Neodymium(III) PVC Membrane Electrodechemical Sensor Based on N-benzoylethylidene-2-aminobenzylamine

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Abstract: The N-benzoylethylidene-2-aminobenzylamine (BEA) was used as a suitable ionophore in construction of neodymium ion selective electrode. The electrode with composition of 30% PVC, 58% solvent mediator (NB), 2% ionophore (BEA) and 10% anionic additive (OA) shows the best potentiometric response characteristics. The Nd³⁺ sensor exhibits a Nernstian slope of 21.2 ± 0.2 mV decade⁻¹ over the concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol L⁻¹, and a detection limit of 6.3×10^{-7} mol L⁻¹ of Nd³⁺ ions. The potentiometric response of the sensor is independent of the solution pH in the range of 2.4–8.5. It has a very short response time, in the whole concentration range (~7 s), and can be used for at least eight weeks. The proposed sensor revealed high selectivity with respect to all common alkali, alkaline earth, transition and heavy metal ions, including members of the lanthanide family other than Nd³⁺. The Nd³⁺ sensor was successfully applied as an indicator electrode in the potentiometric titration of Nd³⁺ ions with EDTA. The electrode was also employed for the determination of the fluoride ion in two mouth wash preparations.

Keywords: Sensor; Potentiometry; Ion-Selective Electrode; 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.¹ There are some instrumental methods for neodymium analysis by ICP-MS, ICP-AES, gravimetric determination, isotope dilution mass spectroscopy, absorption spectra of 4f electron transitions. Despite the fact that these methods are sensitive and precise, they are also expensive and time consuming. In comparison, potentiometric ion selective sensors offer advantages of low cost, portability, selectivity, and simple operatory. They also

provide an analysis method without destruction of sample. Also, they can be used in complex matrix of samples.²⁻²⁰ There are a few reports on neodymium potentiometric sensors.²¹⁻²⁶ In this study, another ion selective sensor has been introduced for the potentiometric Nd^{3+} determination, based on N-benzoylethylidene-2-aminobenzylamine (BEA), demonstrating fast response time, relatively low detection limit and also high selectivity (Figure 1).

Figure 1. The BEA structure.

Experimental

Reagents

The Merck Chemical and the Aldrich Co. were the suppliers for the nitrate and chloride salts of all cations and the reagent grades of benzyl acetate (BA), nitrobenzene (NB), acetophenone (AP), dibutyl phthalate (DBP), oleic acid (OA), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF), and high relative molecular weight PVC. The ionophore N-benzoylethylidene-2-aminobenzylamine (BEA) was prepared as formerly described.²⁷ 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, doubly distilled deionized water was used.

The emf Measurements

The equipment for the emf (electromotive force) measurements consisted of; a) $\text{Ag}-\text{AgCl}$ | internal solution, 1.0×10^{-3} M NdCl_3 | PVC membrane | sample solution | $\text{Hg}-\text{Hg}_2\text{Cl}_2$, KCl (satd.) and b) a Corning ion analyzer with a 250 pH/mV meter for the potential measurements at $25.0 \pm 0.1^\circ\text{C}$.

The activities were calculated according to the Debye–Huckel procedure.²⁸

Electrode Preparation

Membrane solutions were prepared by thoroughly dissolving 2 mg of BEA, 30 mg of powdered PVC, 58 mg of NB and 10 mg OA in 5 mL of fresh THF. The resulting clear

mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d. on top) was dipped into the mixture for about 10 s, so that a transparent membrane of about 0.3 mm thickness was formed.²⁹⁻⁴⁰ The tube was pulled out from the mixture and kept at room temperature for 24 h. The tube was then filled with an internal solution (1.0×10^{-3} M NdCl_3). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M Nd^{3+} ion solution. A silver/silver chloride electrode was used as an internal reference electrode.

Results and Discussion

The Potential Response of the BEA-Based Sensor

The existence of three donating atoms (two nitrogen and one donating oxygen) in the BEA structure was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions, rather than alkali and alkaline earth metal ions. Therefore, in order to check the suitability of BEA as an ion carrier for different metal ions, it was used as a neutral carrier to prepare a number PVC membrane ion-selective electrodes under identical conditions for a large number of metal ions, including alkali, alkaline earth, transition and heavy metal ions. The results revealed that except Nd^{3+} ion with the most sensitive response, in all other cases the slopes of the corresponding emf versus pM^{n+} are much lower than the expected slopes (59, 29, and 19 mV per decade for mono, di and trivalent cations, respectively).

