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Novel Potentiometric PVC-Membrane and Coated Graphite Sensors for Lanthanum(III)

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Abstract

Preliminary theoretical studies revealed the selective complexation of bis (2-mercaptoanil) diacetyl (BMDA) with La^{3+} over several alkali, alkaline earth and heavy metal ions. Thus, novel PVC-based membrane (PBM) and coated graphite membrane (CGM) sensors for $\text{La}(\text{III})$ based on BMDA were prepared. The electrodes display Nernstian behavior over wide concentration ranges (i.e., 1.0×10^{-5} – 1.0×10^{-1} M for PBM and 1.0×10^{-6} – 1.0×10^{-1} M for CGM). The potential response of sensors was pH independent in the range of 4.0–8.0. The sensors possess satisfactory reproducibility, fast response time (< 15 s), and specially excellent discriminating ability for La^{3+} ions with respect to most of the cations. The membrane sensor was used as an indicator electrode in potentiometric titration of lanthanum ions with EDTA. The coated graphite membrane electrode was applied in determination of fluoride ions in mouth wash preparations.

Keywords: Lanthanum ion-selective electrode, PVC membrane, Coated graphite, bis(2-Mercaptoanil)diacetyl, Potentiometry

1. Introduction

In recent decades, many intensive studies on the design and synthesis of highly selective ionophores as sensory molecules for ion-selective electrodes (ISEs) have been reported. In spite of successful progress in the design of highly selective ionophores for various metal ions, there are only a limited number of reports on the development of highly selective ionophores for lanthanum(III) [1–6]. However, these sensors have one, two or in some cases, all of the following problems: 1) high detection limits, 2) short linear ranges and 3) significant interferences from many cations (e.g., Cu^{2+} , Ni^{2+} and Ce^{3+}).

Lanthanum ions accelerate hydrolysis of phosphate ester binding by 13 orders of magnitude. This suggests that phosphate diester in DNA may also suffer such destruction. Thus, lanthanum should be situated among the class of highly toxic metal ions that are potentially effective against micro- and higher organisms. Lanthanum chloride manifests as antitumor. Genotoxicity of lanthanum(III) in human peripheral blood lymphocytes has also been reported. Lanthanum chloride caused changes in lipid peroxidation, the redox system, and ATPase activities in plasma membranes of rice seeding roots [7–9].

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 [10].

Thus, because of the increasing interest in bioinorganic and coordination chemistry and increased industrial use of lanthanum compounds as well as their enhanced discharge, toxic properties, and other adverse effects, determination of the lanthanum ions is very necessary. The available methods for low-level determination of rare-earth ions in solution include spectrophotometry, [11] ICP-MS and ICP-AES [12, 13]. Isotope dilution mass spectrometry, [14] neutron activation analysis, [15] X-ray fluorescence spectrometry, [16] etc, are also used in some laboratories. These methods are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. However, neutral carrier-based ion-selective electrodes (ISEs) can offer an inexpensive and convenient method of analysis of rare-earth ions in solution, provided that acceptable sensitivity and selectivity are achieved. Although the neutral carrier-type ISEs have been successful for determination of a wide variety of metal ions, including the alkali, alkaline-earth, transition, and some other heavy metal ions [17], the use of such electrodes in the determination of rare-earth ions has yet to be realized in a practical sense.

Recently, we have used some S- and N-containing ionophores in construction of PVC-based membrane sensors for different transition and heavy metal ions [18–22]. In

this work, we report novel plasticized polymeric membrane (PBM) and coated graphite electrodes (CGM) for La^{3+} ion based on bis(2-mercaptoanil)diacetyl (BMDA) as a neutral carrier. Our preliminary theoretical studies revealed the increased selectivity of BMDA binding to La^{3+} ion over several alkali, alkaline earth, transition, and heavy metal ions.

