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Design of Highly Selective and Sensitive PVC-Membrane Sensor for Terbium Ions Based on Di(N-succinimidyl)carbonate as a Neutral Ion Carrier

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A highly selective and sensitive Tb^{3+}-PVC membrane sensor was created from poly (vinyl chloride) (PVC) matrix membrane containing Di(N-succinimidyl)carbonate (NSC) as an neutral carrier, oleic acid (OA) as anionic excluder and nitrobenzene (NB) as a plasticizing solvent mediator. The electrode performance includes a Nernstian slope of 19.8 ± 0.3 $mVdecade^{-1}$ across a wide concentration range between 1.0×10^{-6} and 1.0×10^{-2} mol L^{-1} and a detection limit of 5.8×10^{-7} mol L^{-1} in a pH range of 4.0–9.0. The sensor possesses the advantages of short conditioning time, fast response time (~5 s) and, especially, great selectivity towards transition and heavy metal and some mono, di and trivalent cations. The developed Tb^{3+} sensor was successfully used as an indicator electrode in potentiometric titration of Tb^{3+} ions against EDTA as well as for the determination of terbium ions in mixtures of different metal ions.

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

1. INTRODUCTION

Terbium is a chemical element with the symbol Tb and atomic number 65. It is a silvery-white rare earth metal that is malleable, ductile and soft enough to be cut with a knife. Terbium is never found in nature as a free element, but it is contained in many minerals, including cerite, gadolinite, monazite, xenotime and euxenite. Terbium is used to dope calcium fluoride, calcium tungstate and strontium molybdate, materials that are used in solid-state devices, and as a crystal stabilizer of fuel cells which operate at elevated temperatures [1]. Its oxide terbia (Tb_2O_3) is a white powder and the heptaoxide (Tb_4O_7) is a dark maroon color. The heptaoxide contains terbium in both its +3 and +4 oxidation states. The luminescence of Tb^{3+} is important in a significant number of applications.

Terbium is used in color phosphors in lighting applications such as trichromatic lighting and in color TV tubes. It also makes the green color on your Blackberry or other high definition screen [2].

In regards to Tb^{3+}, it has already been determined by different methods such as X-ray fluorescence, isotope dilution mass spectrometry, neutron activation analysis, inductively coupled plasma–mass spectroscopy (ICP-MS), ICP–atomic emission spectrometry (AES), and spectrophotometry [3-5]. However, these methods are either time consuming, involving sample manipulations or too expensive for most analytical laboratories. Potentiometric detection based on ion selective sensors, as a simple method, offer great advantages such as speed and ease of preparation and procedures, relatively short response times, reasonable selectivity, wide linear dynamic range, and low cost [6]. They also provide an analysis method without destruction of sample.

We and other researchers have recently introduced a number of PVC- membrane ion selective electrodes for various metal ions [7-36]. Among these metal ions, a little attention has been paid to the development of terbium sensors [37-39]. In this research, we wish to introduce a highly selective and sensitive Tb^{3+} sensor based on Di(N-succinimidyl)carbonate (NSC) (Fig. 1) as an excellent sensing material for the determination of Tb^{3+} ions in solutions.

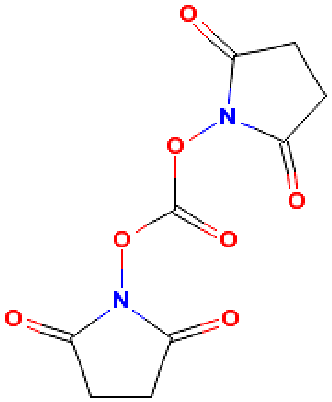


Figure 1. The structure of NSC.

2. EXPERIMENTAL

2.1. Chemicals and reagents

The Merck and the Aldrich Chemical Co. were the providers of the following reagent. grades: benzyl acetate (BA), nitrobenzene (NB), dibutyl phthalate (DBP), acetophenone (AP), oleic acid (OA), ion carrier Di(N-succinimidyl)carbonate, high relative molecular weight PVC, sodium tetraphenyl borate (NaTPB) and tetrahydrofurane (THF). Chloride and nitrate salts of the cations used (from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. During the experiments, doubly distilled de-ionized water was used.