The Membrane Composition Influence

The sensitivity and selectivity of any given membrane electrode is significantly related to the composition of the ion selective membrane, the nature of the solvent mediators and the used additives.⁴¹⁻⁴⁶ Thus, the influence of the membrane composition, the nature and the amount of the plasticizer along with the OA amount (as a suitable lipophilic additive) was investigated on the potential response of the Nd^{3+} sensor and the results are summarized in Table 1. Clearly, among the four plasticizers tested, NB offers the best sensitivity. This phenomenon can be due to the dielectric constant of the plasticizer on membrane phase as well as the mobility of the ionophore and its complex. It should be noted that the presence of lipophilic anions in the cation-selective membrane electrodes not only diminishes the ohmic resistance, but it also enhances their response behavior and selectivity.⁴⁷⁻⁵² The data given in Table 1 reveal that the presence of anionic additive in the construction of cationic sensors has a beneficial influence on the performance characteristics of the membrane electrode. Addition of 10% OA as a suitable additive (No. 6) will increase the slope of the potential response of the sensor from the poor value of mV/decade (No. 4) to a Nernstian value of $21.2 \text{ mV/decade}^{-1}$ (No. 6). Table 1 displays that the optimum response characteristics were obtained with a membrane composition of 30% PVC, 58% NB, 2% BEA and 10% OA (no. 6).

Calibration Graph and Statistical Data

The emf response of the PVC membrane at varying concentrations of neodymium ions (Fig. 2) indicates a rectilinear range from 1.0×10^{-6} to 1.0×10^{-2} M. The slope of the calibration curve was 21.2 ± 0.2 mV per decade of Nd^{3+} ions activity. The detection limit, as determined from the intersection of the two extrapolated segments of the calibration curve, was 6.3×10^{-7} M. The membrane electrode prepared could be used for at least eight weeks without any measurable divergences in the responses.

Table 1. Optimization of the membrane ingredients.

No.	Composition (w/w, %)				Slope (mV/decade)	Dynamic Linear range (M)
	BEA	Plasticizer	Additive	PVC		
1	2	NB, 66	TPB,2; OA,0	30	16.4 ± 0.2	1.0×10^{-5} - 1.0×10^{-2}
2	2	AP, 66	TPB,2; OA,0	30	15.9 ± 0.7	1.0×10^{-5} - 1.0×10^{-2}
3	2	BA, 66	TPB,2; OA,0	30	15.6 ± 0.3	1.0×10^{-5} - 1.0×10^{-2}
4	2	DBP, 66	TPB,2; OA,0	30	13.8 ± 0.5	1.0×10^{-5} - 5.0×10^{-2}
5	2	NB, 63	TPB,0; OA,5	30	17.7 ± 0.3	1.0×10^{-4} - 1.0×10^{-2}
6	2	NB, 58	TPB,0; OA,10	30	21.2 ± 0.2	1.0×10^{-6} - 1.0×10^{-2}
7	2	NB, 53	TPB,0; OA,15	30	17.3 ± 0.4	1.0×10^{-4} - 6.4×10^{-2}
8	2	NB, 56	TPB,2; OA,10	30	14.5 ± 0.3	1.0×10^{-5} - 1.0×10^{-2}
9	2	AP, 58	TPB,0; OA,10	30	20.3 ± 0.5	1.0×10^{-5} - 1.0×10^{-2}
10	2	BA, 58	TPB,0; OA,10	30	20.1 ± 0.6	1.0×10^{-5} - 1.0×10^{-3}
11	2	DBP, 58	TPB,0; OA,10	30	18.1 ± 0.4	1.0×10^{-5} - 1.0×10^{-3}
12	1	NB, 59	TPB,0; OA,10	30	20.3 ± 0.4	1.0×10^{-6} - 1.0×10^{-2}
13	3	NB, 57	TPB,0; OA,10	30	26.8 ± 0.4	1.0×10^{-6} - 1.0×10^{-2}

Figure 2. Calibration curve of the BEA based neodymium electrode.

