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Tb^{3+}-PVC Membrane Sensor Based on 1,4-bis[o-(furan-2-carboxamidophenyl)]-1,4-dithiobutane as a sensing material

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ABSTRACT

In this study, a new terbium(III) membrane sensor was constructed based on 1,4-bis[o-(furan-2-carboxamidophenyl)]-1,4-dithiobutane (FCT) as a suitable materisl. The proposed membrane sensor was fabricated based on a membrane containing 2% sodium tetraphenyl borate (NaTPB) as an anionic additive, 66% dibutyl phthalate (DBP) as solvent mediator, 2% 1,4-bis[o-(furan-2-carboxamidophenyl)]-1,4-dithiobutane (FCT) as an ionophore and 30% poly vinyl chloride (PVC).The proposed Tb^{3+} electrode exhibits a Nernstian slope of 20.7 ± 0.2 decade of activity was demonstrated with a response time of 5 s, and has a lower detection limit of 7.5×10^{-8} M.The linear range of the sensors was 1.0×10^{-7}-1.0×10^{-2} M. It could be used in a pH range of 2.5–7.8.

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

INTRODUCTION

Terbium and other lanthanides are used for gasoline-cracking catalysts, carbon arcs, and in movie projectors. The available methods for the low-level monitoring of terbium ion in solutions are spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), Isotope dilution mass spectrometry, neutron activation analysis and X-ray fluorescence spectrometry. These methods are either time consuming, involving multiple sample manipulation or too expensive for the most analytical laboratories. The potentiometric membrane sensors have shown to be very effective tools for the analysis of a wide variety of metal ions. They are very simple, fast, inexpensive and capable of a reliable response provision in broad concentration ranges [1-10]. We have recently introduced PVC based membrane sensors for different cations based on different neutral ionophores [11-25]. Due to the vital importance of terbium in industry, and the urgent need for a Tb(III)-selective electrode for potentiometric monitoring of terbium, we introduce a selective and sensitive terbium ion selective membrane electrode for potentiometric monitoring of trace

amounts of Tb^{3+} by using 1,4-bis[o-(furan-2-carboxamidophenyl)]-1,4-dithiobutane (FCT) (Fig. 1) as the ionophore for determination of this ion.

EXPERIMENTAL SECTION

The Aldrich and the Merck Chemical Co. were the suppliers for the nitrate and chloride salts of all cations, the reagent grades of benzylacetate (BA), dibutyl phthalate (DBP), acetophenone (AP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and relatively high molecular weight PVC. The ionophore 1,4-bis[o-(furan-2-carboxamidophenyl)]-1,4-dithiobutane was prepared as formerly described [26-29]. All reagents were used without any modification. As far as the nitrate and chloride salts of all employed cations are concerned, they were of the highest available purity and were P_2O_5-vacuum dried. During the experiments, triply distilled deionized water was used.

The PVC membrane was prepared by blending 2 mg FCT ionophore, 2 mg NaTPB, 66 mg DBP and 30 mg PVC and dissolving in 3 mL THF. The resulting homogeneous mixture was transferred into a glass dish with a 2 cm diameter. A Pyrex tube (5 mm i.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm in thickness was formed. The tube was, then, removed from the mixture, kept at room temperature for at least 12 h and filled with an internal filling solution (1.0×10^{-3} M $TbCl_3$) [30-34]. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M Tb^{3+} ion solution. A silver/silver chloride electrode was used as an internal reference electrode.

All emf measurements were carried out with the following assembly:
Ag–AgCl | internal solution, 1.0×10^{-3} M $TbCl_3$ | PVC membrane | sample solution | Hg–Hg_2Cl_2, KC1 (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 DISCUSSIONS

In order to obtain a clue about the stability and selectivity of the ionophore, FCT was used as a neutral carrier to prepare several PVC membrane ion-selective electrodes under identical conditions for a variety of metal ions. The potential responses versus concentration (activity) for different ion-selective electrodes was investigated. From on obtained results, except for the Tb^{3+} ion, for all other ions, the slope of the corresponding potential pM-plots is much lower than the excepted Nernstian slopes of 59, 29.5 and 20mV per decade for the uni, di and trivalent cations, respectively. This is likely due to the high selectivity of the ionophore for terbium ions over other metal ions, as well as the rapid exchange kinetics of the resulting Tb^{3+}-FCT complex.