2.2. The preparation of the sensor membrane

The general procedure to prepare the membrane was as followed: The desired amounts of PVC, plasticizer, the ionic additive, and NSC, summing up to 100 mg, were dissolved in tetrahydrofuran (THF). The solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter, and the solvent was evaporated slowly until an oily concentrated mixture remained. A Pyrex tube (3–5 mmo.d.) was dipped into the mixture for about 10 s. Thus, a transparent membrane of about 0.3 mm thickness formed. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0×10^{-3} mol L^{-1} $TbCl_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} $TbCl_3$ solution [40–56].

2.3. The EMF measurements

The EMF measurements with the polymeric membrane were carried out with the following cell assemblies:

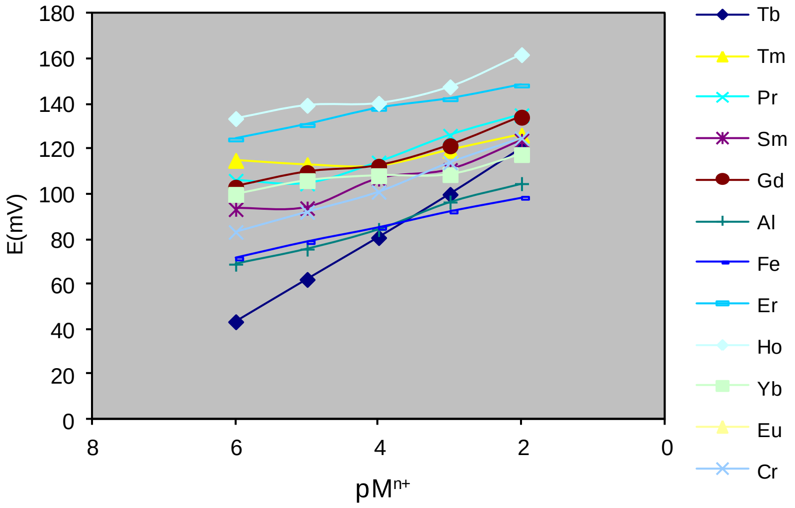
Ag–AgCl| 1.0×10^{-3} mol L^{-1} $TbCl_3$ | PVC membrane: test solution| Hg–Hg_2Cl_2, KCl (satd).

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 [57].

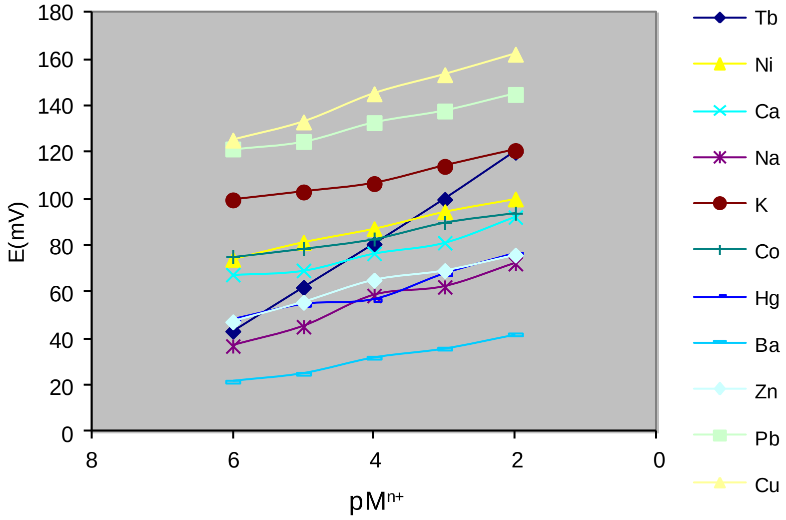
3. RESULTS AND DISCISSION

3.1. The potential response of the Tb^{3+} electrode based on NSC

In preliminary experiments, in order to check the suitability of NSC, it was used as an ion carrier to prepare PVC-based membrane sensors for a variety of common metal ions, including alkali, alkaline earth, transition and heavy metal ions.



(a)



(b)

Figure 2. Potential responses of various ion-selective electrodes based on NSC.