The pH Effect

The pH influence on the membrane electrode response to a Nd^{3+} solution was studied over a pH range of 1.0 to 11.0 (the pH was adjusted using concentrated NaOH and HNO_3) at a neodymium ion concentration solution of 1.0×10^{-3} M. The corresponding results are shown in Figure 3. In the pH range of 2.4 to 8.5, the potential remains fairly constant. Beyond these limits, on the other hand, comparatively drastic drifts in the potential versus pH behavior were observed. At higher pH values, the potential decreases. This is due to the formation of some hydroxyl complexes of Nd^{3+} ions. At lower pH values, potential increases due to the membrane responses to hydronium ions.

Figure 3. The pH effect of the test solution on the potential response of the neodymium sensor.

Response Time

In this research, the dynamic response time⁵³ of the membrane was measured at various concentrations (1.0×10^{-6} to 1.0×10^{-2} M) of the test solutions and results are illustrated in Figure 4. Obviously, in the whole concentration range the electrode reaches its equilibrium response quickly (~ 7 s).

Figure 4. Dynamic response time of the neodymium electrode 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.

The Nd(III) Electrode Selectivity

Selectivity coefficients, which reflects the relative response of the membrane sensor towards the primary ion over the other ions present in the solution, is perhaps the most important characteristic of an ion-selective electrode. In this research, the potential responses of the recommended Nd^{3+} membrane sensor to a wide variety of cations were investigated by matched potential method (MPM)^{54,55}. According to this method, a specified activity of the primary ion (A) is added to a reference solution and the potential is measured. In a separate experiment, an interfering ion (B) is successively added to an identical reference solution (containing the primary ion), until the measured potential matches the one obtained with the primary ions. The matched potential method selectivity coefficient, K^{MPM} , is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{\text{MPM}} = a_A/a_B$. The resulting selectivity coefficient values are summarized in Table 2. In line with the information of this Table, the selectivity coefficients for the monovalent and the divalent tested cations (Na^+ , K^+ , Ca^{2+} , Ni^{2+} , Co^{2+} , Pb^{2+}) are smaller than 3.3×10^{-3} . In the case of trivalent cations (Er^{3+} , Pr^{3+} , Ho^{3+} , Yb^{3+} , Eu^{3+} , Gd^{3+} , Sm^{3+} , Fe^{3+} , Cr^{3+}), the selectivity coefficients are relatively small (from 7.6×10^{-4} to 7.2×10^{-3}). Eventually, it can be stated that because of the good selectivity coefficients values, the disturbance produced by these cations in the function of the developed membrane sensor is negligible.

Table 2. Selectivity coefficients of various interfering ions.

Interfering ions	$K^{\text{MPM}}_{\text{Nd}^{3+},B}$	Interfering ions	$K^{\text{MPM}}_{\text{Nd}^{3+},B}$
Er^{3+}	7.6×10^{-4}	Cr^{3+}	4.3×10^{-3}
Pr^{3+}	8.3×10^{-4}	Pb^{2+}	2.1×10^{-3}
Ho^{3+}	3.2×10^{-3}	Na^+	1.0×10^{-3}
Yb^{3+}	8.5×10^{-4}	K^+	2.1×10^{-3}
Eu^{3+}	8.7×10^{-4}	Ca^{2+}	3.3×10^{-3}
Gd^{3+}	3.8×10^{-3}	Ni^{2+}	2.8×10^{-3}
Sm^{3+}	7.2×10^{-3}	Co^{2+}	2.3×10^{-3}
Fe^{3+}	3.5×10^{-3}		

Table 3 also compares the selectivity coefficients, response times, detection limits, dynamic ranges, and pH range of the Nd^{3+} sensor with those of the best previous Nd^{3+} electrodes reported in the literature by other researchers.²¹⁻²⁶ From the data given in Table 3, the proposed sensor not only in terms of response time, but also in terms of selectivity is superior to the previously reported Nd^{3+} ion-selective membrane electrode.