2. Experimental

2.1. Reagents

Reagent grade dioctyl phthalate (DOP), benzyl acetate (BA), acetophenone (AP), ortho-nitrophenyloctyl ether (NPOE), sodium tetraphenylborate (NaTPB), oleic acid (OA), tetrahydrofuran (THF) and high relative molecular weight PVC (all from Fluka) were used as received. The nitrate and chloride salts of all cations used (all from Merck) were of the highest purity available and were used without any further purification except for vacuum drying over P_2O_5 . Triply distilled deionized water was used throughout.

2.2. Synthesis of BMDA

2-Aminothiophenol (2.50 g, 0.02 mol) was mixed with 150 mL of distilled ethanol in a 500 mL round bottom flask, while magnetic stirring. 2,3-Butanedione (0.86 g, 0.01 mol) dissolved in a 25 mL of distilled ethanol, was then added dropwise using a dropping funnel to the above solution. The contents were refluxed for 50 min to get a yellow solid precipitate of the Schiff base ligand. It was then cooled, filtered, washed with petroleum ether and dried. The pure BMDA was finally recrystallized from chloroform. Anal. calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}_2$: C, 63.88; H, 5.37; N, 9.33; S, 21.34, found: C, 63.88; H, 5.41; N, 9.41; S, 21.27%.

2.3. Electrodes Preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg PVC, 66 mg of plasticizer AP, 2 mg of additive NaTPB and 2 mg of ionophore BMDA in a glass dish of 2 cm diameter. The mixture was completely dissolved in 3 mL of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was

obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 s so that a nontransparent membrane of about 0.3 mm thickness is formed. 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 internal filling solution (1.0×10^{-3} M). The electrode was finally conditioned for 8 h by soaking in a 1.0×10^{-2} M of LaCl_3 . A silver/silver chloride electrode was used as an internal reference electrode.

In order to prepare the coated graphite membrane electrodes, spectroscopic grade graphite rods of 3 mm diameter and 15 mm long were used. A shielded copper wire was glued to one end of the graphite rod, and the electrode was sealed into the end of a PVC tube of about the same diameter by epoxy resin. The working surface of the electrode was polished with fine alumina slurries on a polishing cloth, sonicated in distilled water and dried in air. The polished graphite electrode was dipped into the membrane solution mentioned above and the solvent was evaporated. A membrane was formed on the graphite surface and the electrode was allowed to set overnight. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M solution of LaCl_3 . The pH of all solutions, were fixed at 4.0 using a sodium acetate-acetic acid buffer.

2.4. EMF Measurements

The emf measurement with the plasticized polymeric membrane (PBM) and the coated graphite membrane (CGM) electrodes were carried out with the following cell assemblies:

Ag-AgCl | internal solution 1.0×10^{-3} M LaCl_3 | PVC membrane |

Test solution | Hg-Hg₂Cl₂, KCl (satd) (PBM)

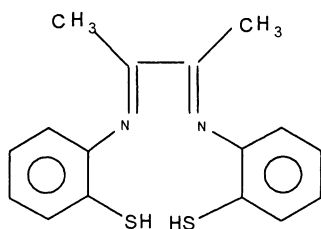
Hg-Hg₂Cl₂, KCl (satd) | sample solution | membrane | graphite surface (CGM)

The EMF observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. Activities were calculated according to the Debye-Hückel procedure [23].

3. Results and Discussion

3.1. Theoretical Studies

Many experimental and theoretical investigations have been carried out to understand better the fundamental interaction between metal ions and neutral molecules and their relationship to molecular recognition. Computational models capable of reliably predicting ligand selectivity in a variety of cations have been shown to be valuable tools for the advancement of practical works [24–27]. In order to have a clear picture about the selectivity of BMDA for various metal ions, in this work, we investigated its binding to Li^+ , K^+ , Sr^{2+} , Ba^{2+} , Cd^{2+} , Pb^{2+} and La^{3+} ions by using the



Scheme 1. BMDA

abinitio theoretical calculations. The influence of the nature, size and charge of metal ions on the complexation reaction with the neutral ligand is explained on the basis of the calculation of gas – phase binding energies.

