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Determination of fluoride ions in mouth wash samples by a Neodymium (III)-PVC Membrane Sensor

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ABSTRACT

5-(methylsulfanyl)-3-phenyl-1H-1,2,4-triazole (MPT) has been used as a suitable ionophore and nitrobenzene (NB) as a plasticizer in order to develop a PVC-based membrane electrode for neodymium ion detection. The sensors exhibits Nernstian response for the Nd^{3+} ions over the concentration range 1.0×10^{-6}-1.0×10^{-2} M at pH 3.0-7.6 with a lower detection limit of 5.9×10^{-7} M. The sensors displays Nernstian slope of 19.8 ± 0.4 mV per decade for Nd(III) ions. The response time was relatively quick in the whole concentration range (~5 s). The electrode shows a good selectivity for Nd(III) ion with respect to most common cations including alkali, alkaline earth, transition and heavy metal ions. The developed sensor was successfully applied as an indicator electrode in the Nd(III) ion potentiometric titration with EDTA, the F^- ions determination in some mouth washing solutions.

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

INTRODUCTION

Neodymium is one of the several metals in alloys commonly used in lighter flints. Neodymium is used in coloring glasses able to adsorb the yellow sodium glare of the flame. Neodymium can be found in houses equipment including color televisions, fluorescent lamps, energy-saving lamps and glasses [1]. Different instrumental methods have been reported for determination of neodymium including inductively coupled plasma mass spectroscopy (ICP-MS) [2-4] and ICP [5, 6]. Nevertheless, almost all of these methods are expensive and time consuming, with the exception of one; the ion selective electrode (ISE) method. As a matter of fact, it is one of the most popular electrochemical methods and it can be employed as a sensor for the determination of ions. These sensors are fast, selective and can be prepared easily [7-20].

There have been some reports of ion-selective neodymium electrodes in the literature [21-26]. Lately, highly selective and sensitive PVC-membrane ion-selective electrodes were reported for some ions [27-35]. The aim of this research is the fabrication of a greatly selective and sensitive Nd^{3+} membrane sensor, based on 5-(methylsulfanyl)-3-phenyl-1H-1,2,4-triazole (MPT) (Figure 1) as a suitable ionophore for the potentiometric measurement of the Nd^{3+} ion amounts for a certain concentration range.

EXPERIMENTAL SECTION

Reagents

The Merck Chemical Co. was the provider for the nitrate and chloride salts of all cations as well as for the following reagents; reagent-grades of dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), acetophenone (AP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and relatively high molecular weight PVC. All reagents were used without any modification. The ionophore 5-(methylsulfanyl)-3-phenyl-1H-1,2,4-triazole (MPT) was prepared as formerly described [36]. 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.

Electrode preparation

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 MPT. 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 $NdCl_3$). Finally, the electrode was conditioned by soaking in a 1.0×10^{-3} M $NdCl_3$ solution for 24 h [24-29]. As an internal reference electrode, a silver/silver chloride electrode was used.

The emf measurements

All emf measurements were carried out with the following assembly:
Ag–AgCl | internal solution, 1.0×10^{-3} M $NdCl_3$ | 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 DISCUSSION

Sensor potential response

In preliminary experiments, in order to check selectivity of MPT toward lanthanide cations, MPT was used as a potential neutral carrier in the construction of PVC membrane ion-selective electrodes for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. Among different cations tested, Nd^{3+} ion illustrated a strong response to the PVC membrane based on MPT. This is likely due to the high ionophore selectivity for neodymium ions over other metal ions, together with the quick exchange kinetics of the resulting Nd^{3+}-MPT complex. Therefore, the ionophore (MPT) was selected as a suitable sensing material for Nd^{3+} ions in PVC matrix.

The membrane composition effect

It is well-known that the sensitivity and selectivity of a given ionophore depend significantly on the membrane ingredients, the nature of the solvent mediator and the used ionic additive [37-39] the membrane composition influence on the potential responses of the Nd(III) sensor was investigated. The results are summarized in Table 1. It can be seen that the ionophore amount increase up to a 2 % value in the presence of 2 % of NaTPB and 66 % of polar solvent (NB) results in the best sensitivity. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules, and the state of ligand [40-42], it was expected to play a key role in determining the selectivity, working concentration range, and response time of the membrane electrode. Among the four different solvent mediators was tested, we found that, in construction of the neodymium membrane sensor, NB acts superior with respect to AP, BA and DBP. It should be noted that the presence of lipophilic anions in cation-selective membrane electrodes not only diminishes the ohmic resistance, but also enhances their response behavior and selectivity [43, 44]. Table 1 displays that the optimum response characteristics were obtained with a membrane composition of 30% PVC, 66% NB, 2% MPT and 2% NaTPB (no. 3).