Table 3. Comparison of different Nd^{3+} 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}	1.0×10^{-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}	6.3×10^{-7}
Response time (s)	10	<15	<5	<10	<10	<15	~7
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	2.4-8.5
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	21.2 ± 0.2
Log $K_{\text{sel}} > -2$	Hg, Ni	La, Gd, Sm, Cu, Yb	Ce, Yb, Gd, Sr, Cu, La, Ag	La, Sm, Gd	La, Dy	La, Gd, Sm, Pr	-

Analytical Application

The proposed Nd^{3+} membrane electrode was found to work well under laboratory conditions. It was also successfully applied to the titration of 1.0×10^{-4} M $\text{Nd}(\text{III})$ solution with a standard 1.0×10^{-2} M EDTA, and the resulting titration curve is shown in Figure 5. As seen, the amount of Nd^{3+} in solution can be accurately determined with the electrode.

Figure 5. Potentiometric titration curve of 25.0 mL from a 1.0×10^{-4} M Nd^{3+} solution with 1.0×10^{-2} M of EDTA.

Because of high selectivity and low detection limit of the developed Nd^{3+} sensor (membrane no. 6), it was also applied for the determination of Nd^{3+} ions concentration in mixtures of

three different ions. The corresponding results in Table 4 reveal that the recovery of Nd^{3+} ions in all mixtures is acceptable.

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

Serial no.	Composition	Observed content (M)
1	0.00010 M $\text{Nd}(\text{NO}_3)_3$ + 0.001 M $\text{Tb}(\text{NO}_3)_3$ + 0.001 M $\text{Eu}(\text{NO}_3)_3$	0.000098
2	0.00010 M $\text{Nd}(\text{NO}_3)_3$ + 0.001 M $\text{Dy}(\text{NO}_3)_3$ + 0.001 M $\text{Ho}(\text{NO}_3)_3$	0.000098
3	0.00010 M $\text{Nd}(\text{NO}_3)_3$ + 0.001 M $\text{Er}(\text{NO}_3)_3$ + 0.001 M $\text{Pr}(\text{NO}_3)_3$	0.000096
4	0.00010 M $\text{Nd}(\text{NO}_3)_3$ + 0.001 M $\text{Ce}(\text{NO}_3)_3$ + 0.001 M $\text{Cu}(\text{NO}_3)_2$	0.000104
5	0.00010 M $\text{Nd}(\text{NO}_3)_3$ + 0.001 M $\text{Tm}(\text{NO}_3)_3$ + 0.001 M $\text{Lu}(\text{NO}_3)_3$	0.000106
6	0.00010 M $\text{Nd}(\text{NO}_3)_3$ + 0.001 M $\text{Cr}(\text{NO}_3)_3$ + 0.001 M $\text{Fe}(\text{NO}_3)_3$	0.000097
7	0.00010 M $\text{Nd}(\text{NO}_3)_3$ + 0.001 M $\text{Ni}(\text{NO}_3)_2$ + 0.001 M KNO_3	0.000105

The BEA sensor was also used to the determination of fluoride ions in two mouth wash samples. 1.0 g of each sample was taken and diluted with distilled water in a 100 ml flask and titrated with a Nd^{3+} solution (1.0×10^{-3} M). The associated results, after triplicate measurements, are summarized in Table 5. As it is seen, there is a satisfactory agreement among the declared fluoride content, the determined values by the sensor.

Table 5. Fluoride ions determination in mouth wash solutions.

Sample	Labeled (ppm)	Found ISE ^a (ppm)
Sodium fluoride mouth wash solution (Aquafresh, Brentford, U.K.)	1350	(1382 ± 18)
Sodium fluoride mouth wash solution (Eurodont, DuroDont GmbH)	1450	(1476 ± 22)

a. Suggested Nd^{3+} sensor.

b. Results are based on three measurements.

Conclusion

A poly vinyl chloride (PVC) membrane sensor for neodymium(III) ions was fabricated based on N-benzoylethylidene-2-aminobenzylamine (BEA) as a new ion carrier. The sensor showed a Nernstian response (slope of 21.2 ± 0.2 mV/decade), low limit of detection (6.3×10^{-7} M), applicable pH range of 2.4-8.5, fast response time (~ 7 s) and 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. Moreover, 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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