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Design and Construction of High-Sensitive and Selective Dysprosium(III) Electrochemical Membrane Sensor Based on a Thiourea Derivative

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A derivative of thiourea (DPDP) have been explored as a neutral ionophore for preparation a highly selective Dy(III) membrane sensor. The best performance was obtained with the sensor having membrane of DPDP-PVC-NaTPB-NB. The proposed sensor exhibits a Nernstian response over a wide concentration range (from 1.0×10^{-7} to 5.0×10^{-1} mol L^{-1} of Dy(III)). The detection limit of designed membrane is 3.9×10^{-8} mol L^{-1}. The sensor response is independent of pH of the solution in the pH range 3.4-8.2 and possess the advantages of fast response time and in particular, good selectivity and sensivity to the dysprosium ions with regard to most common metal ions, and especially all lanthanide ions. The sensor can be used over a period of 11 weeks without any considerable divergence in the potentials. It was applied successfully in the trace determination of Dy(III) ions in some binary mixtures, mouth washing solutions, soil and sediment samples.

Keywords: Membrane sensor, Dy(III) selective, Thiourea derivative, PVC, Potentiometry

1. INTRODUCTION

Dysprosium is disposed of in the environment in many different places, mainly by petrol-producing industries. It can also enter the environment when household equipment is thrown away.

Dysprosium will gradually accumulate in soils and water soils and this will eventually lead to increasing concentrations in humans, animals and soil particles. With water animals dysprosium causes damage to cell membranes, which has several negative influences on reproduction and on the functions of the nervous system [1]. Thus, the fast, simple, and accurate determination of Dy(III) ions in different samples is very important.

Several analytical (and especially spectroscopic) methods have been reported for low-level monitoring of Dy(III) and other lanthanide ions in various sample matrices. But as a result, design of an inexpensive and simple technique, which can provide the necessary selectivity to determine Dy(III) in the presence of other lanthanides that are very similar to Dy(III) is of great value. Potentiometric sensors have shown to be very effective tools for analysis of a wide variety of cations and anions. They are very simple, inexpensive, and capable of reliable response in wide concentration ranges. In addition, sensor based potentiometric detections, offer several other advantages such as speed and ease of preparations and procedures, simple instrumentations, relatively fast responses, wide dynamic ranges, reasonable selectivities, and low costs. This has led to an increasing interest in the development of sensors for several ionic species, increasing the number of available electrodes over the last few years [2-8].

We and other researchers have recently introduced a number of ion selective membrane sensors for lanthanide(III) and other ions based on different noncyclical and macro cyclic ionophores [9-23]. To the best of our knowledge, the first Dy(III) ion selective membrane sensor has prepared in our research group with use of N,N-bis(pyrrolidene)benzene-1,2-diamine [24] and after that some reports were published by us and the other groups [25-30]. This study describes another ion selective sensor for Dy(III) potentiometric determination based on 1-((Dimethylamino)(phenylimino)methyl)-3,3-dimethyl-1- phenylthiourea (DPDP), as a novel neutral ionophore (as shown in Figure 1).

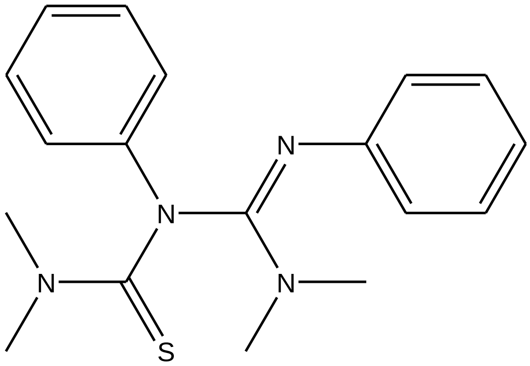

Figure 1. Chemical structure of 1-((Dimethylamino)(phenylimino)methyl)-3,3-dimethyl- 1 phenylthiourea.

Three noticeable benefits demonstrated by this sensor are the fast response time, low detection limit and also great selectivity.

2. EXPERIMENTAL

2.1. Reagents and materials

Reagent grade sodium tetraphenyl borate (NaTPB), oleic acid (OA), benzyl acetate (BA), dibutyl phthalate (DBP), nitrobenzene (NB), acetophenone (AP), tetrahydrofuran (THF), acetonitrile (AN), perchloric acid, hydrofluoric acid and high relative molecular weight PVC of the highest purity available were purchased from Merck and Aldrich, and used without any further treatments, except for the vacuum drying. The nitrate and chloride salts of cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. DPDP was gifted from the Jaber Ibn Hayan research laboratories (NFCRS, Tehran, Iran). Triply distilled deionized water was used in experiments.