The potential responses of various ion-selective electrodes based on NSC are shown in Figure 2a and 2b. The respective potential responses of the ion selective electrodes based on NSC clearly exhibited that only the Tb^{3+} ion illustrated a strong response (with a slope of 19.8±0.3 $mVdecade^{-1}$), which probably stems from the selective tendency of NSC with toward Tb^{3+} ions in comparison with the other tested cations, including other lanthanide ions, and the rapid exchange kinetics of the resulting NSC-Tb^{3+} complex.

3.2. The membrane composition effect

The sensitivity and selectivity of the ion selective electrodes depend significantly on the membrane compositions, the nature of NSC employed, the nature of solvent mediators, the nature of ionic additives as well as the PVC/plasticizer ratio used [58-68]. Thus, the influences of the membrane composition, the nature and amount of plasticizer, NaTPB and OA as the lipophilic additives, and the amount of NSC as neutral carrier on the potential response of the proposed Tb^{3+} ion-selective electrode were investigated, are compared. Table 1 shows the different results with different composition membranes. In this study, a plasticizer/PVC ratio of about 2.0 was found to be the most suitable ratio. The amount of ion carrier (NSC) was also found to affect the sensitivity of the membrane sensor (membrane nos. 5–10). The sensitivity of the response of electrode enhances with increasing NSC content until a value of 2% is reached. Further addition of NSC will however result in diminished response of the sensor (membrane no. 21), most probably due to some inhomogenities and possible saturation of the membrane. Hence, the ionophore with composition of 2% was chosen as the optimum amount of ionophore in the PVC membrane (membrane no. 15). It should be noted that the sensitivity, selectivity, and measuring range of ion-selective membrane sensors are affected by the nature and amount of the plasticizer employed. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules, and the state of the ligands [69-72]. In this experiment, four plasticizers were used. As it was obvious from Table 1, among four plasticizers, NB was found to have the best detection limit and the widest linear range of the membrane electrode. This is because of the ability of NB to extract Tb^{3+} ions with high hydration energy from aqueous solution to the organic membrane phase.

The presence of ionic additives with large lipophilic anions in a cation selective membrane was also considered. Actually, the presence of such lipophilic negatively charged additives in a cation-selective membrane which is based on a neutral ionophore reduces the ohmic resistance, and improves the response behavior and selectivity. Furthermore, in cases where the extraction capability of the ionophore is poor, it enhances the sensitivityof the membrane sensor [73–82]. The results given in Table 2 exhibite that in the absence of a suitable additive, the sensitivity of the PVC membrane based on NSC is low (membrane nos. 5-10). However, the presence of 10% OA as a suitable lipophilic additive in the absence of NaTPB improves the sensitivity of the Tb^{3+} sensor considerably (no. 15 with slope of 19.8 mVdecade^{-1}). All the same, the membranes with a composition of 30% PVC, 2% NSC, 10% OA, and 58% NB exhibit a Nernstian potential response.

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition of the membrane (wt, %)				Slope / mVdecade^{-1}	Dynamic Linear range / molL^{-1}
	PVC	Plasticizer	NSC	Additive		
1	30	NB, 66	2	NaTPB,2;OA,0	18.4 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
2	30	AP, 66	2	NaTPB,2;OA0	6.9 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
3	30	BA, 66	2	NaTPB,2;OA,0	12.4 ± 0.6	1.0×10^{-5}-1.0×10^{-2}
4	30	DBP, 66	2	NaTPB,2;OA,0	8.5 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
5	30	NB, 60	1	NaTPB,9;OA,0	7.1 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
6	30	NB, 60	2	NaTPB,8;OA,0	6.8 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
7	30	NB, 60	3	NaTPB,7;OA,0	6.9 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
8	30	NB, 60	4	NaTPB,6;OA,0	7.9 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
9	30	NB, 60	5	NaTPB,5;OA,0	7.6 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
10	30	NB, 60	6	NaTPB,4;OA,0	7.7 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
11	30	NB, 61	2	NaTPB,2;OA,5	8.3 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
12	30	NB, 56	2	NaTPB,2;OA,10	9.4 ± 0.5	1.0×10^{-5}-1.0×10^{-2}
13	30	NB, 51	2	NaTPB,2;OA,15	6.9 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
14	30	NB, 63	2	NaTPB,0;OA,5	12.8 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
15	30	NB, 58	2	NaTPB,0;OA,10	19.8 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
16	30	NB, 53	2	NaTPB,0;OA,15	13.9 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
17	30	NB, 55	4	NaTPB,1;OA,10	9.2 ± 0.3	1.0×10^{-6}-1.0×10^{-2}
18	30	NB, 55	3	NaTPB,2;OA,10	10.1 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
19	30	NB, 55	2	NaTPB,3;OA,10	7.6 ± 0.4	1.0×10^{-5}-1.0×10^{-2}
20	30	NB, 55	1	NaTPB,4;OA,10	7.8 ± 0.3	1.0×10^{-5}-1.0×10^{-2}
21	30	NB, 55	5	NaTPB,0;OA,10	13.4 ± 0.6	1.0×10^{-5}-1.0×10^{-2}