The molecular structures of the uncomplexed ligand and its complexes with La^{3+} and other metal ions were built with the Chem Office program (Version 5) for structural chemistry on a Pentium 4 workstation. The structures were optimized using the lanl2mb basis set for all atoms at restricted Hartree Fock (RHF) level. No molecular symmetry constraint was applied. Rather, full optimization of all bond lengths, angles and torsion angles was carried out using the Gaussian 98 program. [28]. The binding energy (ΔE) was calculated with the enlarged basis sets using Equation (1):

$$\Delta E = E_{\text{complex}} - (E_{\text{ligand}} + E_{\text{cation}}) \quad (1)$$

Where, E_{complex} , E_{ligand} and E_{cation} are the total energies of the complex, uncomplexed ligand and metal ion, respectively.

Optimization of the uncomplexed ligand was also carried out with the semiempirical AM₁ method using HyperChem software (Version 6.01). No adequate parameterization of the metal ions was available in AM₁, so that semi-empirical calculations could not be carried out on the complexes.

Table 1 summarizes the theoretical data relating the stability of the Schiff base BMDA complexes with Li^+ , K^+ , Sr^{2+} , Ba^{2+} , Cd^{2+} , Pb^{2+} and La^{3+} . Inspection of Table 1 reveals that the cation binding energy with BMDA shows a pronounced dependence on the nature of metal ions used. In fact, the stability of the resulting complexes is expected to decrease in the order $\text{La}^{3+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Sr}^{2+} > \text{Li}^+ > \text{Ba}^{2+} > \text{K}^+$.

Table 1. Binding Energy of Complexes of Different Metal with BMDA

Binding energy (ΔE) [a] (kcal mol ⁻¹)	Total energy of the complex (Hartree)	Total energy of Metal ion (Hartree)	Metal ion
– 370.23	– 765.05	– 29.54	La^{3+}
– 144.33	– 742.29	– 7.14	Li^+
– 62.75	– 762.65	– 27.63	K^+
– 163.15	– 764.72	– 29.54	Sr^{2+}
– 131.78	– 759.52	– 24.39	Ba^{2+}
– 294.93	– 781.11	– 45.72	Cd^{2+}
– 238.45	– 737.80	– 2.60	Pb^{2+}

[a] The total energy of the uncomplexed ligand is – 734.92 Hartree.

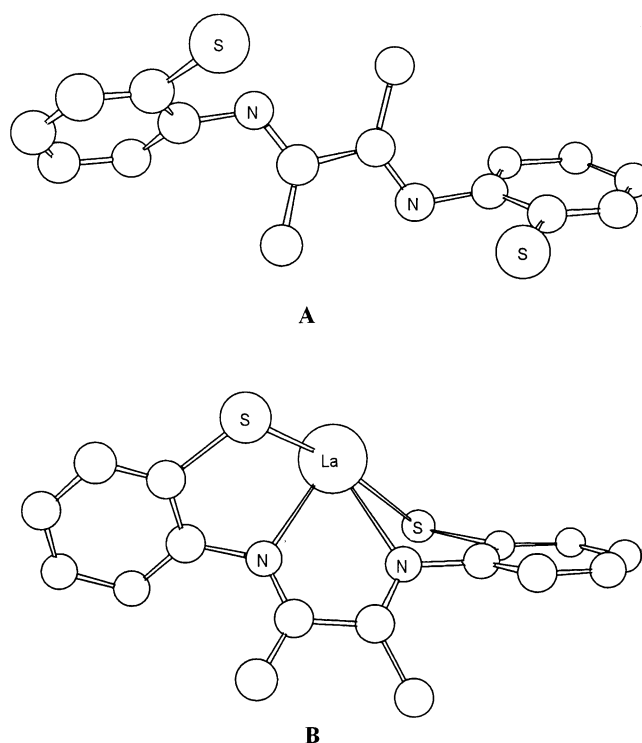


Fig. 1. Optimized structure of uncomplexed BMDA (A) and of La^{3+} complex (B).