2.2. Apparatus

A corning ion analyzer 250 pH/mV meters was used for the potential measurements at 25.0±0.1 ◦C. The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips), with its chamber filled with an ammonium nitrate solution.

2.3. Preparation of membrane

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 62 mg of plasticizer NB and 3 mg of additive NaTPB in 5 ml THF. To this solution was added 5 mg of ionophore DPDP and mixed well. 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 (3-5 mm diameter on top) was dipped into the oily mixture for about 10 s so that a non-transparent film of about 0.3 mm thickness was formed [31-34]. The tube was then pulled out from the mixture and kept at room temperature for at least 1 h. The tube was then filled with an internal filling solution (1.0×10^{-4} mol L^{-1} $Dy(NO_3)_3$). The electrode was finally conditioned for 24h by soaking in a 1.0×10^{-4} mol L^{-1} solution of dysprosium nitrate. Silver – silver chloride electrode was used as an internal reference electrode. The ratio of different membrane ingredients, concentration of equilibrating solution and the time of contact were optimized to provide membranes, which result in reproducible, noiseless and stable potentials.

2.4. EMF measurements

The electromotive force (EMF) measurements with the polymeric membrane electrodes were carried out with the cell assembly of:

Ag–AgCl | internal solution, 1.0×10^{-4} mol L^{-1} $Dy(NO_3)_3$ | PVC membrane | test solution | Hg–Hg_2Cl_2, KCl (Saturated)

The activities were calculated in agreement with the Debye–Huckel procedure.

3. RESULTS AND DISCUSSION

Due to the radii of lanthanum ions (with the range of 1.02-0.80Å from Ce^{3+} to Lu^{3+} respectively), these elements have different properties such as charge densities, size and hydration energy (with the range of 3370–3760 kJ mol^{-1} from Ce^{3+} to Lu^{3+} respectively) [35, 36]. Thus, by using a suitable ionophore having a semi-cavity and relatively high flexibility, it is possible to construct a highly selective lanthanide ion sensor. The existence of donating nitrogen and sulfur atoms in the DPDP structure which causes a semi-cavity and forms a template complex, and considering soft–hard acid–base concept, the charge density and the size of the dysprosium ion, it was expected that DPDP can form a selective complex with dysprosium ion more than the other transition metal ions. Thus, conductivity study of complexation in the acetonitrile solution was carried out as a primary test.

3.1. Preliminary study of DPDP complexation with some metal ions

To examine ligand selectivity against various metal ions and all 14 members of lanthanide series, the interaction of DPDP with metal ions in an acetonitrile solution by conductometric method was investigated [9, 15-20, 37]. In all measurements, the cell should be thermo stated at the temperature of 25.0 °C, using a Phywe immersion thermostat. In this experiment, the ligand to cation mole ratio was equal to 1 in all cases. The formation-constant values of the resulting 1:1 complexes in Table 1 showed that log K_f is 5.97±0.03 for Dy^{3+} and between 2.07±0.01 to 2.92±0.04 for other metal ions used. As can be seen from these results, DPDP can be used as a sensing material in an Dy(III) sensor.

Table 1. The formation constants of DPDP-M^{n+} complexes at 25.0 ± 0.1 ºC.

Ion	Log K_f	Ion	Log K_f
Na^+	< 2.0	Nd^{3+}	2.07 ± 0.01
K^+	< 2.0	Sm^{3+}	2.77 ± 0.02
Cu^{2+}	< 2.0	Eu^{3+}	2.21 ± 0.04
Cd^{2+}	2.18 ± 0.03	Gd^{3+}	2.33 ± 0.05
Ba^{2+}	2.55 ± 0.07	Tb^{3+}	2.92 ± 0.04
Pb^{2+}	2.60 ± 0.03	Dy^{3+}	5.97 ± 0.03
Cr^{3+}	2.25 ± 0.04	Ho^{3+}	2.64 ± 0.02
Fe^{3+}	2.14 ± 0.02	Er^{3+}	2.11 ± 0.05
La^{3+}	2.60 ± 0.03	Tm^{3+}	2.81 ± 0.04
Ce^{3+}	2.46 ± 0.04	Yb^{3+}	2.66 ± 0.03
Pr^{3+}	2.53 ± 0.05	Lu^{3+}	2.35 ± 0.06

In order to check the suitability of DPDP as an ion carrier for Dy(III) and other metal ions, it was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations including a number of lanthanide (La^{3+}, Ce^{3+}, Sm^{3+}, Gd^{3+} and Dy^{3+}) and some common metal ions (K^+, Cr^{3+}, Cu^{2+}, Cd^{2+} and Ba^{2+}). At first experiment we used 30mg PVC, 63mg BA, 5mg DPDP and 2mg NaTPB for membrane fabrication. The potential responses showed that with the exception of Dy(III) ions, all the tested cations showed relatively weak responses in the concentration range 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1}, due to their weak interactions with the ionophore.

