Gadolinium(III) Ion-Selective Electrode Based on 3-Methyl-1*H*-1,2,4-triazole-5-thiol

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Abstract: The 3-methyl-1*H*-1,2,4-triazole-5-thiol (MTH) was used as a suitable ionophore for fabrication of a new gadolinium(III) ion selective potentiometric sensor. Nitrobenzene (NB) was used as plasticizing solvent mediator and sodium tetraphenyl borate (NaTPB) as an anion excluder. It displays a Nernstian response (19.8 ± 0.4 mV/decade) in the concentration range of 1.0×10^{-7} to 1.0×10^{-2} M with the detection limit of 7.3×10^{-8} M. The sensor has a very short response time (< 10 s) and can be used the pH range of 2.9-8.4. The electrode was successfully applied as an indicator electrode for the gadolinium determination in titration with EDTA.

Keywords: PVC membrane, Sensor, Potentiometry, Ion selective electrode

Introduction

The quick determination of minute quantities of ionic species by simple methods is of special interest in analytical chemistry. During the last decade, there has been a renewed resurgence in developing potentiometric membrane electrodes as devices for rapid, accurate, low cost and nondestructive analysis of different samples with small volume samples. Ion-selective sensors based on plasticized PVC membranes were successfully applied to the determination of many cations in various industrial, environmental and biochemical samples¹⁻³.

Many techniques have been used for determination of Gd which most of them have been spectroscopic methods such as inductively coupled Plasma-mass spectrometry (ICP-MS), atomic emission spectroscopy, electron spin resonance, laser-based multi step resonance ionization, phosphorescence opto-sensing, high-resolution ^{13}C -spectroscopy, time-resolved fluorimetry, spectrophotofluorimetric determination, quenching of gadolinium

fluorescence and some nucleic methods. Recently, several greatly selective and sensitive PVC-membrane ion-selective electrodes for various metal ions have been reported^{4,21}. This research focuses on the introduction of a highly Gd(III)-selective sensor based on 3-methyl-1H-1,2,4-triazole-5-thiol (MTH) (Figure 1), as an ionophore for determination of Gd(III) ion concentration.

Figure 1. Chemical structure of MTH

Experimental

The ionophore MTH was synthesized as described elsewhere²². Nitrate and chloride salts of all cations and the reagent grades of dibutyl phthalate (DBP), nitrobenzene (NB) benzyl acetate (BA), acetophenone (AP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were all purchased from Merck Chemical Co. All reagents were used without any further modification. During the experiments, deionized distilled water was used.

Electrode preparation and emf measurements

Blending completely 30 mg of powdered PVC, 66 mg of NB and 2 mg of NaTPB in 5 mL THF was the first step for the PVC membrane construction. The second step involved the addition of 2 mg MTH. After well mixing the resulting mixture, it was transferred into a glass dish of 2 cm in diameter. A Pyrex tube (5 mm i.d.) was dipped into the mixture for about 5 s, so that a non-transparent membrane (about 0.3 mm in thickness) is formed. The tube was, then, removed from the mixture, kept at room temperature for about 12 h and filled with an internal filling solution (1.0×10^{-3} M GdCl_3). Finally, the electrode was conditioned by soaking in a 1.0×10^{-3} M GdCl_3 solution for 24 h²³⁻³³. As an internal reference electrode, a silver/silver chloride electrode was used.

All emf measurements were carried out with the following assembly: Ag–AgCl | 1.0×10^{-3} mol L^{-1} GdCl_3 | PVC membrane: test solution | $\text{Hg-Hg}_2\text{Cl}_2$, KCl (satd). A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. The activities were calculated according to the Debye–Huckel procedure.

Results and Discussion

In the preliminary experiment, MTH was used as a sensing material to prepare the PVC membrane ion-selective electrodes for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. Among different metal ions tested, Gd^{3+} ion seems to be suitably determined with the membrane sensor based on MTH. This observation is most probably due to the proper size of Gd^{3+} ion to the semi cavity of flexible MTH and the rapid exchange kinetics of the resulting MTH – Gd^{3+} complex.

