Articles

La(III) Selective Membrane Sensor Based on a New N-N Schiff's Base

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Bis(2-methylbenzaldehyde)butane-2,3-dihydrazone(TDSB) was used as new N-N Schiff's base which plays the role of an excellent ion carrier in the construction of a La(III) membrane sensor. The best performance was obtained with a membrane containing, 30% poly(vinyl chloride), 60% benzyl acetate, 6% TDSB and 4% sodium tetraphenyl borate. This sensor reveals a very good selectivity towards La(III) ions over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The proposed electrode exhibits a Nernstian behavior (with slope of 19.8 mV per decade) over a wide concentration range $(1.0 \times 10^{-5}\text{-}1.0 \times 10^{-1}$ M). The detection limit of the sensor is 7.0×10^{-6} M. It has a very short response time, in the whole concentration range (~5 s), and can be used for at least twelve weeks in the pH range of 3.0-9.4. The proposed sensor was successfully applied as an indicator electrode for the potentiometric titration of a La(III) solution, with EDTA. It was also successfully applied in the determination of fluoride ions in three mouth wash preparations.

Key Words : La(III) sensor. Potentiometry, PVC. N-N Schiff's base

Introduction

Lanthanum oxide is widely used in the preparation of optical glasses, glass fibers for optical purposes, gasoline-cracking catalysts, polishing compounds and carbon arcs, and in the iron and steel industries to remove sulfur, carbon, and other electronegative elements from iron and steel. Solvent polymeric membrane based ISEs, together with the incorporation of new ion carriers, have shown to be a very useful tool for clinical, environmental, and chemical analyses as well as for process monitoring. In the area of membrane based ISEs, emphasis has been focused on the development of new ion-carriers. Fabrication of a new, ion-specific ISEs with high selectivity and sensitivity, wide linear concentration range, long lifetime and good repro-ducibility, is always in need. There have been many studies about ion-selective electrodes (ISEs) for different metal ions.[1] Among these metal ions, little attention has been paid to the development of La(III) membrane sensors.[2-5]

In recent years, we have reported a number of new PVC-based sensor for selective and sensitive monitoring of lanthanide ions such as Ce(III), La(III), Sm(III), Gd(III), and Yb(III).[6-11] In this work we introduce a highly selective La(III) sensor by incorporating Bis(2-methylbenzaldehyde)-butane-2,3-dihydrazone in a PVC-based membrane.

Experimental Section

Reagents. Reagent grade acetophenone (AP), benzyl acetate (BA), dibutyl phthalate (DBP), *o*-nitrophenyloctyl ether (NPOE), sodium tetraphenyl borate (TPB), tetrahydro-furan (THF) and high relative molecular weight PVC were purchased from Merck Chemical Company and used as received. Reagent grade chloride salts of all cations used (all from Merck), were of the highest purity available and used without any further purification except for vacuum drying. Doubly distilled deionized water was used throughout.

Synthesis of TDSB. TDSB was synthesized in two steps.

Step 1. The synthesis of 2,3-butanedihydrazone. 2,3-butanedihydrazone was prepared by the Bush and Bailar method.[12] To a boiling solution of 11.63 g of aqueous hydrazine (0.24 mol) in 100 mL of methanol, was added 75 mL of biacetyl (0.12 mol, 10.33 g) over a period of 2 hrs. Refluxing was continued for an additional 1 h. Two hundred milliliters of water was then added and the methanol was removed by distillation when the resulting aqueous solution was cooled in an ice-bath, with crystal formed. The crystals were filtered, washed with a little water, recrystallized from 100 mL of hot methanol and dried in vacuum.

Step 2. The synthesis of TDSB. TDSB (Figure 1) was prepared by the reaction of the 2-methylebenzaldehyde with diamine. This can be typified by the following preparation. To an ethanol solution (100 mL) of 2,3-butanedihydrazone (1.14 g, 0.1 mole) was added 2-methylebenzaldehyde (2.40 g, 0.02 mole). This mixture was refluxed in a round bottom flask, fitted with a Dean Stark trap, to remove the water produced during the reaction, and concentrated to yield a yellow solid. The product was collected by filtration,
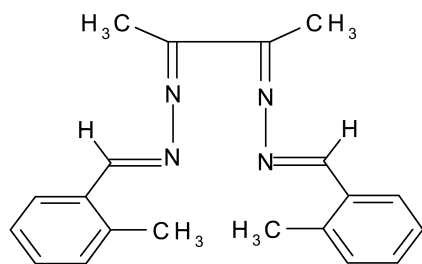
Figure 1. Structure of TDSB.