The optimized structures of uncomplexed BMDA and its La^{3+} complex are shown in Figure 1 and some of their selected geometric parameters are summarized in Table 2. From Figure 1, it is immediately obvious that while the free ligand prefers a transconformation relative to the central C–C bond, the presence of La^{3+} ion induces a quasi *cis*-conformation so that all donating atoms of the molecule (i.e., the two –SH groups and the two =N-groups) can appropriately participate in metal ion binding. As is seen from Figure 1B, in the complexed form, the two benzo groups are not coplanar; they are rotated by an angle of about 90° relative to each other. Table 2 shows that in the complexed species, the nitrogen– La^{3+} distance is shorter than the sulphur– La^{3+} distance, indicating stronger nitrogen– La^{3+} binding.

Based on the theoretical results thus obtained, we decided to examine the suitability of BMDA as a potential ionophore for lanthanide ions. In preliminary experiments, BMDA was used as a potential neutral ion carrier to prepare

Table 2. Selective Geometric Parameters for Free BMDA and its La^{3+} Complex Ion^a

	>CCN	>CNC	>CCS	Atomic Charge N	Atomic Charge S	N–La	S–La	>CNLa	>CSLa
Ligand	128.1, 115.8,	1195	117, 121.3	– 0.244	– 0.161	–	–	–	–
Free	119.7, 122								
Complex with La^{3+}	126.8, 114, 122.6, 119	121.2	115, 122.2	– 0.304	– 0.105	2.42	3.04	122.7, 115.6	91.5

[a] Distances in Å, angles in degrees.

PVC membrane electrodes for a wide variety of transition and heavy metal ions and the potential responses of the resulting electrodes are shown in Figure 2. As can be seen, La^{3+} with the sensitive response seems to be suitably determined with the membrane electrode based on the BMDA.

3.2. Effect of Membrane Composition

It is well known that the membrane composition and, especially in some cases, the nature of the additive may have significant influence on the sensitivity and selectivity obtained for a given ionophore [16–22]. The performance characteristics of several membranes having ingredients of different proportions are summarized in Table 3. It is seen that membrane no. 4 with an optimized composition of 30% PVC, 66% AP, 2% BMDA and 2% NaTPB results in the best sensitivity with a Nernstian slope of 19.7 ± 0.2 mV per decade concentration of La^{3+} ions over a very wide dynamic range. As is obvious from Table 3, the presence of 2% NaTPB provided the electrode with a nice Nernstian potential response. In fact, it has been demonstrated that the presence of lipophilic negatively charged additives such as NaTPB improves the potentiometric behavior of certain selective electrodes, not only by reducing the ohmic resistance, [29] and improving the response behavior and selectivity [30, 31] but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode [31].

3.3. Response Time

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the La^{3+} concentration in solution, over a concentration range 1.0×10^{-1} to 1.0×10^{-5} M. The actual potential versus time traces is shown in Figure 3. As seen, over the entire concentration range the plasticized membrane electrodes reach their equilibrium responses in a very short time (< 15 s). This is most probably due to the fast exchange kinetics of complexation–decom-

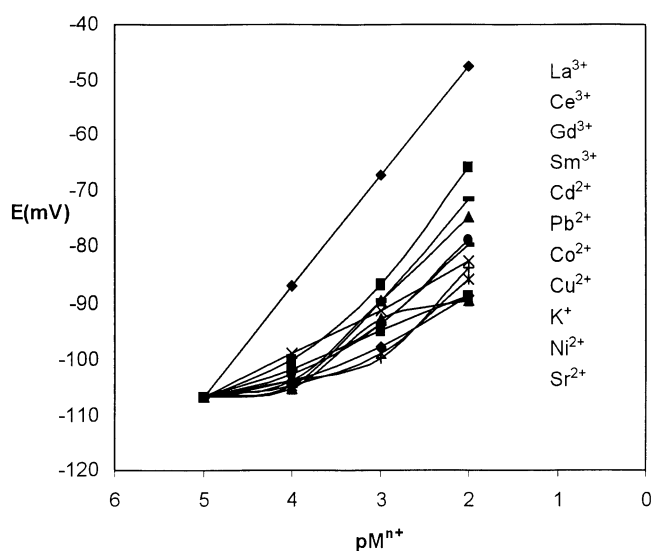


Fig. 2. The potential responses of various cation-selective electrodes based on BMDA.