Calibration graph

The potential response of the suggested MPT based sensor (composition no. 3) at varying neodymium ion concentrations demonstrated a linear response to the neodymium ion concentration in the range 1.0×10^{-6}-1.0×10^{-2} M (Figure 2). The slope of the calibration graph was 19.8 ± 0.4 mV per decade and the standard deviation of eight replicate measurements was ±0.5 mV. The detection limit, as determined from the intersection of the two extrapolated segments of the calibration graph, was 5.9×10^{-7} M. The suggested PVC-based membrane sensor could be used for at least ten weeks (using one hour per day and, then, washed and dried).

The pH effect

The pH influence of the test solution (1.0×10^{-3} M) on the potential electrode response was considered in the pH range of 2.0-10.0 (the pH was adjusted with the use of concentrated NaOH or HCl). The potential remained constant from the pH value of 3.0 up to 7.6, beyond which some drifts in the potentials were observed. The drift at higher pH values could be caused by the Nd^{3+} hydroxyl complex formation in the solution. At lower pH values, the potentials increased, indicating that the membrane sensor responded to protonium ions, as a result of the extent nitrogen atom protonation of the ionophore.

Dynamic response time

Dynamic response time consists of a significant factor for any ion-selective electrode. In this study, the practical response time of the proposed sensor was recorded by changing the Nd(III) concentration in a series of solutions (1.0×10^{-6}-/1.0×10^{-2} M). It can be noticed that in the whole concentration range the plasticized membrane sensor reaches its equilibrium responses rapidly (~5 s).

The sensor selectivity

The potentiometric selectivity coefficient, which reflects the relative response of the membrane sensor for the primary ion over other ions that are present in solution, is perhaps the most important characteristic of an ion-selective electrode. In this work, the potential response of the recommended Nd^{3+} ion-selective sensor was investigated with the aid of the matched potential method (MPM) [45-47]. In accordance with the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B), which gives some potential change in a reference solution. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{\mathrm{MPM}} = \Delta a_{\mathrm{A}}/a_{\mathrm{B}}$. The results are summarized in Table 2. As it is immediately obvious, the selectivity coefficients of the electrode for all the diverse ions are in the order of 6.2×10^{-3} or smaller, indicating they would not significantly disturb the function of the Nd(III) selective membrane sensor.

A comparison is exhibited in Table 3 between the selectivity coefficients of the developed Nd(III) sensor with those of the best previously reported Nd(III) electrodes [21-26]. It is instantly clear that the concentration range, the response time, the detection limit of the recommended electrode and the selectivity coefficients are superior to those stated by other researchers.

Analytical application

The recommended Nd(III) sensor was found to work well under laboratory conditions. It was successfully used as an indicator electrode in the titration of a 1.0×10^{-4} M of Nd(III) with a standard EDTA solution (1.0×10^{-2} M). The resulting titration curve is shown in Figure 5, where it can be noticed that the amount of Nd(III) ions in solution can be determined with the sensor.

Table 1: Optimization of the membrane ingredients

No.	Composition (w/w, %)				Slope (mV/decade)	Concentration range (M)
	MPT	Plasticizer	NaTPB	PVC		
1	2	NB, 68	0	30	12.8 ± 0.5	1.0×10^{-5}-4.3×10^{-2}
2	2	NB, 67	1	30	18.2 ± 0.6	1.0×10^{-6}-1.0×10^{-2}
3	2	NB, 66	2	30	19.8 ± 0.4	1.0×10^{-6}-5.0×10^{-2}
4	2	NB, 65	3	30	18.5 ± 0.3	1.0×10^{-6}-5.0×10^{-2}
5	1	NB, 66	2	30	17.3 ± 0.5	1.0×10^{-6}-5.0×10^{-2}
6	3	NB, 65	2	30	17.8 ± 0.4	1.0×10^{-6}-1.0×10^{-2}
7	2	DBP, 66	2	30	16.7 ± 0.3	1.0×10^{-5}-6.4×10^{-2}
8	2	AP, 66	2	30	17.8 ± 0.5	1.0×10^{-5}-1.0×10^{-2}
9	2	BA, 66	2	30	17.2 ± 0.6	1.0×10^{-5}-1.0×10^{-2}

The electrode was also used in the potentiometric determination of fluoride ions in two mouth wash samples. The results were derived from triplicate measurements and they are listed in Table 4. Clearly, there is a satisfactory agreement between the declared fluoride content and the determined values. Because of the high selectivity and the low detection limit of the developed Nd(III) sensor, it was also used to the direct determination of Nd^{3+} ions in binary mixtures. The corresponding results in Table 5 reveal that the Nd^{3+} ions recovery is quantitative and they support the fact that the neodymium membrane sensor can be used for the direct Nd^{3+} monitoring in real samples.