It is well known that some important features of the PVC based membranes (such as the nature and the amount of the ionophore, the plasticizer properties, the plasticizer/PVC ratio and, especially, the nature of the used additives) significantly influence the sensitivity and the selectivity of the ion-selective electrodes. Also, the perm-selectivity optimization of the membrane sensor is known to be highly dependent on the incorporation of the additional components. The presence of the lipophilic negatively charged additives improves the potentiometric behavior of certain selective electrodes by reducing the ohmic resistance and improving the response behavior and selectivity [35-41]. Therefore, the effect of the membrane composition on the potential response of the Tb(III) electrode was investigated. The results are

summarized in Table 1. It can be seen that increasing the amount of ionophore, up to a value of 2%, in the presence of 2% NaTPB and 66% DBP results in the best sensitivity. The best response was exhibited by the (no. 4) membrane incorporating FCT, PVC, DBP and NaTPB in the ratio of 2:30:66:2 (FCT:PVC:DBP:NaTPB) (wt%), respectively.

The potential response of the electrode at varying concentration of Tb^{3+} ions displays a linear response with respect to the concentration of Tb^{3+} ions in the range of 1.0×10^{-7}-1.0×10^{-2} M (Fig. 2). The slope of calibration graph was 20.7 ± 0.2 mV/decade of the activity of Tb^{3+} ions. The detection limit of the sensor as determined from the intersection of the two extrapolated segments of the calibration graph was 7.5×10^{-8} M.

The effect of pH on the potentiometric response of the terbium membrane sensor in the pH range of 1.5–9.0 for a solution containing 1.0×10^{-3} M of terbium was investigated. The pH was adjusted with HNO_3 and NaOH, and the results are shown in Fig. 3. The response of the sensor is shown to be independent of the solution pH within 2.5–7.8.

Notably, a considerable factor for any ion selective electrode is the dynamic response time. The practical response time of this work was recorded with the change the terbium ion concentration in solution in the range of 1.0×10^{-7} to 1.0×10^{-2} M. The respective resulting data are presented in Fig. 4. It can be observed that in the whole concentration range the electrode reaches quickly (~ 5 s) its equilibrium response.

Table 1. Composition of membrane ingredients

Sensor No.	Composition (wt. %)				Slope (mV/decade)	Linear range (M)
	PVC	Plasticizer	Additive	FCT		
1	30	NB, 66	NaTPB,2	2	18.8 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
2	30	AP, 66	NaTPB,2	2	15.6 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
3	30	BA, 66	NaTPB,2	2	17.3 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
4	30	DBP, 66	NaTPB,2	2	20.7 ± 0.2	1.0×10^{-7}-1.0×10^{-2}
5	30	DBP, 68	NaTPB,2	0	8.4 ± 0.4	5.0×10^{-5}-1.0×10^{-2}
6	30	DBP, 67	NaTPB,2	1	17.9 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
7	30	DBP, 65	NaTPB,2	3	18.2 ± 0.6	1.0×10^{-7}-1.0×10^{-2}
8	30	DBP, 68	NaTPB,0	2	12.5 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
9	30	DBP, 67	NaTPB,1	2	18.2 ± 0.3	1.0×10^{-7}-1.0×10^{-2}
10	30	DBP, 65	NaTPB,3	2	18.6 ± 0.2	1.0×10^{-7}-1.0×10^{-2}

