dimethylamino) naphthalen-1-ylsulfonyl)-N-phenylhydrazinecarbothioamide (L) as a neutral Tb(III)-selective fluoroionophore, in the plasticized PVC membrane containing sodium tetraphenyl borate as a lipophilic anionic additive. The response of the sensor is based on the strong fluorescence quenching of L by Tb(III) ions. At pH 4.7, the proposed sensor displays a calibration curve over a wide concentration range of 1.0×10^{-2} to 1.0×10^{-8} M, with a relatively fast response time of less than 1 min, high stability, high reproducibility and a relatively long working lifetime. The sensor shows a good selectivity towards Tb(III) ion respect to all lanthanide and common coexisting cations. The proposed fluorescence optode was applied successfully to determination of Tb(III) ion in water and phosphate rock samples.

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1. Introduction

During the past decade, an extensive effort has been devoted to developing artificial receptors that are able to transform the binding of ionic species into spectroscopic signals [1,2]. The signal transduction of these receptor systems occurs on the basis of host–guest complexation, in which the absorption or fluorescence properties of the host are perturbed by selective binding of metal ions. Fluorescence is particularly a suitable optical sensing method for designing these optical sensors. This is mainly due to its inherent sensitivity, its almost complete inertness to turbidity and its flexibility with respect to geometric arrangements [3–6]. There is an increasing current interest in the development of fluorescent sensors for metal ions such as Li^+ [7], Na^+ [8,9], Ag^+ [10], Hg^{2+} [11], Co^{2+} [12], Cu^{2+} [13], Ni^{2+} [14], Al^{3+} [15], and Zn^{2+} [16] as well as a number of anionic species [17–19].

Terbium is used to dope calcium fluoride, calcium tungstate and strontium molybdate materials that are used in solid-state devices. It is used as a crystal stabilizer of fuel cells which operate at elevated temperatures together with ZrO_2 , and is also used in alloys and in production of electronic devices. Its oxide is used in green

phosphors in fluorescent lamps and color TV tubes. Sodium terbium borate is used in solid solid-state devices. As with the other lanthanides, terbium compounds are of low to moderate toxicity, although their toxicity has not been investigated in detail. Thus, separation, concentration and sensitive determination of Tb(III) ions are of increasing interest [20,21].

In recent years a number of techniques including isotope dilution mass spectrometry, neutron activation analysis, X-ray fluorescence spectrometry [22–24], flow injection analysis [25], fluorescence enhancement [26,27], raman spectrometry [28], capillary zone electrophoresis [29], fluorescence methods [30] and electrochemical methods [31,32] have been reported in literature for the selective and sensitive determination of Tb(III) ions. Although these methods are sensitive and accurate, most require a tedious sample pre-treatment (e.g. separation from other elements present and the use of a pre-concentration step prior to terbium determination) and expensive equipment with sophisticated performance, which in turn, cannot be used for direct field application or on-site screening. Also, due to the high sensitivity of the optical sensors, they have a lower detection limits and wider linear range (10^{-8} to 10^{-2} M) than the other methods.

However, to the best of our knowledge, there is no previous report on an efficient and selective fluorimetric membrane optode for terbium ion detection in aqueous solutions.

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In this work, we found that the strong fluorescence of 2-(5-(dimethylamino) naphthalen-1-ylsulfonyl)-N-phenylhydrazine-carbothioamide (L) to be quenched considerably in a selective manner upon complexation with Tb(III) ions. Thus, we decided to prepare highly sensitive and selective fluorimetric optode membrane for the determination of trace amounts of Tb(III) ions in real samples.

2. Experimental

2.1. Reagents

Reagent grade benzyl acetone (BA), dibutyl phthalate (DBP), dioctyl phthalate (DOP), potassium tetrakis(*p*-chlorophenyl)-borate (KTPClPB), sodium tetraphenyl borate (NaTPB), high relative molecular weight PVC, tetrahydrofuran (THF) and methanol (MeOH) were purchased from Fluka chemical company at the highest purity available, and used without any further purification except for vacuum drying. Doubly distilled deionized water was used throughout. pH of samples was adjusted at 4.7 using a diluted hydrochloride acid/glycin buffer solution.

2.1.1. Synthesis of L

The fluorogenic reagent L (Fig. 1) was prepared as follows: A mixture of hydrazine (2 mmol) and dansyl chloride (2 mmol) in dichloromethane and triethylamine (35 mL) was refluxed at -20°C for 5 h. Then, the resulted salt was extracted with water. The residue dansyl hydrazine was then added to the phenyl isocyanate solution in ambient temperature. Then, the precipitate washed with dichloromethane (5 mL). The solid was recrystallized from 1:1 acetone–ethanol and the product was obtained as yellow crystals. Yield: 80%; M.P.: 148–149; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3310, 3290 and 3270 (NH), 1672 (C=O), 1150 (SO₂), 1552, 1483, 1273, 1153, 1034, 951, 841, 696; ¹H NMR (90 MHz, CDCl₃): 2.99 (6H, s, NMe₂), 7.35 (1H, t, *J* = 7.5 Hz, CH), 7.38 (1H, d, *J* = 6.5 Hz, CH), 7.43 (1H, dd, *J* = 8.9 Hz, *J* = 6.0 Hz) CH, 7.64 (1H, dd, *J* = 8.5 Hz, *J* = 6.3 Hz) CH, 7.70–7.75 (4H, m, 4CH), 8.22 (1H, d, *J* = 6.3 Hz, CH), 8.30 (1H, d, *J* = 8.5 Hz, CH), 8.35 (1H, d, *J* = 8.9 Hz, CH), 8.9 (1H, br, NH), 10.05 (1H, s, NH); ¹³C NMR: 45.20 (NMe₂), 112.25, 114.39, 119.65, 126.69 (4CH), 126.95, 127.43 (2CH), 128.33, 129.05 (2CH), 129.61 (C), 130.15, 133.64 (2CH), 133.17 (C), 135 (CH) 153.72 (C), 190.39 C=S.