3.2. The influence of membrane composition on the sensor response

The properties of the ion-selective membrane sensors depend on the nature and amount of ionophore, the plasticizer properties, the plasticizer/PVC ratio and, especially, the nature of additives used [2, 3]. Thus, in this work, ten PVC membranes with plasticizer/PVC ratios of about 1.93-2.17, but with varying nature and amount of other ingredients were prepared (Table 2). It is noteworthy that the best membrane characteristics are reported to be usually obtained at a plasticizer/PVC ratio of about 1.6–2.3 [11, 13, 15, 24, 31-34].

Table 2. Optimization of membrane ingredients during design of Dy(III) selective membrane sensor.

No.	Composition (wt.%)				Slope (mV decade^{-1})	Linear Range (mol L^{-1})
	PVC	Plasticizer	DPDP	Additive		
1	30	BA, 63	5	NaTPB, 2	18.8 ± 0.2	1.0×10^{-7} to 1.0×10^{-2}
2	30	DBP, 63	5	NaTPB, 2	17.4 ± 0.4	5.0×10^{-7} to 1.0×10^{-2}
3	30	NB, 63	5	NaTPB, 2	19.1 ± 0.4	1.0×10^{-7} to 5.0×10^{-1}
4	30	AP, 63	5	NaTPB, 2	16.8 ± 0.6	1.0×10^{-6} to 1.0×10^{-2}
5	30	NB, 64	4	NaTPB, 2	17.7 ± 0.3	1.0×10^{-7} to 5.0×10^{-1}
6	30	NB, 62	6	NaTPB, 2	18.5 ± 0.1	1.0×10^{-7} to 5.0×10^{-1}
7	30	NB, 58	5	OA, 7	17.6 ± 0.5	5.0×10^{-7} to 5.0×10^{-1}
8	30	NB, 62	5	NaTPB, 3	20.5 ± 0.3	1.0×10^{-7} to 5.0×10^{-1}
9	30	NB, 65	5	-	14.9 ± 0.5	1.0×10^{-6} to 5.0×10^{-2}
10	30	NB, 65	0	NaTPB, 3	8.3 ± 0.2	1.0×10^{-6} to 1.0×10^{-2}

As it is well known, plasticizers are solvent mediators that lead to optimum physical properties as well as ensure high mobility of ions in the membrane. The presence of 61–65% plasticizer can influence the working concentration range of ISEs [2, 6, 7]. The effect of different plasticizers on Dy(III) selective membrane sensor was first investigated. The potential response obtained for prepared membrane sensors with use of BA, DBP, NB and AP at the same membrane composition (having DPDP – PVC – NaTPB – Plasticizer with the ratio 5.0: 30.0: 2.0: 63.0) is shown in Figure 2. Due to the increased polarity of NB over BA, DBP and AP It can be seen that membrane with NB as plasticizer gave better slope (19.1 ± 0.4 mV decade^{-1}) and higher order of magnitude widening of the measuring concentration range of the corresponding membrane sensor over the membrane based on other plasticizers. Also the result is in tune with earlier reports that high dielectric constant of plasticizers cause better sensivity to lanthanide(III) ions [15-28].

