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Determination of Tb³⁺ Ions in Solution Samples by a Tb³⁺-Polyvinyl Chloride Membrane Sensor

Hassan Ali Zamani and *Mohammad Reza Abedi

Department of Applied Chemistry, Quchan Branch, Islamic Azad University, Quchan, Iran

ABSTRACT

In this work, a highly terbium PVC-membrane sensor based on N-phenyl-2-(phenylcarbamoithiyl) hydrazinecarboxamide as a suitable ion carrier was created. The resulting data illustrated that the electrode presents a Nernstian slope of 19.7 ± 0.5 mV per decade for the Tb³⁺ ions across a broad working concentration range from 1.0×10^{-6} to 1.0×10^{-2} M. The detection limit of the electrode is 5.6×10^{-7} M. It has a useful working pH range of 2.8 –8.5. The potentiometric response of the proposed electrode is independent of the pH of the solution in the pH range of 3.0 –7.5. The sensor possesses the advantages of short conditioning time, fast response time (~10 s), and especially, very good selectivity towards transition and heavy metal, and some mono, di and trivalent cations. The practical applicability of the electrode was demonstrated by its use the determination of Tb(III) ions in water solutions (tap water and river water) and in various binary mixtures.

Keywords: PVC Membrane, Ion-Selective Electrode, Potentiometry, Sensor.

INTRODUCTION

With the increase of the rare earths applications in agricultural, metallurgical and functional material areas, etc., convenient, fast and sensitive analysis methods are urgently required. Terbium is used for carbon arcs, gasoline-cracking catalysts, and in movie projectors. There are some expensive and time consuming methods which have been used for the Tb(III) determination such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectrometry, Isotope dilution mass spectrometry and neutron activation analysis. It is important to find a sensitive and selective method which is quick and inexpensive. Thus, a selective sensor was constructed for the potentiometric determination of this element. Currently, the usage of the ion selective electrode as sensor element for potentiometric determination is popular because it demonstrates some special properties. At first, this method is simple and it is

not necessary to equip with expensive instrument. Secondly, this method is fast and also it is a selective method that can determine the ions value while some other lanthanides ions are present in low concentrations [1-15]. We have recently reported a number of highly selective and sensitive PVC-membrane ion-selective electrodes for alkaline earth and transition metal ions [16-32]. This study exhibits the development of a new ion selective sensor for the Tb(III) determination in real sample solutions and, in particular, the use of N-phenyl-2-(phenylcarbamothioyl) hydrazinecarboxamide as an excellent ionophore for the preparation of a highly Tb(III) ion-selective electrode.

EXPERIMENTAL SECTION

Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), nitrobenzene (NB), acetophenone (AP), 2-nitrophenyl octyl ether (NPOE), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Merck and Aldrich, used as received. The nitrate and chloride salts of all cations used (all from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P₂O₅. Doubly distilled de-ionized water was used throughout.

The phenylcarbamic chloride (1mmol, 0.155gr) was solved in hot ethanol, after that the N-Phenylhydrazinecarbothioamide (1mmol, 0.167gr) was added to the solution of phenylcarbamic chloride. The mixture of reaction was refluxed for hour. Then the solid product was crystallized in solution of Acetone and ethanol (1:1) [33-35].

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 65 mg of plasticizer DBP, 2 mg of additive NaTPB, and 3 mg of ionophore in 5 mL of fresh THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5mm o.d.) 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 then pulled out from the mixture and kept at the room temperature for about 12 h. The tube was then filled with internal filling solution (1.0×10^{-3} M of TbCl₃). The electrode was finally conditioned by soaking in a 1.0×10^{-2} M TbCl₃ solution for 24 h [5-15]. A silver/silver chloride wire was used as an internal reference electrode.

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

Ag–AgCl | internal solution, 1.0×10^{-3} M TbCl₃ | PVC membrane | sample solution | Hg–Hg₂Cl₂, KCl (satd.).

