A new triazene-1-oxide derivative, immobilized on the triacetyl cellulose membrane as an optical Ni\(^{2+}\) sensor

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An optical sensor for the direct measurement of Ni\(^{2+}\) ion was developed. The basic element of this optode is the immobilization of 1-p-toly1-3-(3-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide on a triacetyl cellulose membrane. Spectrophotometric studies of complex formation between the triazene-1-oxide derivative, L with Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\), Ag\(^{+}\), Co\(^{2+}\), Pb\(^{2+}\), Mn\(^{2+}\), Hg\(^{2+}\) and Cd\(^{2+}\) metals in acetonitrile solution indicated a substantially larger stability constant for the Nickel ion complex. Consequently, the new triazene-1-oxide derivative L was used as an appropriate ionophore for the preparation of a selective Ni\(^{2+}\) optical sensor, by its immobilization on a transparent triacetyl cellulose tapes. The effects of pH, reagent concentration and reaction time on the immobilization of L were studied. A linear response curve was observed for the membrane sensor in Ni\(^{2+}\) concentration range of 1.18 \times 10^{-9} - 7.34 \times 10^{-5} M with a \(R^2\) value of 0.998 at pH 5.7. The detection limit (3\(\sigma\)) of the method for Ni\(^{2+}\) was 1.0 \times 10^{-9} M. No significant interference from 100 times concentrations of a number of potentially interfering ions was observed for the nickel ion determination. The sensor showed a good durability and short response time with no evidence of reagent leaching. The sensor was successfully applied for the determination of Ni\(^{2+}\) in environmental water samples.

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1. Introduction

In the recent years, pollution of the environment by heavy metals has received considerable attention. Nickel is a moderate toxic element compared to other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including respiratory system cancer. Moreover, nickel can cause a disorder known as nickel-eczema. Nickel is an excellent alloying metal in steel industry and is the metal component of the enzyme urease and as such is considered to be essential to plants and some domestic animals [1]. This metal normally occurs at very low level in the environment, so sensitive methods are needed to detect it in most environmental samples. Thus, the development of simple methods for selective determination of nickel in trace amounts in different matrices is critical.

Atomic spectroscopic methods are powerful analytical techniques for the determination of elements in a great number of samples. However, these techniques are rather expensive and time consuming and may not be available in all the laboratories. Optical chemical sensors (optodes), on the other hand, are simple and selective tools for the determination of heavy metal ions that have been extensively developed in recent years [2–4]. Optodes are generally used in combination with inexpensive spectrophotometric or spectrofluorometric techniques to provide simple and fast determination methods with enhanced selectivity and low detection limits [5–7].

Immobilization of ionophores on transparent membranes is one of the essential steps in fabrication of optical sensors. The ionophore immobilized is accomplished by either physical entrapment [8], sol–gel [9,10], multilayered films [11] or chemical (covalent) bonding methods [12]. Physical entrapment and multilayered films methods suffer the problem of slow dye leakage and sensors of these types have relatively short life times [13]. Sensors with covalent bonding, on the other hand, have reproducible responses and long life times [14]. Different approaches to covalent immobilization can be found in the literature [15].

In construction of optical sensors, ionophores play an important role. The compounds contain some donor atoms have been frequently used as ionophores in construction of membrane sensors because of their ability to form stable complexes with transition metal ions. They produce remarkable selectivity, sensitivity and stability for a specific ion [16–18].

Some Ni\(^{2+}\) optodes based on liquid or solid state membranes have been reported in the literature, but generally with in sufficient detect ion limits, lack of sufficient selectivity for
environmental sensing or reagent leaching problems [19–21]. In the present study, a newly synthesized ligand 1-p-tolyl-3-[3-(trifluoromethyl)phenyl]triaz-1-ene 1-oxt, \( \text{L} \), was covalently immobilized on a triacetyl cellulose membrane to be used as an effective ionophore with N and O donor atoms for construction of a selective optical sensor for the spectrophotometric determination of Ni\(^{2+} \) in aqueous solutions.

2. Experimental

2.1. Materials and instruments

All reagents used in this work were of analytical grade. Double-distilled water was used throughout and test solutions were buffered in a 0.05 mol L\(^{-1} \) solution of acetic acid/sodium acetate and pH adjusted with drop wise addition of 0.5 mol L\(^{-1} \) solution of HCl or NaOH. The synthesized ligand \( \text{L} \), with the chemical name of 1-p-tolyl-3-[3-(trifluoromethyl)phenyl]triaz-1-ene 1-oxt, was synthesized and purified as reported [22].

A Jenway (USA) model 3020 pH meter with a combined glass electrode was used after calibration against standard Merck buffers for pH determinations. A Shimadzu (Japan) model 1650PC double-beam spectrophotometer was used for running the electronic absorption spectra. A home-made polycrylamide holder was used for holding triacetyl cellulose membranes inside the quartz cells of the spectrophotometer. A totally glass Fisons (UK) double distiller was used for preparation of doubly distilled water.

2.2. Procedures

For spectrophotometric titrations, 2 mL of the ionophore solution (5 × 10\(^{-5} \) mol L\(^{-1} \)) in acetonitrile was transferred into a quartz cell of the spectrometer. Micro liter amounts of 5 × 10\(^{-3} \) mol L\(^{-1} \) solution of each metal ion were transferred to the ionophore solution by a 50 μL microsyringe. Each spectrum was recorded immediately after various mixing of the solution. All the absorbances data were corrected for the dilution.

A method described elsewhere was used for the preparation of transparent triacetyl cellulose membranes that were produced from waste photographic film tapes, which were previously treated with commercial sodium hypochlorite for several seconds in order to remove the colored gelatinous layers [5,23]. The triacetyl cellulose transparent film was hydrolyzed in order to deesterify the acetyl groups and to increase the porosity of the membrane by treating the membrane into 0.10 M NaOH solution for 24 h. The films were treated with a solution of 0.006 g of the compound \( \text{L} \), in 10 mL ethylene diamine for 2 min at ambient temperature. Afterwards, they were washed with water for the removal of ethylene diamine and the loosely trapped indicator. The prepared membranes with a thickness of 0.15 mm were kept under water, when not in use. A 1 cm × 2 cm peace of the fabricated membranes sensor was cut and mounted in a polycrylamide holder and placed inside the quartz cell of the spectrophotometer. The cell was then used as usual for the absorbance determinations. All the measurements on the transparent triacetyl cellulose membranes were performed in aqueous medium.

To test the reliability of the recommended procedure, the method was applied to the determination of nickel in several natural water samples collected from the west of Iran. The pH adjusted on 5.7 before analysis, without any further treatment. For analysis, about 2 mL of a sample was transferred into a 1 cm quartz cell equipped with the membrane sensor. The absorbances were then measured at 344 nm and subtracted from an absorbance reading for a buffer solution at the same wavelength. The Ni\(^{2+} \) concentration was then derived using an ordinary calibration curve method.

![Fig. 1. Chemical structure of 1-p-tolyl-3-[3-(trifluoromethyl)phenyl]triaz-1-ene 1-oxt.](image1)

![Fig. 2. Absorbance spectra of \( \text{L} \) (5.0 × 10\(^{-5} \) mol L\(^{-1} \)) in acetonitrile, solution, at different Ni\(^{2+} \) concentrations.](image2)

![Fig. 3. Absorbance of \( \text{L} \) (5.0 × 10\(^{-5} \) mol L\(^{-1} \)) in acetonitrile at 352 nm, as a function of [M\(^{2+} \)]/[triazene-1-oxt] mole ratio for different metal ions.](image3)