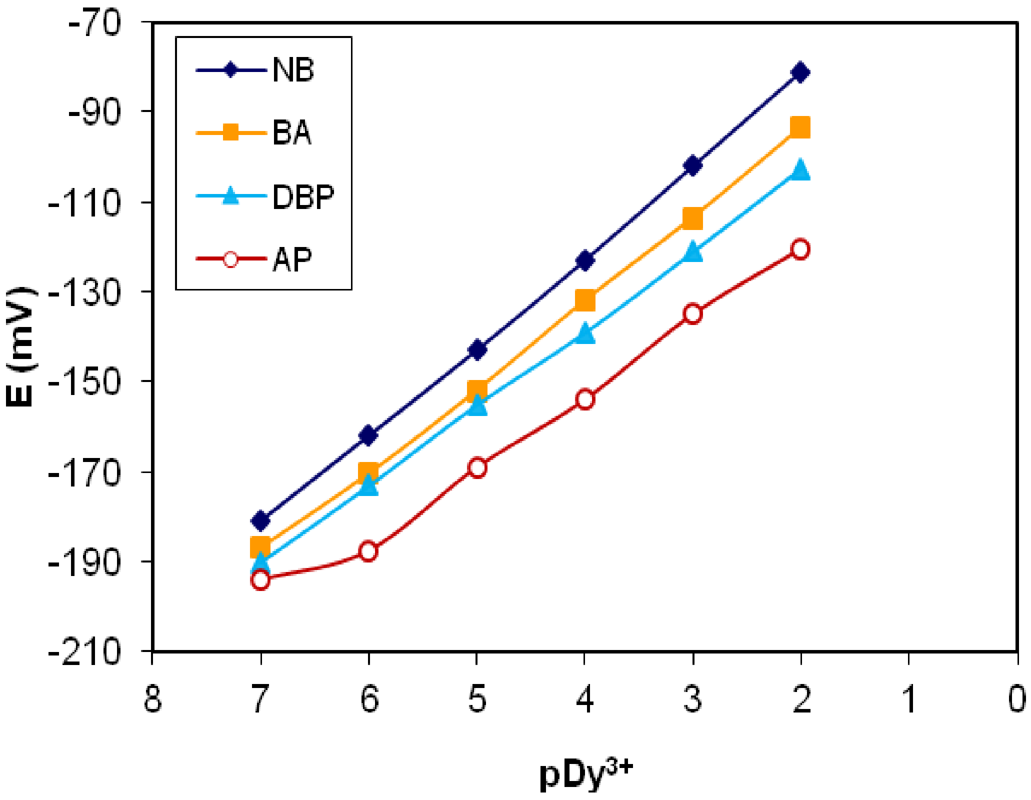

Figure 2. The potential responses of the Dy(III) membrane ISEs prepared with different plasticizers.

It has been well established that, the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain cationic selective electrodes [3, 11, 38, 39]. Table 2 shows that in the absence of ionic additive, the slope of the proposed sensor is 14.9 mV decade^{-1} (No. 9) whereas in the presence of 3% NaTPB as a suitable additive, the slope increases 20.5 mV decade^{-1} (No.8). It is interesting to note that a membrane, having a composition like membrane 8, but lacking DPDP, (No.10) showed no promising responses towards Dy(III) ions. However, membrane with a PVC: NB: DPDP: NaTPB percent ratio of 30: 62: 5: 3 had a Nernstian behavior over a wide concentration range.

3.3. Linear concentration range and detection limit

The critical response characteristics of the Dy(III) sensor were assessed according to IUPAC recommendations [40]. The potential response of the membrane at varying concentrations of Dy(III) ions was investigated. Figure 3 indicates a rectilinear range from 1.0×10^{-7} to 5.0×10^{-1} mol L^{-1}. The slope of the calibration curve was 20.5 ± 0.3 mV decade^{-1} of Dy(III) concentration. The detection limit, as determined from the intersection of the two extrapolated segments of the calibration graph, was 3.9×10^{-8} mol L^{-1}.

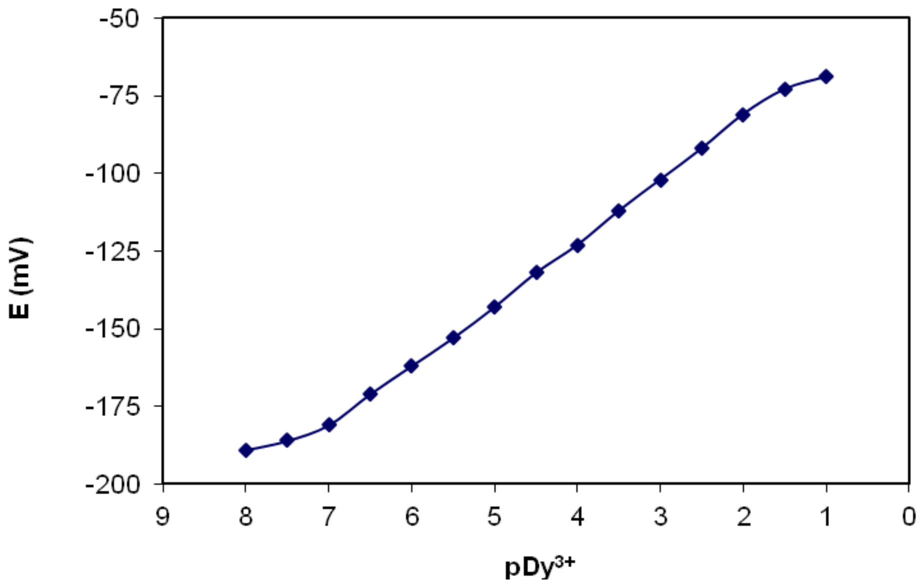

Figure 3. The Calibration curve of the Dy(III) membrane sensor based on DPDP.