A Corning ion analyzer with a 250 pH/mV meter for the potential measurements at 25.0 ± 0.1 °C. The activities were calculated according to the Debye–Hückel procedure.

RESULTS AND DISCUSSION

At first, the N-phenyl-2-(phenylcarbamothioyl) hydrazinecarboxamide was used as ionophore in fabricating of a Tb(III)-PVC membrane sensor. Then, different aspects (such as the nature and the amount of the ionophore, the kind of plasticizer, the plasticizer/PVC ratio and, especially, the nature of the used additives) [36-40] of the constructed Tb(III)-selective membrane were optimized. On the obtained results, the membrane incorporating 65% DBP and 30% PVC, in the presence of 2% ionophore and 2% NaTPB, showed the best sensitivity, with a good Nernstian

slope of 19.7 ± 0.5 mV per decade of Tb(III) concentrations (1.0×10^{-6} to 1.0×10^{-2} M). The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5.6×10^{-7} M. The dependence of sensor's potential response on the pH has been tested over a range of 2.0–10.0 for 1.0×10^{-3} M of Tb^{3+} ion. The operational range was studied by varying the pH of the test solution with nitric acid or sodium hydroxide solutions. The potential of the Tb(III) sensor is independent of pH in the range of 2.5–8.5. The dynamic response time of the membrane was measured at various concentrations (1.0×10^{-6} to 1.0×10^{-2} M) of the test solutions. In the whole concentration range, the electrode reaches its equilibrium response, very fast (~10 s). For the determination of selectivity coefficients, matched potential method (MPM) was used [39]. For all tested ions, indicating they would not radically disturb the function of the developed Tb(III) membrane sensor.

Because of high selectivity and low detection limit of the developed Tb^{3+} sensor, it was successfully applied to the determination of Tb^{3+} ions in tap water and river water samples and the results of triplicate measurements are summarized in Table 1. The corresponding results in Table 1 reveal that the recovery of Tb^{3+} ions in all mixtures is acceptable.

The proposed Tb^{3+} sensor was also applied for the monitoring of the concentration of Tb^{3+} ions in various binary mixtures, and the results are given in Table 2. As it is seen, the recoveries of the Tb^{3+} ions in all mixtures are acceptable and in the range of 96.8-103.7%.

Table 1: Determination of Tb^{3+} in water samples solutions using the constructed sensor

Sample	Tb^{3+} added (mg/mL)	Found (mg/mL)	Recovery (%)
River water	0.25	$(0.28^a \pm 0.04)$	112
	0.5	(0.57 ± 0.03)	114
Tap water	0.25	(0.27 ± 0.02)	108
	0.5	(0.54 ± 0.04)	108

a. Results are based on three measurements

Table 3: Recovery of Tb^{3+} ions from binary mixtures by the proposed Tb^{3+} ion-selective electrode

Tb(III) (ppm)	Added cation (ppm)	Recovery (%)
20	Dy^{3+} , 100	$103.4^a \pm 0.4$
20	La^{3+} , 100	98.6 ± 0.2
20	Nd^{3+} , 100	101.7 ± 0.3
20	Gd^{3+} , 100	99.4 ± 0.6
20	Sm^{2+} , 100	101.6 ± 0.3
20	Yb^{2+} , 100	99.7 ± 0.5
20	Lu^{2+} , 100	97.3 ± 0.2
20	Tm^{3+} , 100	98.6 ± 0.6
20	Fe^{3+} , 100	102.8 ± 0.6
20	Cr^{3+} , 100	99.6 ± 0.5
20	Zn^{2+} , 100	103.7 ± 0.2
20	Ni^{2+} , 100	101.1 ± 0.3
20	Co^{2+} , 100	99.2 ± 0.7
20	Pb^{2+} , 100	101.5 ± 0.4
20	Ca^{2+} , 100	96.8 ± 0.6
20	Mg^{2+} , 100	102.3 ± 0.3
20	K^+ , 100	97.9 ± 0.5
20	Na^+ , 100	102.7 ± 0.2

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