Table 2: Selectivity coefficients of various interfering ions

Interfering ions	$K^{MPM}_{Nd^{3+},B}$	Interfering ions	$K^{MPM}_{Nd^{3+},B}$
Gd^{3+}	3.2×10^{-3}	Fe^{3+}	4.2×10^{-3}
Eu^{3+}	2.8×10^{-3}	Cr^{3+}	5.8×10^{-3}
Tm^{3+}	8.3×10^{-4}	K^{+}	2.2×10^{-3}
La^{3+}	8.9×10^{-4}	Na^{+}	3.1×10^{-3}
Dy^{3+}	8.2×10^{-4}	Ca^{2+}	2.5×10^{-3}
Tb^{3+}	5.5×10^{-3}	Co^{2+}	4.5×10^{-3}
Pr^{3+}	5.7×10^{-3}	Ni^{2+}	4.8×10^{-3}
Sm^{3+}	4.6×10^{-3}	Cd^{2+}	5.4×10^{-3}
Ho^{3+}	6.2×10^{-3}	Pb^{2+}	2.6×10^{-3}

Table 3: Comparison of different Nd(III) electrodes

Parameter	Ref. 21	Ref. 22	Ref. 23	Ref. 24	Ref. 25	Ref. 26	This work
LR (M)	5.0×10^{-7}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-5}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}-1.0×10^{-1}	5.0×10^{-6}-1.0×10^{-2}
DL (M)	1.0×10^{-7}	7.0×10^{-6}	7.9×10^{-7}	2.0×10^{-6}	6.2×10^{-7}	8.0×10^{-7}	5.9×10^{-7}
Response time (s)	10	<15	<5	<10	<10	<15	<10
pH range	4.0-8.0	4.0-8.0	4.0-6.5	3.5-8.5	3.7-8.3	3.0-7.0	3.0-7.6
Slope (mV/decade)	19.8±0.3	19.6±0.3	20.1±0.2	19.6±0.3	19.7±0.4	19.4±0.3	19.8±0.4
Log K_{sel}>-2	Hg, Ni	La, Gd, Sm, Cu, Yb	Ce, Yb, Gd, Sr, Cu, La,Ag	La, Sm, Gd	La, Dy	La, Gd, Sm, Pr	-

Table 4: Determination of fluoride ions in mouth wash solutions

Sample	Labeled (ppm)	Found ISE[a] (ppm)
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1350	($1378^{b} \pm 22$)
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	($1476^{b} \pm 17$)

a. Proposed Nd^{3+} sensor
b. Results are based on three measurements

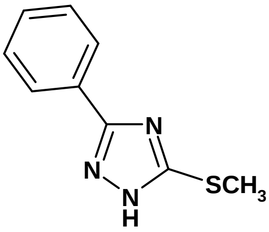

Fig 1: The MPT chemical structure.

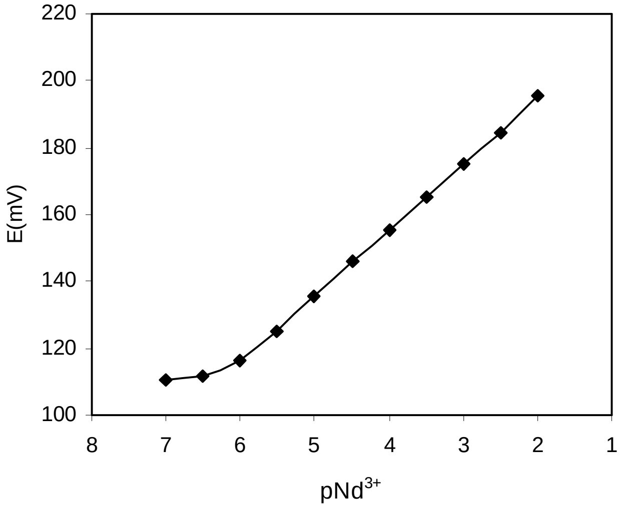

Fig 2: Calibration curve of neodymium electrode based on MPT.