3.3. The calibration curve

Critical response characteristics of the sensor were evaluated according to IUPAC recommendations [83]. For the best sensor composition, the emf response of the Tb^{3+} sensor (Figure 3) indicated a Nernstian slope of 19.8±0.3 mVdecade^{-1} across an extended terbium concentration range from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}. The lower limit of detection, determined by extrapolating two segments of the calibration graph, was estimated to be 5.8×10^{-7} mol L^{-1}.

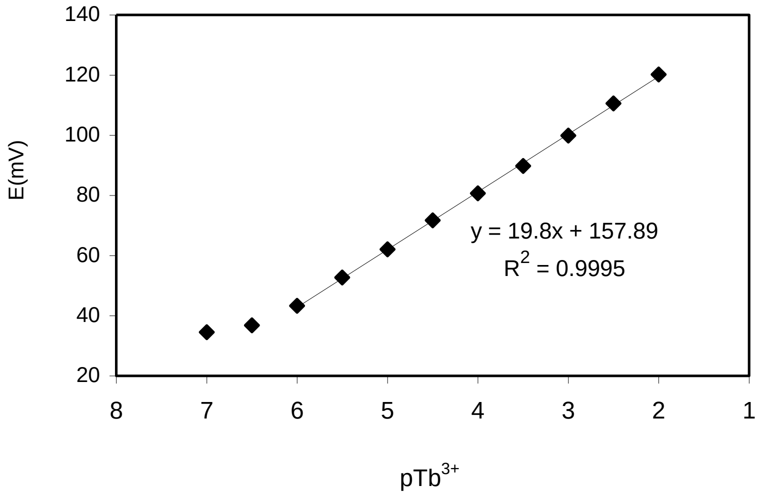


Figure 3. Calibration curve of the terbium sensor based on NSC.

3.4. The effect of pH

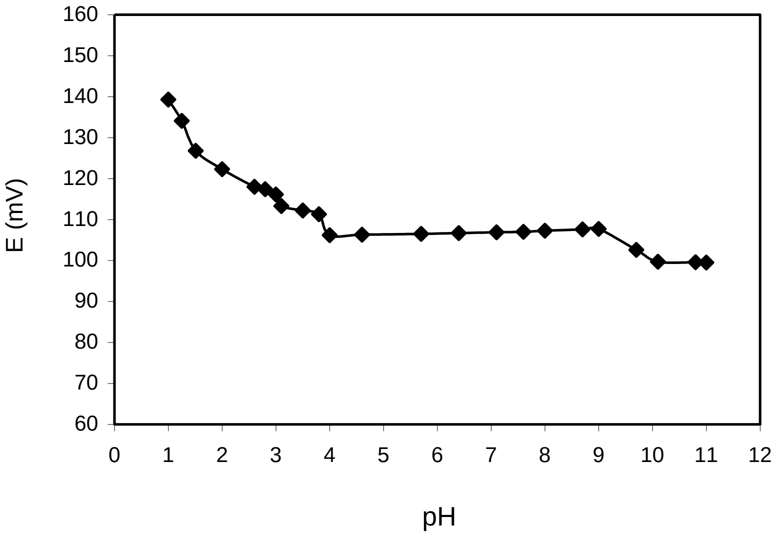


Figure 4. pH effect of the test solution (1.0×10^{-3} mol L^{-1} of Tb^{3+}) on the potential response of the Tb^{3+} sensor.

