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Sensors and Actuators B 120 (2007) 487–493
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Fabrication of a highly selective and sensitive Gd(III)-PVC membrane sensor based on *N*-(2-pyridyl)-*N*′-(4-nitrophenyl)thiourea

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Received 26 December 2005; received in revised form 1 March 2006; accepted 2 March 2006

Abstract

In this work we report the development of a highly selective and sensitive Gd(III) membrane based on *N*-(2-pyridyl)-*N*′-(4-nitrophenyl)thiourea ($PyTu4NO_2$) as an excellent neutral ion carrier. The Gd(III) sensor exhibits a Nernstian slope of 19.95 ± 0.3 mV per decade over the concentration range of 3.0×10^{-7} to 1.0×10^{-1} M, and a detection limit of 3.0×10^{-7} M of Gd(III) ions. The potentiometric response of the sensor is independent of the solution pH in the range of 4.0–9.0. It manifests advantages of low detection limit, fast response time (∼10 s), and most significantly, very good selectivity with respect to a number of lanthanide ions (La, Ce, Sm, and Eu ions). It can be used at least for a period of 8 weeks without any significant divergences in its potential response. To assess its analytical applicability the proposed Gd(III) sensor was successfully applied as an indicator electrode in the titration of Gd(III) ion solutions with EDTA and for the determination of the fluoride ion in two mouth wash preparations. It was also used for the direct monitoring of Gd(III) ions in binary mixtures.

Keywords: Gd(III) sensor; Potentiometry; PVC; *N*-(2-pyridyl)-*N*′-(4-nitrophenyl)thiourea ($PyTu4NO_2$)

1. Introduction

Gadolinium and other lanthanide oxides are widely used in the preparation of optical glasses, glass fibers for optical purposes, gasoline-cracking catalysts, polishing compounds and carbon arcs, and in the iron and steel industries to remove sulfur, carbon, and other electronegative elements from iron and steel [1].

There are many methods for low-level monitoring of lanthanide ions in solution such as spectrophotometry, inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectroscopy. Isotope dilution mass spectrometry, neutron activation analysis, X-ray fluorescence spectrometry, etc., are also used in some laboratories. These methods have either low sensitivity and are time-consuming, involving multiple sample manipulations, or are too expensive for most analytical laboratories.

Potentiometer monitoring, based on the ion-selective membrane sensor as a simple method, offers several advantages such as speed and ease of preparation and procedure, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost.

Literature survey revealed that only three Gd(III) membrane sensors with Nernstian response have been reported. These sensors, although they revealed relatively good selectivities over other common and lanthanide metal ions, have comparatively narrow linear ranges [2–4]. In this research, we present a highly selective and sensitive Gd(III) sensor, based on *N*-(2-pyridyl)-*N*′-(4-nitrophenyl)thiourea ($PyTu4NO_2$). The best performance was obtained with a membrane contain 2% potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB) as an anionic additive, 63% benzylacetate (BA) as a solvent mediator, 5% $PyTu4NO_2$, and 30% poly(vinyl chloride) (PVC). The Gd(III) sensor exhibits a Nernstian slope of 19.95 ± 0.3 mV per decade over the concentration range of 3.0×10^{-7} to 1.0×10^{-1} M, and a detection limit of 3.0×10^{-7} M of Gd(III) ions.

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doi:10.1016/j.snb.2006.03.001

2. Experimental section

2.1. Reagents

Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), *o*-nitrophenyloctyl ether (NPOE), potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB), tetrahydrofuran (THF) and high relative molecular weight poly(vinyl chloride) (PVC) were purchased from Merck and Aldrich and used as received. All chloride and nitrate salts of cations used (all from Merck, Aldrich and Fluka) were of the highest available purity and used without any further purification, except for vacuum drying over P_2O_5. $PyTu4NO_2$ (Fig. 1) was synthesized as described elsewhere [5]. Triply distilled de-ionized water was used throughout.