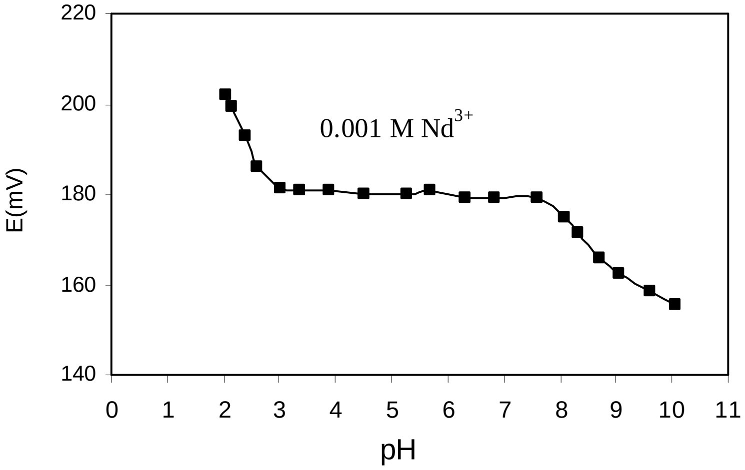

Fig 3: The pH effect of the test solution on the potential response of the neodymium sensor (no. 3).

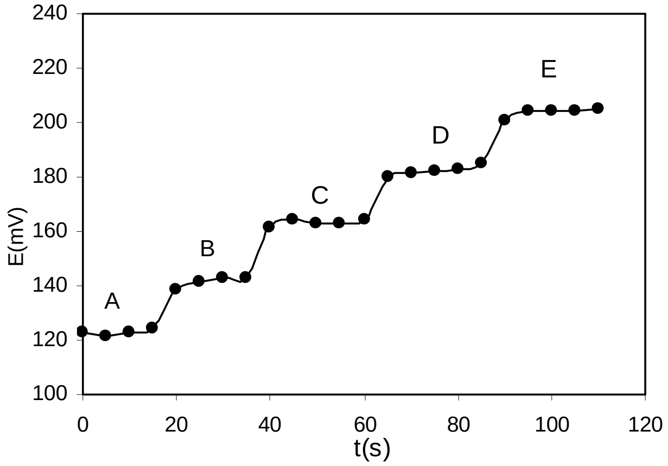

Fig 4: Dynamic response time of the neodymium electrode (no. 3) for step changes in the Nd^{3+} concentration: A) 1.0 × 10^{-6} M, B) 1.0 × 10^{-5} M, C) 1.0 × 10^{-4} M, D) 1.0 × 10^{-3} M, E) 1.0 × 10^{-2} M.

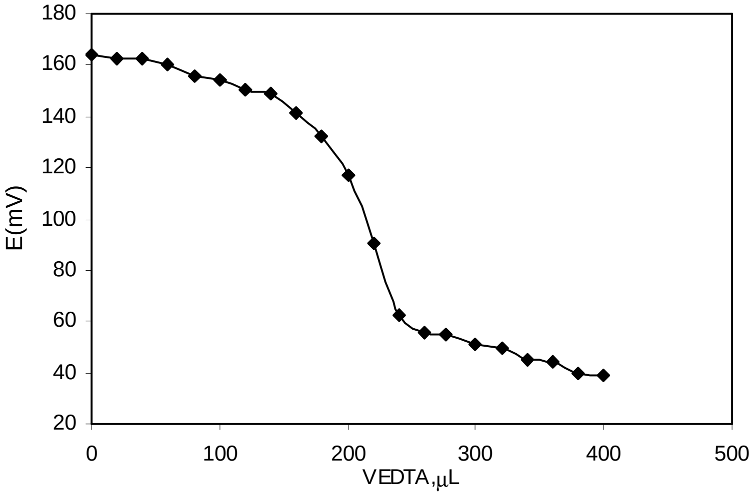

Fig 5: Potential titration curve of 20.0 mL from a 1.0 × 10^{-4} M Nd^{3+} solution with 1.0×10^{-2} M of EDTA.

CONCLUSION

Application of 5-(methylsulfanyl)-3-phenyl-1H-1,2,4-triazole (MPT) in PVC membrane electrode as a suitable carrier with NB as plasticizer creates a Nd^{3+}-PVC membrane sensor. The sensor displayed a Nernstian response (slope of 19.8±0.4 mV/decade) with a low limit of detection (5.9 × 10^{-7} M). It has a very short response time (~7 s), in the whole concentration range with the pH range of 3.0-7.6, wide linear range (1.0×10^{-6}-1.0×10^{-2} M) and very low interference from common alkali, alkaline earth, transition and heavy metal ions. It was successfully applied as an indicator electrode to the neodymium ion titration with EDTA as well as to the fluoride ions detection in mouth wash samples.

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