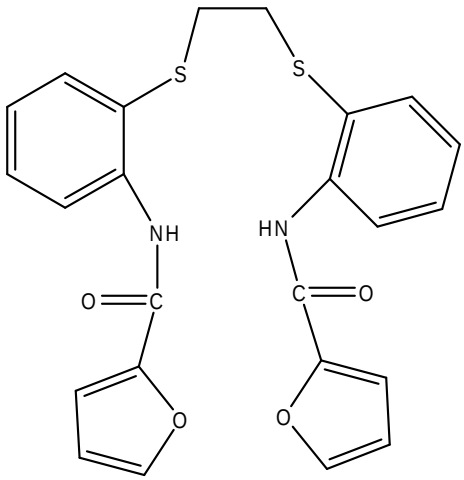

Figure 1. FCT structure

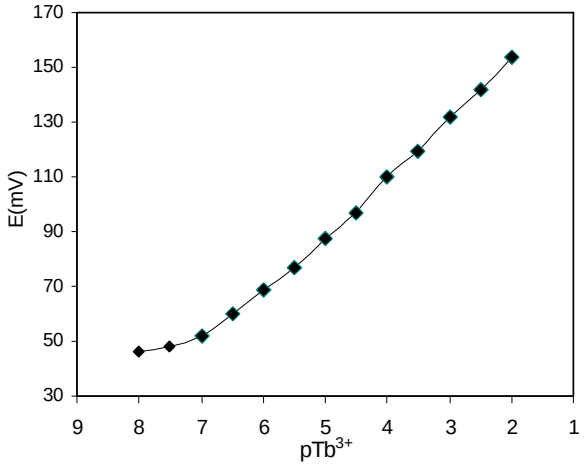

Figure 2. Calibration curve of Tb^{3+} sensor based on FCT.

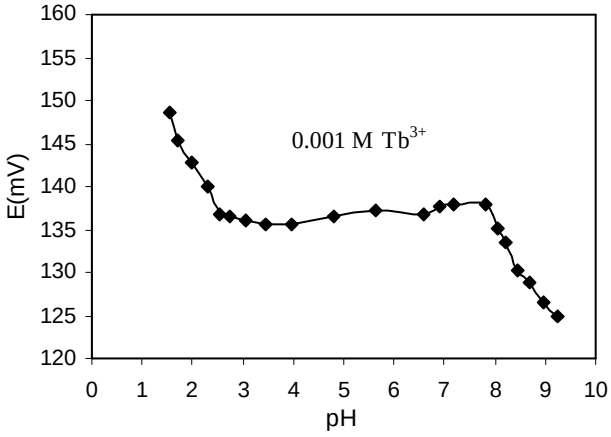

Figure 3. pH effect of the test solution (1.0×10^{-3} M of Tb^{3+}) on the potential response.

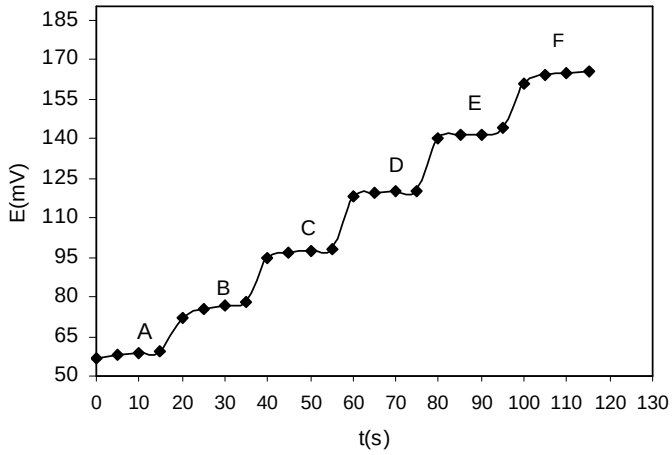

Figure 4. Dynamic response time of the terbium electrode for step changes in the Tb^{3+} concentration: A) 1.0×10^{-7} M, B) 1.0×10^{-6} M, C) 1.0×10^{-5} M, D) 1.0×10^{-4} M, E) 1.0×10^{-3} M, F) 1.0×10^{-2} M.

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