In this research to understanding the impact of pH on the sensor response, the potential was recorded at one particular concentrations of the Tb^{3+} activity of 1.0×10^{-3} mol L^{-1}. The pH of the solutions was adjusted by drop-wise addition of a solution of either HCl or NaOH, and the potential of the sensor was recorded at each pH value, in a pH range of 1–11. In agreement with the resulting data (Figure 4), the potential remained constant despite the pH changes in the range of 4.0 to 9.0, indicating the applicability of this electrode in the specific pH range. The deviation in potentials at the pH above 9.0 may be due to the formation of insoluble $Tb(OH)_3$ and the pH below 4.0, the potentials increased, indicating that the membrane sensor responded to protonium ions, as a result of the extent protonation of the ionophore nitrogen atoms.

3.5. Dynamic response time of the Tb^{3+} sensor

The response time of the Tb^{3+} sensor was evaluated by measuring the time required to achieve a 95% of the steady potential. In this research, the Tb^{3+} concentration was rapidly increased 10 fold from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} and then the practical response time was recorded. Figure 5, clearly shows that the response time is about 5 s. The low response time of the sensor is most probably due to the fast exchange of Tb^{3+} between ionophore and the bulk solution occurring at the membrane interface.

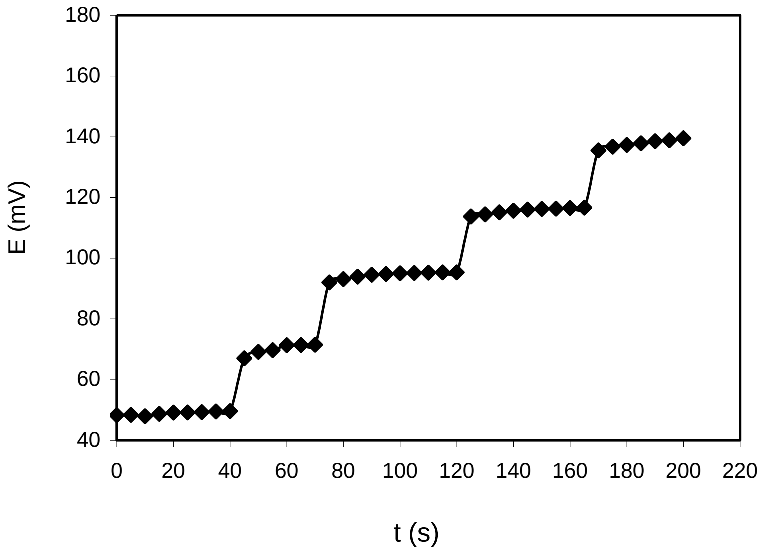


Figure 5. Dynamic response time of the terbium sensor for step changes in the Tb^{3+} concentration: A) 1.0×10^{-6} mol L^{-1}, B) 1.0×10^{-5} mol L^{-1}, C) 1.0×10^{-4} mol L^{-1}, D) 1.0×10^{-3} mol L^{-1}, E) 1.0×10^{-2} mol L^{-1}.

3.6. The selectivity of the Tb^{3+} sensor based on NSC

The potentiometric selectivity coefficients of the terbium sensor were evaluated by the matched potential method (MPM) [84-87]. According to MPM, a specified activity of the primary ions (A) is added to a reference solution and then the potential is measured. In a separate experiment, the interfering ions (B) are successively added to the identical reference solution until the measured potential matches the one obtained before the primary ions addition. MPM selectivity coefficient, $K^{\mathrm{MPM}}_{A,B}$, is then given by the resulting primary ion to the interfering ion activity ratio, $K^{\mathrm{MPM}}_{A,B}=a_A/a_B$. The resulting values of the selectivity coefficients are given in Table 2.

It is immediately obvious from these data, that the proposed Tb(III) sensor is highly selective with respect to the most of metal ions. In the case of lanthanide ions (Yb^{3+}, Pr^{3+}, Gd^{3+}, Tm^{3+}, Ho^{3+}, Dy^{3+}, Nd^{3+}, Lu^{3+}, Sm^{3+}, La^{3+} and Er^{3+}), the selectivity coefficients are in the order of 7.6×10^{-3} or smaller, which seems to indicate that the Tb(III) ions can be determined in the presence of other lanthanide ions. The selectivity coefficients for other metal ions (Cr^{3+}, Fe^{3+}, Na^{+}, K^{+}, Ba^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, and Zn^{2+}) are smaller than 9.0×10^{-3} and they can not disturb the functioning of the proposed Tb(III) sensor. The surprisingly high selectivity of the sensor for Tb(III) ions over other cations used most probably arises from the strong tendency of the carrier molecule for Tb(III) ions.