Figure 2. Potential responses of different ionselective electrodes based on TDSB.

washed with a little water, recrystallized from 100 mL of hot ethanol and dried in vacuum (yield ~87%). mp = 126-127 °C, ^{1}H-NMR (200 MHz, CDCl$_3$), δ 2.42 (6H, s, CH$_3$), 2.62 (6H, s, CH$_3$), 7.45-7.60 (8H, m, phenyl), 8.42 (2H, s, CH=N); ^{13}C NMR data; δ 12.70 and 19.95 (2CH$_3$), 128.77, 128.96, 130.23 and 131.49 (4 CH), 135.82, 139.33 (2 C), 159.75 (CH), 164.31 (C). Anal. Calcd for CxHyNz: C, 75.44; H, 6.96; N, 17.59. Found: C, 75.23; H, 6.86; N, 17.64%, IR (KBr, cm^{-1}): 1608 ($\nu_{C=N}$); 1550 ($\nu_{C=C}$).

Electrode Preparation. Membrane solutions were prepared by thoroughly dissolving 6.0 mg of TDSB, 30 mg of powdered PVC, 60 mg of BA and 4.0 mg of TPB in 3 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 5 s, so that a nontransparent membrane of about 0.3 mm thickness was formed.[13,14] The tube was pulled out from the mixture and kept at room temperature for 12 hrs. The tube was then filled with an internal solution (1.0 × 10^{-3} M LaCl$_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0 × 10^{-2} M lanthanum chloride solution. A silver/silver chloride electrode was used as the internal reference electrode.

The pH of all solutions was adjusted at 4.0, using a buffer of acetic acid/lithium acetate.

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

Ag-AgCl | internal solution, 1.0 × 10^{-3} M LaCl$_3$ | PVC membrane | test solution | Hg-Hg$_2$Cl$_2$ | KCl (satd)

The activities were calculated according to the Debye-Hückel procedure.[15]

Results and Discussion

The existence of four donating nitrogen atoms in TDSB, was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions.[6,11,12,16] Thus, in order to check the suitability of TDSB as an ion carrier for different metal ions, it was used to prepare a number of PVC membrane ion-selective electrodes for a wide variety of cations, including alkali, alkaline earth and transition metal ions. The potential responses of the most sensitive ion-selective electrodes based on TDSB are given in Figure 2a and 2b. As can be seen, except for the La(III) ion-selective electrode, in the case of all other cations tested,
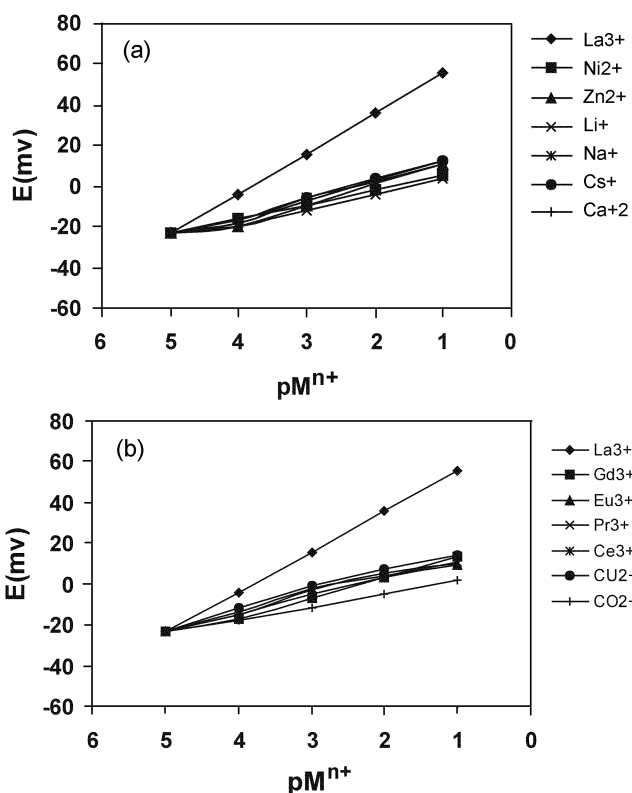
the slopes of the corresponding potential pM^{n+} plots, is much lower than the expected Nernstian slopes of 59, 29.5 and 20 mV per decade for the univalent, bivalent and trivalent cations, respectively. However, La(III) with the most sensitive response among all cations tested seems to be suitably determined with the membrane electrode based on TDSB. This is likely due to the high selectivity of the ion carrier towards La(III) ions, over other metal ions as well as the rapid exchange kinetics of the resulting La(III)-TDSB complex.