3.4. Response time

In analytical application, response time of an electrochemical sensor is very important. It is evaluated through measuring the average time required to achieve potential values within ±0.1 mV of the steady-state potential of the electrode after its immersion in a series of solutions of the target ions, each having a ten-fold difference in concentration [15, 16].

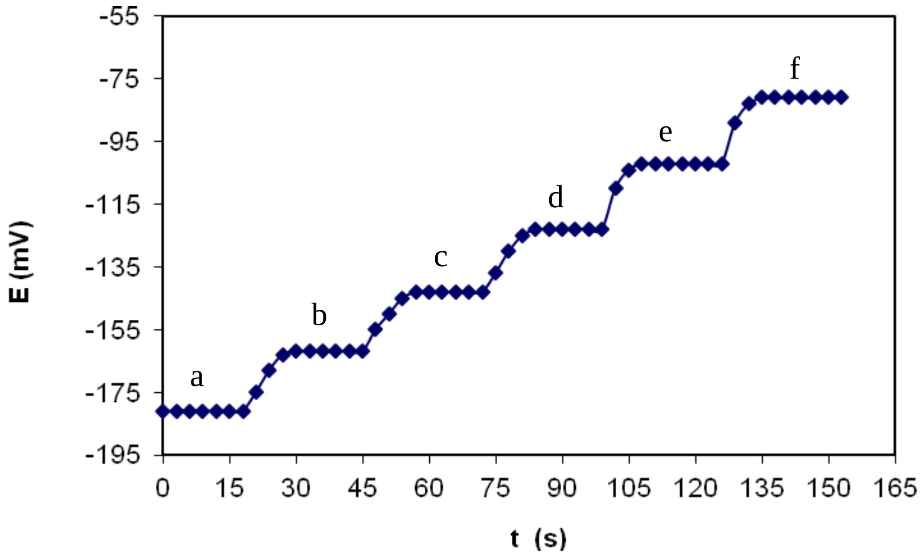

Figure 4. The practical response time of the Dy(III) membrane sensor for step changes in the Dy(III) concentration: (a) 1.0 × 10^{-7} mol L^{-1}, (b) 1.0 × 10^{-6} mol L^{-1}, (c) 1.0 × 10^{-5} mol L^{-1}, (d) 1.0 × 10^{-4} mol L^{-1}, (e) 1.0 × 10^{-3} mol L^{-1}, (f) 1.0 × 10^{-2} mol L^{-1}.

A numbers of experimental parameters such as temperature of testing solution, type and speed of stirring, the concentration and composition of each test solution, and preconditioning of the electrode can affect the response time of any sensor [31-34]. In this study, the practical response time was recorded by changing the Dy(III) concentration in solution, over a concentration range from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1}, and the results are shown in Figure 4. The response time of the proposed membrane sensor was between 6 s (for high concentrations) to 9 s (for low concentrations) of Dy(III) ions.

3.5. pH effect on the electrode response

The pH response profile for the electrode was tested by using 1.0×10^{-3} mol L^{-1} and 1.0×10^{-4} mol L^{-1} $Dy(NO_3)_3$ solutions over the pH range of 2.0-10.5. The pH was adjusted by introducing small drops of HCl or NaOH (0.1-0.01 mol L^{-1}). The influence of pH on the response of PVC membrane electrode is shown in Figure 5.