Table 2. Selectivity coefficients of the developed Tb^{3+} electrode.

Interfering Ion	K^{MPM}
Yb^{3+}	7.6×10^{-3}
Pr^{3+}	6.8×10^{-3}
Gd^{3+}	6.3×10^{-3}
Tm^{3+}	2.5×10^{-3}
Ho^{3+}	2.2×10^{-3}
Dy^{3+}	1.0×10^{-3}
Nd^{3+}	8.9×10^{-4}
Lu^{3+}	7.8×10^{-4}
Sm^{3+}	6.7×10^{-4}
Er^{3+}	6.2×10^{-4}
La^{3+}	8.9×10^{-4}
Cr^{3+}	3.2×10^{-3}
Fe^{3+}	9.0×10^{-3}
Na^{+}	4.5×10^{-3}
K^{+}	2.7×10^{-3}
Ba^{2+}	3.3×10^{-3}
Ca^{2+}	1.0×10^{-3}
Ni^{2+}	3.7×10^{-3}
Cu^{2+}	4.3×10^{-3}
Cd^{2+}	5.4×10^{-4}
Zn^{2+}	4.3×10^{-3}
Co^{2+}	1.0×10^{-3}
Concentration Range (mol L^{-1})	1.0×10^{-6}-1.0×10^{-2}
Detection Limit (mol L^{-1})	5.8×10^{-7} mol L^{-1}
pH Range	4.0-9.0
Slope (mVdecade^{-1})	19.8 ± 0.3
Response Time (s)	~5 s

Table 3 compares the linear range, detection limit, slope, pH range, response time and major interfering ions of the proposed sensor with those reported for the only previously reported Tb^{3+} sensor in the literature [37-39]. As it is seen, the sensor not only in the case of detection limit, but also in the case of selectivity coefficients is superior to the previously reported Tb^{3+} ion-selective membrane electrode.

Table 3. Comparison of different Tb(III) electrodes.

Parameter	Ref. 37	Ref. 38	Ref. 39	This work
LR (mol L^{-1})	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-1}	1.0×10^{-5}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-2}
DL (mol L^{-1})	8.0×10^{-7}	8.6×10^{-7}	7.0×10^{-6}	5.8×10^{-7}
Response time (s)	~10	15	<20	~5
pH range	3.5-8.0	3.8-8.2	3.5-7.7	4.0-9.0
Slope (mVdecade^{-1})	19.7	19.4	19.8	19.8
Log K_{sel}>-2	Gd	Gd	Ce, La, Dy, Yb, Sm	-

3.7. Analytical application

3.7.1. Titration with EDTA

The proposed Tb^{3+} sensor was successfully used as an indicator electrode in the titration of 25.0 mL of a 1.0×10^{-4} mol L^{-1} Tb^{3+} solution with a 1.0×10^{-2} mol L^{-1} EDTA. The resulting titration curve is given in Figure 6. Clearly, the amount of Tb^{3+} ions in the solution can be effectively determined with the electrode.