It is well understood that the sensitivity, linear dynamic range, and selectivity of the ISEs depend on, not only the nature of the carrier used, but also significantly on the

Table 1. Optimization of the membrane ingredients

Number of membrane	Composition (wt.%)				Slope (mV per decade)
	PVC	Plasticizer	TDSB	NaTPB	
1	30	BA. 65	5	–	8.4 ± 0.1
2	30	BA. 64	6	–	10.7 = 0.2
3	30	BA. 63	7	–	8.8 = 0.1
4	30	BA. 62	6	2	13.2 = 0.2
5	30	BA. 61	6	3	17.7 = 0.3
6	30	BA. 60	6	4	19.8 = 0.3
7	30	AP. 60	6	4	18.8 = 0.5
8	30	DBP. 60	6	4	17.7 = 0.2
9	30	NPOE. 60	6	4	19.6 = 0.3
10	30	BA. 66	–	4	3.7 = 0.1

membrane composition and the properties of the additives employed.[17,18,19,20] Thus, the influence of the membrane composition, nature, and amount of the plasticizer, and lipophilic additives, on the potential response of the membranes were investigated and the results are given in Table 1. As it can be seen, in the composition 6, the membrane incorporating 60% BA and 30% PVC, in the presence of 6% TDSB and 4% TPB, shows the best sensitivity, with a Nernstian slope of 19.8 mV per decade of La(III) concentration.

The potentiometric response of the membranes was greatly improved in the presence of a lipophilic cationic additive (from slope of 10.7 to 19.8 mV per decade for the membrane Nos. 2 and 6, respectively). It is well known that not only do the lipophilic salts reduce the membrane resistance, but they also enhance the response behavior and selectivity, and reduce interference from sample anion.[21]

The effect of the concentration of the internal solution on the potential response of the sensor was investigated. The lanthanum chloride concentration was changed from 1.0×10^{-1} to 1.0×10^{-2} M and the corresponding EMF versus pLa^{3+} plots were obtained. It was found that the concentration of the internal solution has a negligible effect on the potential response of the electrode, except for an expected shift in the intercept of the resulting plots. A 1.0×10^{-3} M concentration of the filling solution was used for further studies.

The plot of EMF *vs.* pLa^{3+} obtained under optimal membrane ingredients for the sensor (Fig. 3), indicate that it has a Nernestian behavior over wide concentration ranges of La(III) ion. The slope and linear range of the resulting calibration graph were 19.8 mV per decade and 1.0×10^{-5}-1.0×10^{-1} M, respectively. The limit of detection (LOD), defined as the concentration of La(III) ion, obtained when the linear regions of the calibration graph extrapolated to the base line potential, is 7.0×10^{-6} M.

The optimum equilibration time for the membrane sensor in the presence of 1.0×10^{-3} M lanthanum chloride was investigated and found to be 24 h, after which the electrode
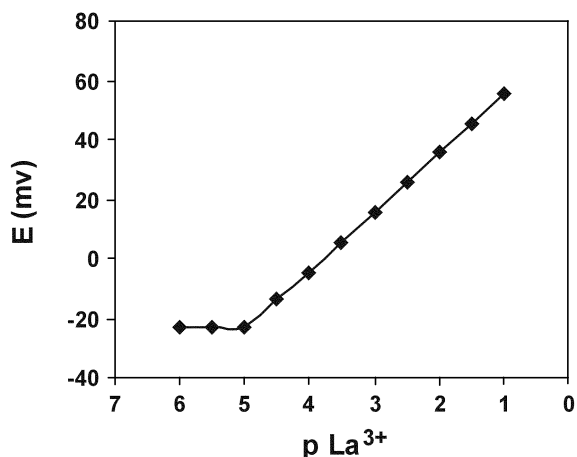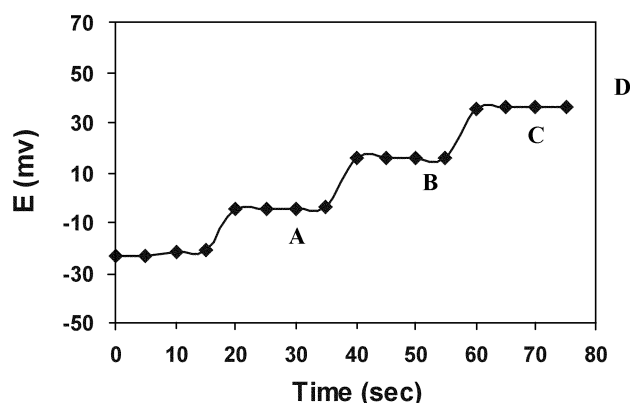
Figure 4. Dynamic response time of the lanthanum electrode for step changes in the concentration of La³⁺: (A) 1.0×10^{-5} M, (B) 1.0×10^{-4} M, (C) 1.0×10^{-3} M, (D) 1.0×10^{-2} M.

generated stable potentials in contact with La(III) ion solutions. The standard deviation of 10 replicate potential measurements for proposed electrode was at the most = 0.3 mV. The proposed electrode was very stable and could be used for at least 2 months without observing any change in its response characteristics.

