Materials Science and Engineering C 31 (2011) 307–312

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Praseodymium analysis in aqueous solution by Pr^{3+}–PVC membrane sensor based on *N*,*N*′-bis(4-hydroxysalicylidene)-1-3-phenylenediamine

Hassan Ali Zamani [a,*], Ali Arvinfar [a], Fatemeh Rahimi [a], Alihossien Imani [a], Mohammad Reza Ganjali [b], Soraia Meghdadi [c]

[a] Department of Applied Chemistry, Quchan branch, Islamic Azad University, Quchan, Iran
[b] Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran
[c] Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

ARTICLE INFO

Article history:
Received 29 January 2010
Received in revised form 13 August 2010
Accepted 24 September 2010
Available online 1 October 2010

Keywords:
Potentiometry
Sensor
Ion-selective electrode
PVC membrane

ABSTRACT

A new Pr^{3+} poly vinyl chloride PVC membrane sensor based on a membrane containing 3% *N*,*N*′-bis(4-hydroxysalicylidene)-1-3-phenylenediamine (HSPDA) as an ionophore, 2% sodium tetraphenyl borate (NaTPB) as an anionic additive, 65% benzyl acetate (BA) as solvent mediator and 30% poly(vinyl chloride) was prepared. This sensor responds to praseodymium ion in a wide linear dynamic range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} with Nernstian slope of 19.8 ± 0.4 mV per decade and a detection limit of 5.7×10^{-7} mol L^{-1} in pH range of 3.1 to 9.8. It has a fast response time of ~5 s in the whole concentration range, and can be used for at least 2 months without any considerable divergences in the potentials. The proposed sensor displays an excellent selectivity for Pr^{3+} ions with respect to a large number of alkali, alkaline earth, transition and heavy metal ions. The developed sensor was successfully applied as an indicator electrode in Pr^{3+} ion potentiometric titration with EDTA, and in direct determination of fluoride ion in two mouth wash samples.

1. Introduction

Praseodymium is one of the rare chemicals that can be found in houses, in equipment such as color televisions, fluorescent lamps, energy-saving lamps and glasses. Praseodymium used as a core material for carbon arc lights is used by the motion picture industry. Praseodymium is added to fiber optic cables as a doping agent where it is used as a signal amplifier. Praseodymium salts are used to give glasses and enamels a yellow color. Praseodymium is dumped in the environment in many different places, mainly by petrol-producing industries. It can also enter the environment when household equipment is thrown away. Praseodymium will gradually accumulate in soils and water soils and this will eventually lead to increasing concentrations of Pr^{3+} in humans, animals and soil particles [1,2].

The biological properties of praseodymium ion as well as other lanthanide ions, due to their similarity to Ca^{2+} ion, have been the basis for therapeutic applications of lanthanides since the twentieth century. The lanthanide ions have similar ionic radii to calcium, but by virtue of possessing a higher charge, they have a high affinity for Ca^{2+} sites on biological molecules [3]. They have been used as biochemical probes to study calcium transport in mitochondria and other organelles.

Many techniques have been developed in order to determine the amount of Pr^{3+} ion in real samples including; absorption spectra of the 4f electron transitions [4], derivative spectroscopy [5] and some other spectroscopic methods [6–11]. These methods are time consuming, involving multiple sample manipulations and are too expensive for most analytical laboratories. In this paper we are going to introduce a new simple and inexpensive electrochemical sensor based on a sensing component *N*,*N*′-bis(4-hydroxysalicylidene)-1-3-phenylenediamine (HSPDA) (Fig. 1).

Lately, several studies concerning selective and sensitive PVC membrane ion-selective electrodes were reported for some other ions [12–14]. In this work, we introduce a new selective and sensitive Pr^{3+} PVC membrane sensor based on HSPDA for potentiometric determination of a wide concentration range of Pr^{3+} ion.

2. Experimental

2.1. Reagents and materials

Reagent grade dibutylphthalate (DBP), nitrobenzene (NB), acetophenon (AP), benzyl acetate (BA), high-molecular weight polyvinylchloride (PVC) and tetrahydrofuran (THF) were purchased from Fluka and Aldrich. The ligand *N*,*N*′-bis(4-hydroxysalicylidene)-1-3-phenylenediamine (HSPDA) was synthesized and purified as described elsewhere [15]. Reagent grade of chloride and nitrate salts of used cations were purchased from from Merck and Aldrich. All solutions were prepared using doubly distilled deionized water.

* Corresponding author. Tel.: +98 581 224 1801; fax: +98 581 2226093.
E-mail address: haszamani@yahoo.com (H.A. Zamani).

0928-4931/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2010.09.016

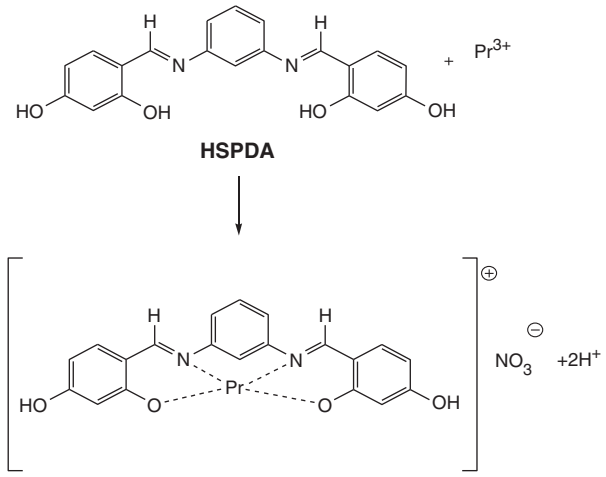

Fig. 1. The HSPDA chemical structure and its interaction with Pr^{3+} ion.