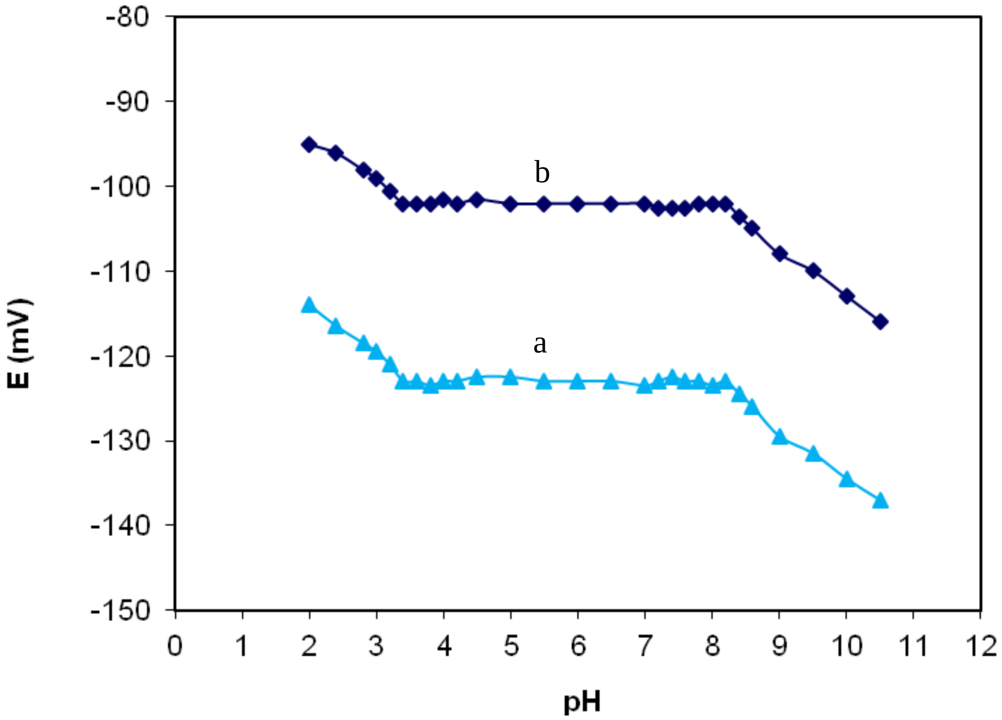

Figure 5. pH effect on the potential response of the Dy(III) membrane sensor based on DPDP in the test solutions of Dy(III) ions: (a) 1.0×10^{-4} mol L^{-1}, (b) 1.0×10^{-3} mol L^{-1}.

As is seen, the potential remained constant from pH 3.4 to 8.2, beyond which some drifts in the potentials were observed. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Dy(III) in the solution. At the lower pH values, the potentials decreased, indicating that the membrane sensor also responded to H^+ ions, by the protonation of the nitrogen atoms of the ionophore.

3.6. Potentiometric selectivity

Potentiometric selectivity coefficients of the Dy(III) membrane sensors were evaluated by a matched potential method (MPM) [5, 38, 39]. Table 3 shows potentiometric selectivity coefficients of the DPDP-based Dy(III) selective membrane sensor. For all diverse ions, the selectivity coefficients of the electrode are in the order of 9.2×10^{-3} or smaller, indicating they would not significantly disturb the function of the Dy(III) PVC-membrane sensor.

Also, Table 4 compares the ionophore, linear range, detection limit, Nernstian slop and response time of the described sensor with those of the best previously reported dysprosium sensors [24-30]. It is clear that characterizations of designed electrode are superior to those of the formerly stated dysprosium sensors.

Table 3. The selectivity coefficients of various interfering cations for the membrane sensor.

Cation	$K^{MPM}_{\mathrm{Dy}^{3+},B}$	Cation	$K^{MPM}_{\mathrm{Dy}^{3+},B}$
Tb^{3+}	9.2×10^{-3}	Cd^{2+}	1.1×10^{-5}
Tm^{3+}	1.3×10^{-4}	Fe^{3+}	1.8×10^{-5}
Pb^{2+}	1.6×10^{-4}	Eu^{3+}	2.2×10^{-5}
Sm^{3+}	2.4×10^{-4}	Lu^{3+}	2.6×10^{-5}
Ba^{2+}	3.5×10^{-4}	K^{+}	3.4×10^{-5}
Ho^{3+}	6.2×10^{-4}	Gd^{3+}	4.0×10^{-5}
Yb^{3+}	6.9×10^{-4}	Er^{3+}	5.1×10^{-5}
La^{3+}	7.1×10^{-4}	Cu^{2+}	5.9×10^{-5}
Pr^{3+}	7.7×10^{-4}	Nd^{3+}	7.3×10^{-5}
Ce^{3+}	8.6×10^{-4}	Al^{3+}	1.5×10^{-6}
Cr^{3+}	9.3×10^{-4}	Na^{+}	1.8×10^{-6}

For the investigation of the stability and lifetime of the Dy(III) membrane sensor, two electrodes were tested over a period of 14 weeks and the results are in Table 5. The main factor limiting the lifetime of the ion-selective membrane in potentiometric measurements is the leakage of ionophore into the aqueous solutions. The proposed PVC-based membrane sensor could be used for at least 11 weeks (use of 1 hour daily). After its utilization, it was washed and kept dry. During this certain time period, the membrane sensor could be used without any measurable divergence. After 11 weeks changes were observed in the slope and detection limit (from 20.5 to 18.9 mV decade^{-1} and 3.9×10^{-8} from 1.2×10^{-7} mol L^{-1}, respectively) [21, 22, 24-30].

Table 4. Comparative study of best responsive membrane sensor (No. 8) and conventional Dy(III) chemical sensors.