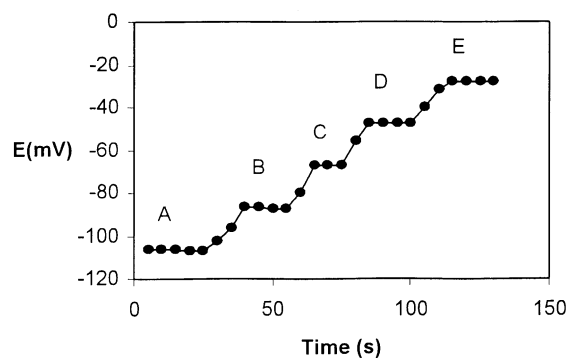


Fig. 3. Dynamic response of La^{3+} sensor for step changes in concentration of lanthanum(III) ion: A) 1.0×10^{-5} M, B) 1.0×10^{-4} M, C) 1.0×10^{-3} M, D) 1.0×10^{-2} M, E) 1.0×10^{-1} M.

plexation of La^{3+} ion with the ionophore at the test solution-membrane interface. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations and the results

Table 3. Optimization of Membrane Ingredients.

Membrane number	Composition [%]				Slope [mV/decade]
	BMDA	PVC	Additive	Plasticizer	
1	–	30	NaTPB, 2	AP, 68	≈ 0
2	2	30	–	AP, 68	11.2
3	2	30	OA, 15	AP, 53	15.6
4	2	30	NaTPB, 2	AP, 66	19.7
5	1	30	NaTPB, 2	AP, 67	14.2
6	4	30	NaTPB, 2	AP, 64	16.4
7	2	30	NaTPB, 2	NPOE, 66	12.0
8	2	30	NaTPB, 2	BA, 66	6.28
9	2	30	NaTPB, 2	DOP, 66	6.63

are shown in Figure 4. Here it is seen that the potentiometric response of the sensor is reversible, although the time needed to reach the equilibrium values were longer than that for the low-to-high sample concentration procedure. It is well documented that, in the case of high-to-low concentrations, the time needed to attain a stable potential is some 100 times larger than that required for the case of low-to-high concentrations (for a 10 times change in the cation concentration) [15].

3.4. Effect of pH

The influence of pH of the test solution on the potential response of the membrane sensor was tested in the pH range 2.5–10.0 and the results are shown in Figure 5. As can be seen, potential remains constant over a pH range of 4.0–8.0, beyond which the potential changes considerably. The observed drift at higher pH values could be due to the formation of some hydroxy complexes of La^{3+} ions in solution. The observed increase in potential at low pH values indicates that the protonated ionophore possesses a poor response to the La^{3+} ions and strong response to H_3O^+ in solution.

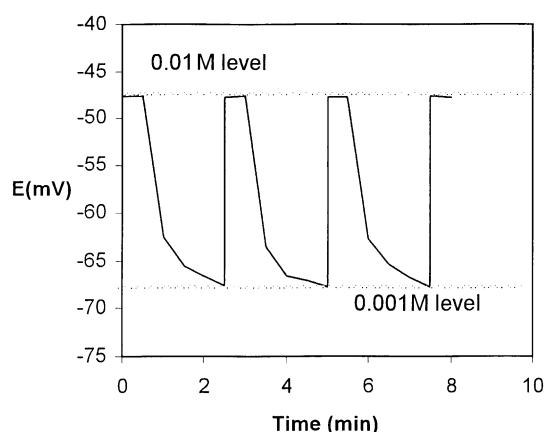


Fig. 4. Dynamic response characteristics of the La^{3+} electrode for several high-to-low sample cycles.