In the next step, membrane ingredients effect (the nature and the amount of the ionophore, the nature and the amount of the used additive and the kind of plasticizer) were investigated on the potential response of the Gd^{3+} electrode³⁴⁻³⁹. The results are shown in Table 1. Among four plasticizers tested, NB offers the best sensitivity. This phenomenon can be due to the effect of plasticizer dielectric constant on the organic phase of the membrane. In accordance with Table 1, using 2% of MTH in the membrane electrode

displays Nernstian slope towards Gd(III) ion (membrane No. 3). However, the membrane sensor with the composition of 30% PVC, 66% NB, 2% NaTPB and 2% MTH displays a very nice Nernstian behavior.

Table 1. Optimization of the membrane ingredients

Sensor No.	Composition of the membrane, wt, %				Slope (mV decade ⁻¹)	Dynamic Linear range (M)
	PVC	Plasticizer	MTH	NaTPB		
1	30	NB, 68	0	2	9.4 ± 0.3	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻²
2	30	NB, 67	1	2	22.3 ± 0.5	1.0 × 10 ⁻⁷ - 1.0 × 10 ⁻²
3	30	NB, 66	2	2	19.8 ± 0.4	1.0 × 10 ⁻⁷ - 1.0 × 10 ⁻²
4	30	NB, 65	3	2	19.4 ± 0.3	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻²
5	30	NB, 68	2	0	14.9 ± 0.7	1.0 × 10 ⁻⁷ - 6.0 × 10 ⁻²
6	30	NB, 67	2	1	14.2 ± 0.2	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻²
7	30	NB, 65	2	3	16.6 ± 0.3	1.0 × 10 ⁻⁷ - 1.0 × 10 ⁻²
8	30	AP, 66	2	2	17.9 ± 0.2	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻²
8	30	BA, 66	2	2	16.8 ± 0.5	1.0 × 10 ⁻⁶ - 1.0 × 10 ⁻²
9	30	DBP, 66	2	2	17.3 ± 0.4	1.0 × 10 ⁻⁵ - 1.0 × 10 ⁻²

The potential response of the suggested MTH based sensor (composition no. 3) at varying gadolinium ion concentrations demonstrated a linear response to the gadolinium ion concentration in the range 1.0 × 10⁻⁷ - 1.0 × 10⁻² M (Figure 2). The slope of the calibration graph was 19.8 ± 0.4 mV per decade. The detection limit was 7.3 × 10⁻⁸ M.

The pH dependence of the membrane electrode was evaluated over a pH range of 2.0-11.0 at a 1.0 × 10⁻³ M of gadolinium ion concentration and the results are depicted in Figure 3. As can be seen, the potential remains fairly constant in the pH range of 2.9 - 8.4 (the pH of the solutions was adjusted by either HNO₃ or NaOH solutions). Beyond this range, a gradual change in the potential was detected. The observed potential drift at the higher pH values could be due to the formation of some hydroxyl complexes of Gd(III) and insoluble gadolinium hydroxide, that in both cases, the concentration of free Gd(III) reduces in the solution. At the lower pH values than 2.9, the potentials increase, indicating that the membrane sensor responds to hydrogen ions protonation of nitrogen atom in structure of MTH.

Figure 2. Calibration curves of the MTH-based gadolinium electrode

Figure 3. pH effect of the test solution (1.0 × 10⁻³ M of Gd³⁺) on the potential response of the Gd³⁺ ion-selective electrode

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the concentration of gadolinium

ion in solution in the range of 1.0×10^{-7} to 1.0×10^{-2} M and the results are shown in Figure 4. As can be seen, in the whole concentration range the electrode reaches its equilibrium response, very fast (<10 s).

The gadolinium membrane sensor was used as an indicator electrode in the successful titration of a gadolinium ion solution (1.0×10^{-4} M) with EDTA (1.0×10^{-2} M). The resulting titration curves are depicted in Figure 5. As seen from Figure 5, the amount of gadolinium can be determined with the proposed sensor.

Figure 4. Dynamic response time of the gadolinium electrode for step changes in the Gd^{3+} concentration: A) 1.0×10^{-7} M, B) 1.0×10^{-6} M, C) 1.0×10^{-5} M, D) 1.0×10^{-4} M, E) 1.0×10^{-3} M, F) 1.0×10^{-2} M

Figure 5. Potential titration curve of 20.0 mL from a 1.0×10^{-4} M Gd^{3+} solution with 1.0×10^{-2} M of EDTA

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