Ref.	Ionophore	LR[a] (mol L^{-1})	DL[b] (mol L^{-1})	Slope (mV $decade^{-1}$)	Response Time (s)
24	N,N-bis(pyrrolidene)benzene-1,2-diamine	1.0×10^{-5} to 1.0×10^{-1}	6.0×10^{-6}	20.6 ± 0.2	< 20
25	(E)-N-(2-hydroxybenzylidene)benzohydraide	1.0×10^{-6} to 1.0×10^{-2}	8.0×10^{-7}	20.1 ± 0.8	< 20
26	Procaine	1.0×10^{-6} to 1.0×10^{-1}	7.9×10^{-7}	20.1 ± 0.1	< 10
27	6-hydrazino-1,5-diphenyl-6,7-dihydropyrazolo[3,4-d]pyrimidine-4(5H)-imine	8.0×10^{-7} to 1.0×10^{-1}	4.2×10^{-7}	19.6 ± 0.3	< 10
28	Benzoxazoleguanidine	1.0×10^{-6} to 1.0×10^{-1}	4.7×10^{-7}	19.5 ± 0.4	< 10
29	Derivative of bis(5-bromo-2-thienyl)methane	5.4×10^{-8} to 1.0×10^{-2}	4.1×10^{-8}	19.4 ± 0.2	10
30	N,N'-bis(naphthalidene)-2-aminobenzylamine	1.0×10^{-6} to 1.0×10^{-2}	5.2×10^{-7}	20.7 ± 0.4	~ 7
This Work	1-((dimethylamino)(phenylimino)methyl)-3,3-dimethyl-1-phenylthiourea	1.0×10^{-7} to 5.0×10^{-1}	3.9×10^{-8}	20.5 ± 0.3	~ 8

[a] Linear Range
[b] Detection Limit

3.7. Stability and lifetime

Table 5. Lifetime of Dy(III) selective membrane sensor.

Week	**Slop (mV $decade^{-1}$)**	**DL[a] (mol L^{-1})**
1	20.5 ± 0.3	3.9×10^{-8}
2	20.4 ± 0.2	4.0×10^{-8}
3	20.5 ± 0.2	3.9×10^{-8}
4	20.3 ± 0.4	4.0×10^{-8}
5	20.4 ± 0.1	4.1×10^{-8}
6	20.4 ± 0.3	4.3×10^{-8}
7	20.5 ± 0.4	4.4×10^{-8}
8	20.5 ± 0.1	4.6×10^{-8}
9	20.5 ± 0.2	4.9×10^{-8}
10	20.4 ± 0.3	5.1×10^{-8}
11	20.3 ± 0.1	5.5×10^{-8}
12	18.9 ± 0.3	1.2×10^{-8}
13	17.5 ± 0.3	3.8×10^{-7}
14	16.4 ± 0.2	6.7×10^{-7}

[a] Detection Limit

3.8. Analytical applications

Due to the high selectivity and the very low detection limit of the constructed Dy(III) sensor, it was applied for the monitoring of the dysprosium ions concentration in various binary mixtures [24] and the resulting data are given in Table 6. It is clear from the table that the recoveries of the Dy(III) ions in all mixtures are in the range of 98.7-103.4%, therefore being acceptable the high degree of dysprosium selectivity exhibited by the membrane sensor.

The proposed sensor was used for the determination of fluoride ion concentration in two mouth wash preparations [17, 18]. One gram of each sample of the sodium fluoride mouth wash solutions was taken and diluted with distilledwater in a 100 mL flask and titrated with a Dy(III) solution (1.0×10^{-3} mol L^{-1}). The corresponding results (after triplicate measurements) are summarized in Table 7. Evidently, there is a satisfactory agreement among the declared fluoride content, the determined values by the sensor and the commercial solid fluoride sensor.

Table 6. Determination of Dy(III) ions in various binary mixtures by the designed selective membrane sensor.

Dy^{3+} (ppm)	Added cation (ppm)	Recovery[a] (%)
30	La^{3+}, 90	102.3 ± 0.3
30	Nd^{3+}, 90	102.6 ± 0.1
30	Gd^{3+}, 90	99.8 ± 0.5
30	Tb^{3+}, 90	98.7 ± 0.2
30	Er^{3+}, 90	101.5 ± 0.4
30	Tm^{3+}, 90	103.1 ± 0.5
20	Pn^{2+}, 90	102.0 ± 0.3
20	Ba^{2+}, 90	102.4 ± 0.6
20	Cd^{2+}, 100	100.3 ± 0.1
20	Cu^{2+}, 100	99.9 ± 0.4
20	K^{+}, 100	101.8 ± 0.5
20	Na^{+}, 100	103 ± 0.2

[a] Results are based on three measurements.

