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Design of an efficient uranyl ion optical sensor based on 1′-2,2′-(1,2-phenylene)bis(ethene-2,1-diyl)dinaphthalen-2-ol

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ABSTRACT

A new optical uranyl (IV) selective sensor by incorporation of 1,1′-2,2′-(1,2-phenylene)bis(ethene-2,1-diyl) dinaphthalen-2-ol (PBED), dibutyl phthalate (DBP) and sodium tetraphenylborate (Na-TPB) in the plasticized poly vinyl chloride membrane matrices has been constructed. In the proposed optode, PBED functions as both ionophore and chromoionophore while DBP has synergistic effect on the complexation of uranyl ion (UO_2^{2+}) by PBED. Following the optimization of influences of variables, the proposed sensor due to its high stability, reproducibility and relatively long lifetime has good selectivity and sensitivity for uranyl ion over a large number of alkali, alkaline earth, transition, and heavy metal ions. The response of the proposed optode is linear over the concentration range of 3.99×10^{-6} up to 8.06×10^{-5} mol L^{-1} of UO_2^{2+} within a detection limit of 9.99×10^{-7} mol L^{-1} and response time less than 10 min. The proposed optical sensor was applied successfully for the determination and evaluation of UO_2^{2+} ion content in water samples.

1. Introduction

The importance of detection and determination of metal ions, especially toxic ones in environmental, waste and drinking waters is a challenging requirement [1,2]. Among metal ions, uranium ion usually mostly appearing in natural waters at low levels [3] is known to cause acute toxicological effects in mammals and as carcinogen agent [4–6]. Uranium is generally found at low levels within all rock, soil and water samples, especially in earth combined with other elements. The increase in nuclear power production predominantly based on uranium fuel cycle causes the release of uranium and other radionuclides into the waste of such industrial process. One health risk from large intakes of uranium is toxic damage to the kidneys, due to its radioactive and toxic properties [7]. Radiological impact and chemical toxicity of uranium depend on its chemical form and concentration and may be as reproductive toxicant [8–10]. Uranyl (UO_2^{2+}) ions (uranium trioxide or uranyl nitrate and other hexavalent uranium compounds) have been shown to cause birth defects and immune system damage in laboratory animals [11]. Uranyl is present in low quantities (10^{-5} to 10^{-3} mol L^{-1}) in aqueous and nonaqueous waste of nuclear reactors [12]. The World Health Organization (WHO), Health Canada and Australian drinking water guidelines approved that the maximum allowable uranyl concentration in drinking waters be less than 9, 20, and 20 g/L, respectively [13]. Therefore, there is a development of new accurate and sensitive procedure for determination of uranyl ion content [14].

The methods including inductively coupled plasma atomic emission spectrometry (ICP-AES) [15], inductively coupled plasma-mass spectrometry (ICP-MS) [16], ion chromatography (IC) [17], capillary zone electrophoresis (CZE) [18], graphite furnace atomic absorption spectrometry (GFAAS) [19], fluorimetry [20], spectrophotometry [21], neutron activation analysis [22] and voltammetry [23] have been used for determination of uranium. These methods in spite of their own advantages suffer from limitations such as expensive instruments, maintenance cost and tedious procedure.

Optical sensors (optode) due to several great advantages such as simplicity, rapidity, low cost, capability for incorporation into easy-to-use kits with moderate selectivity and sensitivity are particularly suitable for determination of metal ions [24]. Until now, only a few optical sensors have been developed for determination of uranyl ion [14,25–30] and most of the reported uranyl ion optical sensors have narrow working range. Thus, sensitive and simple uranyl optodes with relatively short response times and large working concentration range are required.

To improve the analytical signal, selective binding of analyte ions to especial receptor is required to improve the method performances [31–38]. In optic sensor based on plasticized polymer matrix the analyte interacts with ionophore to produce a distinctive optical property change. It is one of the advanced techniques that attain much attention for the determination of toxicologically relevant ions present in aqueous medium [39,40].

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In the present work, a new ionophore based optical sensor for the simultaneous preconcentration and determination of UO_2^{2+} from aqueous samples has been developed. The optode is based on physical inclusion of 1,1′-2,2′-(1,2-phenylene)bis(ethene-2,1-diyl)dinaphthalen-2-ol (PBED) into plasticized poly vinyl chloride membrane. The influence of experimental parameters such as composition of membrane, pH, and interference of cations and anions on the determination of UO_2^{2+} was optimized. At optimum values of all variables, the response time, and detection limit were calculated and compared with the conventional spectrophotometry. Finally, the optode has been tested for quantitative determination of UO_2^{2+} in the real water samples.

2. Experimental

2.1. Reagent

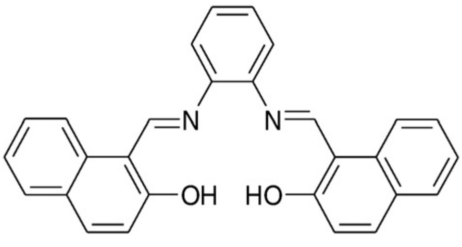
Standard UO_2^{2+} ion solutions were prepared daily by appropriate dilution of stock 0.5 mol L^{-1} $UO_2(NO_3)_2$ solution. Acetate buffer, dimethyl sebacate (DMS), dibutyl phthalate (DBP), diethyl sebacate (DES), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF) and sodium tetraphenylborate (Na-TPB) all from Fluka or Merck Chemical Companies were used as received. All other chemicals were of analytical reagent grade and were used without further purification. Doubly distilled deionized water was used throughout the experiments. The pH of the solutions was kept constant by using acetate buffer at pH 3.0.