For analytical purposes, response time is one of the most important factors that are taken into account. In this work, the practical response time was recorded by immediate and successive changing of La(III) concentration from 1.0×10^{-5} to 10×10^{-1} M and the results are shown in Figure 4. As it can be seen, in the whole concentration range, the electrode reaches to its equilibrium response in a very short time (5 s).

The pH dependence of the membrane sensor was tested over a pH range of 1.0-12.0 in a 1.0×10^{-3} M La(III) solution, and the results are illustrated in Figure 5. As it can be seen, the potential remains fairly constant in a pH range of 3.0-9.4. Beyond this range, a gradual change in the potential was detected. The observed potential drift at the higher pH values could be due to the formation of some hydroxy complexes of La(III) in the solution. At lower pH values, the potentials increased, indicating that the membrane sensor responds to proton ions, too.

The potentiometric selectivity coefficients, which reflected the relative response of the membrane sensor towards the
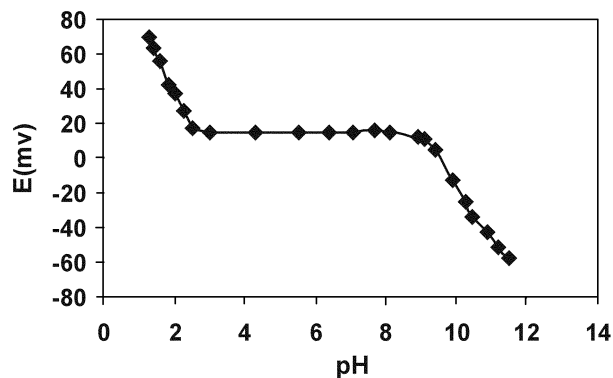
Figure 3. Calibration curves of lanthanum(III) electrode based on TDSB.

Figure 5. The effect of the pH of the test solution on the potential response of the lanthanum Sensor.

Table 2. Selectivity coefficients for various interfering ions

Cation	$K_{A,B}^{MPM}$
Pr^{3-}	7.84×10^{-3}
Gd^{3-}	2.21×10^{-3}
Eu^{3-}	3.12×10^{-3}
Ce^{3-}	9.33×10^{-3}
Zn^{2-}	9.34×10^{-4}
Ni^{2-}	3.64×10^{-4}
Cu^{2+}	3.09×10^{-2}
Ca^{2-}	4.38×10^{-3}
Na^+	9.64×10^{-4}
Co^{2+}	1.45×10^{-4}
Cs^+	5.91×10^{-3}
Li^-	2.38×10^{-4}
K^1	4.60×10^{-4}
NH_4	2.39×10^{-4}

primary ion, over other ions present in solution, is perhaps the most important characteristics of an ion-selective electrode. In this work, the potential responses of the proposed La(III) membrane sensor to a wide variety of cations, were investigated by the matched potential method (MPM). According to the MPM,[22] the selectivity coefficient is defined as the activity ratio of the primary ion ($A=10^{-5}$-10^{-3} M of La(III) ion) and the interfering ion ($B=10^{-1}$-10^{-3} M) that gives the same potential change in a reference solution (1.0×10^{-5} M of La(III) ion). Thus, first the change in potential upon changing the primary ion activity is measured, and then the interfering ion would be added to an identical reference solution until the same potential change is obtained.

The selectivity coefficient $K_{A,B}^{MPM}$, is determined as:

$K_{A,B}^{MPM} = \Delta A/a_B$, where $\Delta A = á_A \Delta a_A$, a_A is the initial primary ion activity and $á_A$ the activity of A in the presence of interfering ion, a_B. The resulting selectivity coefficient values thus obtained for the La(III) membrane electrode, are summarized in Table 2. As it is seen, for all the monovalent cations tested (Li^-, Na^-, K^-, NH_4^+, Cs^+) the selectivity coefficients are smaller than 5.91×10^{-3}. Selectivity coefficients obtained for divalent cations tried (Zn^{2+}, Ni^2, Ca^{2-}, Co^{2-}) are also very small, and in the range 1.45×10^{-4}-4.38×10^{-3}, (except for Cu^{2-}). In the case of trivalent cations (Pr^{3-}, Gd^{3-}, Eu^{3+}, Ce^{3+}) the selectivity coefficients are relatively small (in the range 2.21×10^{-3}-9.33×10^{-3}). The obtained selectivity coefficients indicate that the disturbance produced by these cations in the functioning of the proposed membrane sensor is negligible.