Table 7. Determination of fluoride ions in mouth washes.

Sample	Labeled (ppm)	Found ISE[a,b] (ppm)	Commercial fluoride ISEb (ppm)
Sodium fluoride mouth wash solution (Aquafresh, Brentford, UK)	1350	1371 ± 21	1347 ± 15
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	1478 ± 12	1445 ± 19

[a] Designed Dy(III) membrane sensor

[b] Results are based on three measurements

Table 8. Comparison between the determination of Dy(III) ions by proposed sensor, ICP-AES and FFT-CCV.

Solution	Real amount (ppm)	Found amount (ppm)		
		ISE[a,b]	ICP-AES[b]	FFT-CCV[b]
Monazite	6.0	6.50 ± 0.08	6.49 ± 0.12	6.50 ± 0.06
Xenotime	8.6	8.98 ± 0.13	9.09 ± 0.03	8.85 ± 0.24

[a] Designed Dy(III) membrane sensor.
[b] Results are based on three measurements

Monazite $[(Ln,Th)PO_4]$ Bastnasite $[LnFCO_3]$ and Xenotime $[(Y,Ln)PO_4]$ are three important lanthanide ores and have large amounts of these elements. The first and second one is richer in earlier lanthanides and the last one is richer in later lanthanides. So, three solutions were prepared with the same ingredients of monazite and xenotime and diluted 1000 times to provide sample solutions The results obtained for Dy(III) ions in samples under investigation are given in Table 8. For these determinations three replicate analyses were performed for each sample. From the results it can be seen that within the precision of both measuring procedures the concentration values of these ions determined by proposed sensor, ICP-AES and fast Fourier transform continuous cyclic voltammetry (FFT-CCV) [41-43] are in fair agreement with each other.

The proposed sensor was effectively employed for the determination of dysprosium ions in soil and sediment samples [16]. A sample (1 g) was weighed into a PTFE beaker. Then, 5mL of 70% $HClO_4$ and 10mL of 48% HF were added. The sample was heated in a sand bath to incipient dryness. The acid attack with $HClO_4$ and HF (1 + 2) was repeated three times to complete the digestion of the silicate matrix. Afterwards, the samples were transferred into flasks, diluted with 5mL of NaOH 5% and distilled water to 50mL (pH~5) [44].

Table 9. Determination of Dy(III) ions in soil samples.

Sample No.	Designed membrane sensora (ppm)	Arsenazo methoda (ppm)
1	66.6 ± 0.4	65.2 ± 0.2
2	37.8 ± 0.1	37.0 ± 0.5
3	49.5 ± 0.3	48.4 ± 0.1
4	55.4 ± 0.2	53.8 ± 0.4
5	61.3 ± 0.2	60.5 ± 0.2

[a] Results are based on three measurements

Then, the potential of these solutions was measured by employing the developed Dy(III) sensor as well as its calibration curve (1.0×10^{-7} to 1.0×10^{-1} mol L^{-1}), which was obtained after measuring a series of dysprosium ion standard solutions. Afterwards, the Dy(III) ion concentration in the samples was determined. The result, derived from triplicate measurements with the same sensor, was found to be in satisfactory agreement with that determined by the Arsenazo method (This is a spectrophotometric method in which the Arsenazo reagent (*o*-(1,8-dihydroxy-3,6- disulfo-2-naphthylazo)benzene arsenic acid, tri-sodium salt) forms a colored complex with the lanthanide ions and it is also used as a standard method for determination of lanthanides. There was a color change from red-orange to blue-violet, denoting the complex formation.) [45] as it can be seen from Table 9.

4. CONCLUSION

The above studies showed that 1-((Dimethylamino)(phenylimino)methyl)-3,3-dimethyl- 1-phenylthiourea (DPDP) is a selective ionophore for Dy(III) ions. This can be related to the presence of four intermediately soft N-donor atoms in its structure, and also to the size of the semi-cavity formed as a result of the arrangement of the different parts of the ligand around the desired ion in the solution. Another determining property which leads to the applicability of DPDP as a proper ion carrier, is the relatively fast ion exchange kinetics that governs the formation of its complexes, at least those with Dy(III) ions. This can be indirectly concluded from the relatively short response time of the sensor (~8 s). The lipophilicity of the ionophore, decreasing its leaching from the membrane to the test solution drastically, is the reason for the long life-times of the electrodes based on DPDP. All these advantages, together with the other improvements that are the result of the optimized composition of the membrane ingredients make DPDP-based membrane sensors, acceptable potentiometric devices for the determination of Dy(III) concentrations in different samples.

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