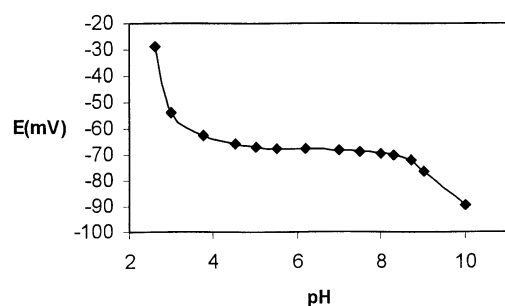


Fig. 5. Effect of pH of the test solution (1.0×10^{-3} M of La^{3+}) on the potential response of the La^{3+} ion-selective electrode. The pH was adjusted with nitric acid or sodium hydroxide solutions.

3.5. Calibration Plot and Statistical Data

The potential responses of the proposed sensors at varying concentration of $\text{La}(\text{III})$ ion show a linear response to the concentration of La^{3+} ions in the range of 1.0×10^{-1} to 1.0×10^{-5} M for PBM and 1.0×10^{-1} to 1.0×10^{-6} M for (Figure 6). The slope of calibration plots was 19.7 ± 0.2 mV per decade of the activity of La^{3+} ions. The limit of detections as determined from the intersection of the two extrapolated segments of the calibration plots were 6.5×10^{-6} M and 5.0×10^{-7} M for PBM and CGM, respectively. The standard deviation of 12 replicate measurements was ± 0.3 mV. The membrane electrodes prepared could be used for at least 2 months without any measurable divergence.

In Table 4, the response characteristics of the two electrodes are compared. Table 4 shows that, while both electrodes show Nernstian behaviors with fast responses, the linear range and limit of detection of the CGM are greatly enhanced relative to those of the PBM. The improved performance characteristics of the CGM over those of the PBM presumably originate from the coated graphite technology, where an internal 1.0×10^{-3} M LaCl_3 solution, in the case of PBM, has been replaced by a copper wire of much higher electrical conductivity, in the case of CGM.

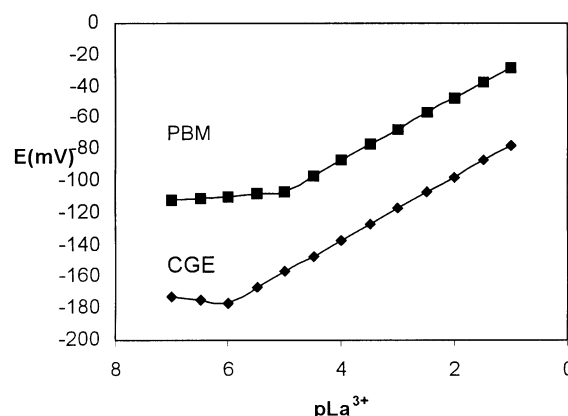


Fig. 6. Calibration plot of La^{3+} ion-selective electrode with membrane No. 4.

Table 4. Comparison of Response Characteristics of PBM and CGM

	PBM	CGM
Slope	19.7	19.7
Limit of detection	6.5×10^{-6}	5.0×10^{-7}
Linear range	1.0×10^{-1} M -1.0×10^{-5} M	1.0×10^{-1} M -1.0×10^{-6} M
Response time	< 15 s	< 15 s

Table 6. Results of determination of fluoride in different mouth wash solutions

Sample	Labeled (mg per tablet)	Found (mg per tablet)
Sodium fluoride mouth wash solution (Chimia Daru Co., Tehran, Iran)	2.0%	(2.02 ± 0.03)%
Sodium fluoride mouth wash solution (Shahre Daru Co., Tehran, Iran)	0.2%	(0.20 ± 0.02)%
Sodium fluoride tablets (Loghman Pharmaceutical Co., Tehran, Iran)	1.0	(0.999 ± 0.021)%