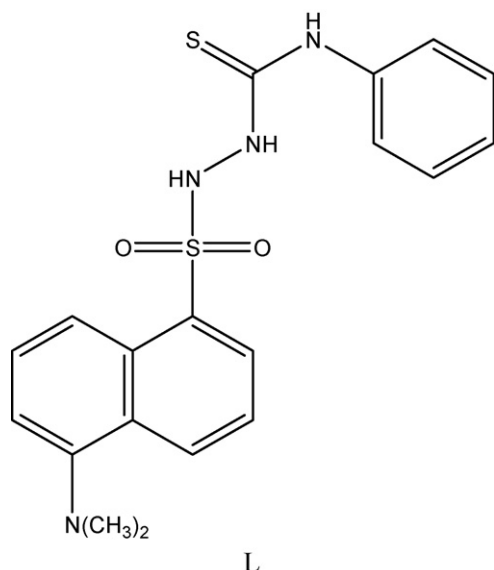


Fig. 1. Structure of L.

2.2. Apparatus

All fluorescence measurements were carried out on a Perkin-Elmer LS50B luminescence spectrometer. A corning ion analyzer 250-pH/mV meter was used for the pH measurements.

2.3. Membrane preparation

The membrane solutions were prepared by thoroughly dissolving of 30 mg powdered PVC, 65 mg of plasticizer, 2 mg of additive NaTPB and 3 mg of fluorogenic ligand L in 3 mL THF. A volume of 0.2 mL of this solution was then pipetted and spread onto a 7 mm × 50 mm dust-free quartz plate located in a THF-saturated desiccators. In this way, a membrane of approximately 0.1 mm thickness was coated on the plate, and it was allowed to stand in ambient air before use.

3. Results and discussion

The ionophores having nitrogen and sulfur atoms as donor atoms are known to form very stable complexes with transition metal ions [33]. The resulting 1:1 complexes have been frequently used as catalysts in such diverse processes, e.g. oxygen and atom-transfer [34]. Due to the radii of lanthanum ions (from Ce³⁺ to Lu³⁺ with the range of 1.02–0.80 Å, respectively), these elements have different properties such as charge densities, size and hydration energy (from Ce³⁺ to Lu³⁺ with the range of 3370–3760 kJ mol⁻¹) [35,36]. Thus, by using a suitable ionophore having a semi-cavity and relatively high flexibility, it is possible to construct a highly selective lanthanide ion sensor. The existence of donating nitrogen and sulfur atoms in the L structure which causes a semi-cavity and forms a template complex, and considering soft–hard acid–base concept, the charge density and the size of the terbium ion, it was expected that L can form a selective complex with terbium ion more than the other transition metal ions. Thus, fluorescence study of complexation in the acetonitrile solution was carried out as a primary test.

3.1. Preliminary studies

To evaluate whether L could be used as a selective fluorescent chemosensor for Tb³⁺ ion, its emission fluorescence spectra variations that occur upon addition of increasing amounts of metal ion to an acetonitrile solution of the ligand (5×10^{-6} M) were recorded at $25.0 \pm 0.1^{\circ}\text{C}$. The shape and position of the fluorescence emission bands did not change in the presence of the terbium ion compared to those of the free ligand, whereas emission intensities sharply decreased as a function of Tb³⁺/L molar ratio according to the curve reported in Fig. 2. The fluorescence intensity–mole ratio data for the other lanthanides ions are also included in Fig. 2. As it is obvious from Fig. 2, a rather pronounced chelation enhancement of quenching of the fluorescence (CHEQ effect) is observed for L upon addition of increasing the quantity of Tb³⁺ ion, which begins to level off at a ligand/metal ion molar ratio of 1. From such a sharp inflection point at a molar ratio of 1, it can be immediately concluded that a 1:1 [TbL]³⁺ complex cation is formed in acetonitrile solution. The formation constant of the resulting complex was evaluated by fitting the fluorescence intensity/[Tb³⁺] molar ratio data to a 1:1 model using a nonlinear least-squares curve-fitting program, as described elsewhere [37], and results showed that log *K*_f is 7.2 ± 0.1 for Tb³⁺, 3.86 ± 0.1 , for Dy³⁺, 4.46 ± 0.1 for La³⁺, 3.86 ± 0.1 for Eu³⁺ and <2 for other metal ions used. It is interesting to note that a much weaker CHEQ effect was observed upon addition of other lanthanide ions such as Pr³⁺, Yb³⁺, Sm³⁺ and Ce³⁺ to an acetonitrile solution of L.

To obtain more information about the conformational changes of L upon complexation to the terbium ion, the molecular struc-

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