Table 3. Comparison of the selectivity coefficients of different La(III) electrodes

Ions	Selectivity Coefficient		This work
	Ref. 21	Ref. 22	
Co^{2-}	2.5×10^{-2}	5.0×10^{-3}	1.45×10^{-4}
Cu^{2-}	–	2.0×10^{-2}	3.09×10^{-2}
Ni^{2-}	2.5×10^{-2}	1.5×10^{-2}	3.64×10^{-4}
Zn^{2-}	–	2.1×10^{-2}	9.34×10^{-4}
Sm^{3+}	–	1.5×10^{-2}	–
Ce^{3-}	5.2×10^{-1}	5.0×10^{-2}	9.33×10^{-3}
UO_2^{2+}	–	3.0×10^{-3}	–
Ag^+	–	8.1×10^{-4}	–
Pb^{2-}	–	5.0×10^{-2}	–
Hg^{2+}	–	5.0×10^{-3}	–
Pr^{3-}	–	–	7.84×10^{-3}
Eu^{3-}	–	–	3.12×10^{-3}
Na^+	–	–	9.64×10^{-4}
Ca^{2-}	–	–	4.38×10^{-3}
Cs^-	–	–	5.91×10^{-3}
Li^-	–	–	2.38×10^{-4}
Gd^{3+}	–	–	2.21×10^{-3}

Table 3, compares the selectivity coefficients of the La(III) sensor with those of the best previously La(III) electrodes, reported in the literature.[20-23] From the data given in Table 3, it is immediately obvious that the selectivity coefficients of the sensor are superior to those reported by other researchers, especially for interfering cations such as Co^{2+}, Cu^{2-}, Ni^{2-}, Zn^{2-}, Ce^{3+}, Pr^{3+}, Eu^{3+}, Na^+, Ca^{2+}, Cs^-, Li^+, and Gd^{3-}.

The La(III) sensor was successfully used as an indicator electrode in the titration of 25.0 mL of 1.0×10^{-1} La(III) solution with a 1.0×10^{-2} M EDTA, and the resulting titration curve is given in Figure 6. As it is seen, the amount
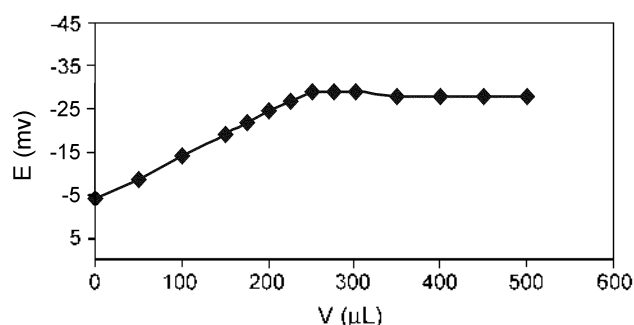
Figure 6. Potentiometric titration curve of 25.0 mL 1.0 × 10⁻¹ M solution of La³⁻ with 1.0 × 10⁻² M of EDTA at pH 5.0.

Table 4. Results of the determination of the fluoride in the three different mouth wash samples

Sample	Labeled	Fluoride electrode[a]	Found ISE[b]
Sodium fluoride mouth wash solution (Chimia Daru Co., Tehran, Iran)	2.0%	$(1.99 \pm 0.05)\%$	$(2.03 \pm 0.02)\%$
Sodium fluoride mouth wash solution (Shahre Daru Co., Tehran, Iran)	0.2%	$(0.21 \pm 0.01)\%$	$(0.24 \pm 0.03)\%$
Sodium fluoride tablets (Loghman Pharmaceutical Co., Tehran, Iran)	1.0 mg per tablet	$(1.01 \pm 0.03)\%$	$(0.98 \pm 0.024)\%$ mg per tablet

[a]Solid state fluoride electrode. [b]Proposed lanthanum membrane sensor

of La(III) ion in the solution can be determined with the electrode.

The membrane sensor was used to the determination of fluoride ions in two mouth wash preparation samples. 1.0 g of each sample was weighed, and diluted with distilled water in a 100 mL flask and titrated with a La^{3+} solution (1.0 × 10^{-3} M), and the results of three measurements are summarized in Table 4. As it is seen, there is a satisfactory agreement among the declared fluoride content, the values determined by the proposed sensor, and commercial solid fluoride sensor.

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