3.6. Potentiometric Selectivity

The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients, $K_{A,B}^{\text{pot}}$. In this work the matched potential method was chosen for determination of selectivity coefficient [32]. According to the MPM, a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before by adding primary ions. The selectivity coefficient, $K_{A,B}^{\text{pot}}$, is determined as

$$K_{A,B}^{\text{pot}} = \Delta A / A_B$$

where, $\Delta A = a_A' - a_A$; that a_A is the initial primary ion activity and a_A' is the activity of A in the presence of interfering ion, a_B . The experimental conditions employed and the resulting values are given in Table 5. As is seen, for all diverse ions used, the selectivity coefficients are in the order of 3.0×10^{-2} (for PBM) and 7.0×10^{-3} (for CGM) or smaller, indicating they would not significantly disturb the functioning of the La^{3+} ion-selective electrodes. It is also worth noting that the potentiometric response of the proposed sensor was found to be insensitive to the nature of the anions used.

Table 5. Selectivity coefficients ($K_{A,B}^{\text{pot}}$) of various interfering cations. Reference solution (1.0×10^{-6} and 1.0×10^{-7} M of La^{3+} for PBM and CGM, respectively). Primary ion (1.0×10^{-5} – 1.0×10^{-3} M of La^{3+}), interfering ions (1.0×10^{-2} – 1.0×10^{-3} M).

Cations	$K_{A,B}^{\text{pot}}$	
	PBM	CGM
Ce^{3+}	5.0×10^{-2}	3.5×10^{-3}
Gd^{3+}	6.5×10^{-3}	4.0×10^{-4}
Sm^{3+}	3.5×10^{-3}	6.6×10^{-4}
Sr^{2+}	2.0×10^{-4}	2.1×10^{-5}
Co^{2+}	6.5×10^{-4}	4.2×10^{-5}
Ni^{2+}	3.0×10^{-4}	1.2×10^{-5}
Cu^{2+}	3.5×10^{-4}	3.3×10^{-5}
Zn^{2+}	3.5×10^{-4}	1.3×10^{-5}
Cd^{2+}	8.5×10^{-4}	5.9×10^{-5}
Pb^{2+}	5.5×10^{-4}	5.7×10^{-5}
K^{+}	2.0×10^{-4}	2.7×10^{-5}

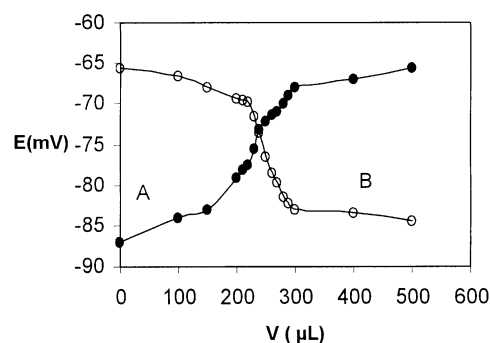


Fig. 7. Potentiometric titration curves of 25.0 mL 1.0×10^{-4} M solution of La^{3+} with 1.0×10^{-2} M of EDTA (A) and 25.0 mL 1.0×10^{-4} M solution of EDTA with 1.0×10^{-2} M of La^{3+} (B).

3.7. Analytical Applications

The proposed La^{3+} -ion-selective electrodes were found to work well under laboratory conditions. The PBM sensor was successfully applied as an indicator electrode in titration of La^{3+} (1.0×10^{-4} M) with an EDTA solution (1.0×10^{-2} M) and vice versa, and the resulting titration curve is shown in Figure 7. As seen, the amount of La^{3+} ions in solution can be determined with the electrode.

The CGM sensor was used in the determination of fluoride ions in two mouth wash preparation samples. 1.0 g of each sample was taken 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 triplicate measurements are summarized in Table 6. As seen, there is a satisfactory agreement between the declared fluoride content and the determined values.

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