2.2. Apparatus and measurement procedures

A Jenway model 691 (Metrohm) pH meter was used to measure the pH. A UV–vis spectrophotometer (model V-530, Jasco, Japan) with two 1-cm glass cells was used for absorbance measurements. All of the experiments were operated at room temperature, 25 ± 1 °C. The absorbance measurements were carried out with respect to air as well as blank optode sample.

2.3. Preparation of 1,1′-2,2′-(1,2-phenylene)bis(ethene-2,1-diyl) dinaphthalen-2-ol

A solution of 1,2-phenylenediamine (0.540 g, 5 mmol) in absolute EtOH (20 mL) was added to a solution of 2-hydroxy-1-naphthaldehyde (1.722 g, 10 mmol) in absolute EtOH (20.0 mL) and boiled under reflux for 3–5 h. After several hours, the product was obtained as orange powder. The powder was filtrated and washed twice with cooled ethanol and dried under air (81% yields). Elemental analysis, % $C_{28}H_{20}N_2O_2$: C, 80.75; H, 4.84; N, 6.73; found: C, 79.9; H, 4.6; N, 6.9. IR(KBr, cm^{-1}): 3300–3500(bs, νOH), 3058(w, CH-Aromatic), 1621(vs, $-C{=}N$), 1563(m, $C{=}C$), 1470(s, $C{=}C$), 1396(m, $C{=}C$), 1324(m, $C-N$), 1245(w), 1180(m, $C-O$), 1160(m, $C-O$), 1082(m), 969(m), 825(s), 746(s), 670(m), 612(w). The structure of this ligand is illustrated in Scheme 1.



Scheme 1. The structure of ligand PBED.

2.4. Preparation of membrane optode

For membrane preparation, high molecular weight PVC, dibutyl phthalate (DBP) as a plasticizer, extractant and freshly distilled tetrahydrofuran (THF) were used. After complete dissolution, the casting solution was prepared by mixing the required volumes of the solutions containing known amounts of the components. Na-TPB was used as an additive (in the membranes) and as the ionic strength stabilizer in the spectrophotometric studies. The metal cations tested were of their nitrate salt. Doubly distilled and deionized water was used throughout.

The optode membranes were prepared by mixing 60.0 mg plasticizer (DBP), 30.0 mg PVC, 2.0 mg of PBED and 4.0 mg Na-TPB dissolved. The membrane components were dissolved in exactly 2.0 mL THF. A 200.0 μL of the THF cocktail was pipetted and transferred on the glass plate. Prior to coating, all of the glass plates were cleaned with pure THF and HNO_3 to remove organic impurities and dust. After 50 s spinning (using a spin-on device) with rotation frequency of 600 rpm, the membrane was allowed to dry in air for a few minutes. The optimal membrane had a thickness of approximately 5–7 μm. The thickness of the membranes was calculated from the amount of solvent and solutes employed for the preparation of the membrane layer. In all studies, the reference membrane had the same composition as the proposed membranes except that the PBED was absent.

2.5. Procedure

The optical sensor membrane was mounted into the spectrophotometer cell already filled with 2.5 mL of acetate buffer (pH 3.0). Then, UO_2^{2+} ion solution with specific concentration was added and the absorption spectrum against a reference membrane was recorded over the wavelength range of 340–700 nm at 1 nm interval. All measurements were performed at ambient temperature.

3. Results and discussion

3.1. Spectral characteristic

PBED is a chelating agent able to react with some metal ions. The proposed sensor is based on bulk phenomenon, where the organic phase of the plasticized PVC membrane is in equilibrium with the contacting aqueous solution. In this optical sensor PBED acts as both ionophore and chromoionophore. When uranyl ion diffuses into the membrane, it forms a complex with PBED and consequently a change in the optical property occurred.

The absorption spectra of the membrane obtained after being equilibrated in acetate buffer solution (pH 3.0) containing different concentrations of uranyl ion are shown in Fig. 1. The spectral change is a result of addition of UO_2^{2+} ions and complex formation. The spectral characteristic of this sensor showed two maxima at 381 and 457 nm. The wavelength of 381 nm was selected for further studies because of higher sensitivity at this wavelength.

3.2. Influence of amount of PBED on the response of the proposed optode

The influences of PBED amount in the range of 0.5–2.5 mg at fixed concentration of UO_2^{2+} (8.06×10^{-5} mol L^{-1}) were investigated and respective results are presented in Fig. 2a. In the absence of PBED due to low complexation, the low sensitivity is achieved. By addition of PBED up to 2.0 mg the amount of UO_2^{2+} ion that migrates to the membrane significantly increased and the amount of complex significantly increased. Further addition of PBED did not significantly affect the response and sensitivity of this optode. Therefore, 2.0 mg of PBED is recommended for subsequent works. For membranes with different amounts of PBED, absorbance signal was recorded at 381 nm for