2.2. Electrode preparation

For the preparation of the membrane, according to Table 2, certain amounts of powdered PVC (30 mg), different plactisizers (63–66 mg), $PyTu4NO_2$ (4–6 mg) and KTpClPB (0–2 mg) were completely dissolved in 5 ml of fresh THF. The mixture was transferred into a glass dish of a 2 cm diameter and its solvent was allowed to evaporate slowly so as to gain an oily concentrated mixture. In the next step, a Pyrex tube (with an outer diameter of 3–5 mm) was dipped into the mixture for about 10 s so that a transparent membrane of 0.3 mm thickness was formed on its tip [6–9]. The tube was then pulled out of the mixture and kept at room temperature for 12 h, before being filled with its internal filling solution (1.0×10^{-3} M $GdCl_3$). The final step involved electrode conditioning for 24 h by its soaking in a 1.0×10^{-2} M solution of Gd(III) nitrate. The ratio of different membrane ingredients, the concentration of the equilibrating solution and the contact time were optimized to provide membranes, which resulted in reproducible, noiseless and stable potentials.

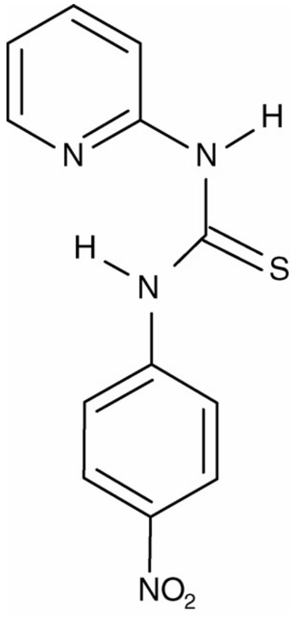

Fig. 1. Structure of $PyTu4NO_2$.

2.3. Emf measurements

All emf measurements were carried out with the following assembly: Ag–AgCl| internal solution (1.0×10^{-3} M $GdCl_3$)| PVC membrane| test solution| $Hg–Hg_2Cl_2$, KCl (satd).

A Corning ion analyzer 250 pH/mV meter was used for potential measurements at 25.0 ± 0.1 °C.

3. Results and discussion

Recently, a number of lanthanide membrane sensors based on different ion carriers containing nitrogen and sulfur donor atoms have been reported during recent years [2–4,6–26]. Due to its flexible structure and, especially, because of the presence of three donating nitrogen atoms in its structure, $PyTu4NO_2$ was expected to act as a suitable neutral ion carrier in the PVC membranes with respect to transition and heavy metal ions of proper size and charge.

Thus, at primary experiments, the complexation of $PyTu4NO_2$ with a number of lanthanide and common ions was investigated by a conductometric method.

3.1. Conductance study of complexation of $PyTu4NO_2$ with metal ions in acetonitrile solution

The existence of three donating nitrogen atoms, in the structure of $PyTu4NO_2$ was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions, more than other metal ions. Thus, at first experiment, the complexation of the $PyTu_4NO_2$ with a number of lanthanide and common metal ions was investigated conductometrically in acetonitrile solutions (1.0×10^{-4} M of cation solution and 1.0×10^{-2} M of ligand) at 25 ± 0.1 °C [27], in order to obtain a clue about the stability and selectivity of resulting complexes. The formation constants (K_f) of the resulting 1:1 complexes are given in Table 1. As can be seen, the $PyTu_4NO_2$ with the most stable complex with Gd(III) ion is expected to act as a suitable ion-carrier for fabrication of a Gd(III) ion-selective membrane sensor.

In the next experiments, $PyTu4NO_2$ was used as a neutral ion carrier to fabricate a number of PVC-based membrane sensors for a variety of alkali, alkaline earth and transition metal ions. The potential responses of the most sensitive metal ion sensors are shown in Fig. 2. As it can be seen from Fig. 2, except for Gd(III) ion, the slopes of emf versus pM^{n+} were smaller than the expected Nernstian response for mono-, di- and tri-valent cations. Among the different metal ions used, only Gd(III) ion with the most sensitive response can be suitably determined with the PVC membrane sensor based on $PyTu4NO_2$. This is most probably due to the proper size of Gd(III) ion to the semi-cavity of the $PyTu4NO_2$.

It is well established that some important features of the PVC membranes such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of the ion carrier, and