2.2. Preparation of the membrane

Membrane solutions were prepared by thoroughly dissolving 3.0 mg of HSPDA, 30 mg of powdered PVC, 65 mg of BA and 2.0 mg of NaTPB in 3 mL of fresh THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm o.d. on top) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm thickness was formed. The tube was pulled out from the mixture and kept at room temperature for 12 h [16]. The tube was then filled with an internal solution (1.0×10^{-3} mol L^{-1} $PrCl_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} Pr^{3+} ion solution. A silver/silver chloride electrode was used as an internal reference electrode.

2.3. Electro motive force (emf) measurements

The emf measurements of polymeric membrane were carried out with the following cell assembly:

Ag–AgCl|internal solution, 1.0×10^{-3} mol L^{-1} $PrCl_3$|PVC membrane|test solution|Hg–Hg_2Cl_2, KC1 (satd.).

A Corning ion analyzer 250 pH/mV meter was used for potential measurements at 25.0 °C. The activities were calculated according to Debye–Huckel procedure [17].

2.4. Conductometric study

In all measurements, the cell is thermostated at 25.0 °C, using a Phywe immersion thermostat. In typical experiments, 25 mL of an ion solution (1.0×10^{-4} mol L^{-1}) are placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, it should be noted that both the starting solution and the titrant have the same ion concentration. Then, a known amount of an ionophore or a ligand (1.0×10^{-2} mol L^{-1}) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition.

The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved.

3. Results and discussion

The major problem in the field of lanthanide potentiometric membrane sensors was finding a selective ionophore. Lanthanide series are rather similar. Having different radii of the lanthanum ions (from Ce^{3+} to Lu^{3+} their radii vary from 1.02 to 0.80°A, respectively) causes their different properties, such as charge densities and hydration energy (from Ce^{3+} to Lu^{3+} their hydration energy ranges from 3370 to 3760 kJ mol^{-1}) [18]. The only way to design an ion-selective electrode for the lanthanide ions is using ionophores having semi cavity, heteroatoms (N, O and S as donor atoms), and high flexibility. Such an ionophore can easily form a template with reference to the size of the cation [19]. Furthermore, these kinds of ionophores are able to form a stronger complex with one of the lanthanide cations than the other ones with the optimum free energies. This phenomenon can be attributed to type, number and site of its donor atoms, its flexibility as well as the size and the charge density of the cation. Schiff's base compounds, like HSPDA, refer to the branch of supramolecules that can be used as a suitable sensing material in the construction of potentiometric ion-selective electrodes for lanthanide series.

For checking the selectivity of HSPDA, initially, its interaction with numerous metal ions was monitored conductometrically in an acetonitrile solution [20,21]. The complex formation constant (Table 1), K_f, shows the selectivity of the used ionophore toward Pr^{3+} ions (K_f: 5.6×10^6) among the all other cations tested.

3.1. Potential response of Pr^{3+} sensor

The HSPDA-based PVC membrane electrode creates stable potential response to praseodymium ions in aqueous solutions after conditioning for 24 h in a 0.01 mol L^{-1} praseodymium solution. The potential responses of all lanthanide membrane sensors were studied in a wide range of concentration of lanthanide solutions. Except Pr^{3+} ion-selective electrode, the slope of calibration curve plots of all other metal ions, were much lower than the expected Nernstian slope of 20 mV per decade for the trivalent ions. Among the lanthanide ions tested, Pr^{3+} with the most sensitive response seems to be suitably determined with PVC membrane based HSPDA. This is probably due to the selective behavior of the ion carrier toward Pr^{3+} ion in comparison with other lanthanide ions tested, and the rapid exchange kinetics of the resulting HSPDA–Pr^{3+} complex.

3.2. Effect of membrane composition

The sensitivity and selectivity of an ion-selective electrode resulted from membrane ingredients, nature of solvent mediators and the additives used [22,23]. To investigate these effects, the nature

Table 1
Formation constant of HSPDA with some metal ions.

Ion	K_f
Pr^{3+}	5.6×10^6
La^{3+}	2.0×10^4
Sm^{3+}	1.1×10^4
Yb^{3+}	9.6×10^3
Ho^{3+}	7.3×10^3
Nd^{3+}	4.2×10^3
Eu^{3+}	4.1×10^3
Lu^{3+}	3.5×10^3
Tm^{3+}	3.3×10^3
Er^{3+}	1.4×10^3
Gd^{3+}	9.1×10^2
Tb^{3+}	8.7×10^2
Dy^{3+}	8.3×10^2
Co^{2+}	6.6×10^2
Ni^{2+}	5.4×10^2
Fe^{3+}	$<10^{-2}$
Cr^{3+}	$<10^{-2}$
Na^{+}	$<10^{-2}$
K^{+}	$<10^{-2}$
Ca^{2+}	$<10^{-2}$
Pb^{2+}	$<10^{-2}$