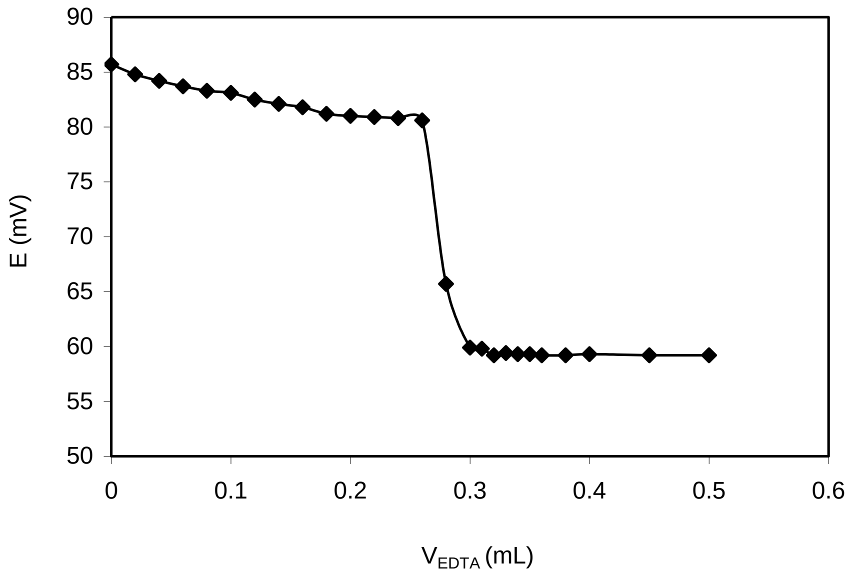


Figure 6. Potential titration curve of 25.0 mL from a 1.0×10^{-4} mol L^{-1} Tb^{3+} solution with 1.0×10^{-2} mol L^{-1} of EDTA.

3.7.2. The accuracy test of the Tb^{3+} sensor

To evaluate the accuracy of the developed sensor, it was also applied for the determination of Tb^{3+} ion concentration in mixtures of two and three different metal ions. The corresponding results in Table 4 reveal that Tb^{3+} sensor can be used as an alternative tool in determination of Tb^{3+} ions in presence of other metal ions.

Table 4. Determination of Tb^{3+} ions in mixtures of different ions.

Serial no.	Composition	Observed content (mol L^{-1})
1	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Nd(NO_3)_3$ + 0.0001 mol L^{-1} $La(NO_3)_3$	0.0000103
2	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Tm(NO_3)_3$ + 0.0001 mol L^{-1} $Ho(NO_3)_3$	0.0000097
3	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Lu(NO_3)_3$ + 0.0001 mol L^{-1} $Gd(NO_3)_3$	0.0000096
4	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Pr(NO_3)_3$ + 0.0001 mol L^{-1} $Dy(NO_3)_3$	0.0000098
5	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Eu(NO_3)_3$ + 0.0001 mol L^{-1} $Sm(NO_3)_3$	0.0000102
6	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Yb(NO_3)_3$ + 0.0001 mol L^{-1} $Er(NO_3)_3$	0.0000104
7	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Ba(NO_3)_2$+ 0.0001 mol L^{-1} $Fe(NO_3)_3$ + 0.0001 mol L^{-1} $Zn(NO_3)_2$	0.0000098
8	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Cr(NO_3)_3$+ 0.0001 mol L^{-1} $Ca(NO_3)_2$ + 0.0001 mol L^{-1} $Ni(NO_3)_2$	0.0000097
9	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Al(NO_3)_3$+ 0.0001 mol L^{-1} $Cu(NO_3)_2$ + 0.0001 mol L^{-1} $NaNO_3$	0.0000096
10	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Zn(NO_3)_2$+ 0.0001 mol L^{-1} $Co(NO_3)_2$ + 0.0001 mol L^{-1} KNO_3	0.0000102
11	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Pb(NO_3)_2$+ 0.0001 mol L^{-1} $Ba(NO_3)_2$ + 0.0001 mol L^{-1} $Zn(NO_3)_2$	0.0000097
12	0.000010 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Ni(NO_3)_2$+ 0.0001 mol L^{-1} $Mn(NO_3)_2$ + 0.0001 mol L^{-1} KNO_3	0.0000102

4. CONCLUSION

In this research, the terbium PVC membrane sensor based on the Di(N-succinimidyl)carbonate (NSC) ligand with the composition 2% ionophore, 10% OA, 30% PVC and 58% NB exhibited the best performance characteristics with Nernstian behavior over the concentration range of 1.0×10^{-6}–1.0×10^{-2} mol L^{-1} Tb^{3+}, a detection limit of 5.8×10^{-7} mol L^{-1} with very low interference from common alkali, alkaline earth, transition and heavy metal ions and a fast response time of 5 s. The proposed sensor potential responses are independent of pH in the range of 4.0–9.0. Moreover, it was successfully used as an indicator electrode in the terbium ion titration with EDTA as well as in the terbium ion detection in solution.

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