

Lanthanum(III) PVC Membrane Electrodes Based on 1,3,5-Trithiacyclohexane

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Novel plasticized polymeric membrane (PPME) and membrane-coated graphite (MCGE) electrodes based on 1,3,5-trithiacyclohexane for highly selective determination of La³⁺ ion have been developed. The electrodes exhibit Nernstian responses over very wide concentration ranges (8.0×10^{-6} – 5.0×10^{-2} M for PPME and 4.0×10^{-8} – 1.0×10^{-2} M for MCGE). The limit of detections were 5.0×10^{-6} and 2.0×10^{-8} M for PPME and MCGE, respectively. The electrodes possess a fast response time of ~ 10 s and can be used for at least 6 months without observing any deviation. The proposed electrodes revealed excellent selectivities for La³⁺ over a wide variety of alkali, alkaline earth, transition, and heavy metal ions and could be used in a pH range of 5.0–8.0. The practical utility of the electrodes has been demonstrated by their use as indicator electrodes in the potentiometric titration of La³⁺ ions with EDTA and in determination of F[−] in some mouthwash preparations.

Lanthanides are widely distributed in low concentrations throughout the earth's crust.¹ The vapors or dusts of these elements are very toxic when are inhaled. Lanthanum chloride manifests as an antitumor agent.^{2,3} The genotoxicity of lanthanum(III) in human peripheral blood lymphocytes has also been reported.⁴ Recently, attempts were made to promote germination of natural rice seeds by treating them with lanthanum nitrate;⁵ the results revealed that lanthanum may be used to pretreat seed before sowing. Lanthanum chloride caused changes in lipid peroxidation, the redox system, and ATPase activities in plasma membranes of rice seedling roots.⁶ Lanthanum oxide is extensively used in the making of optical glasses.⁷ Lanthanum and other rare earth elements are used as 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.⁷

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, the selective separation and determination of these compounds have been of a recent increasing concern. Many methods described for assay of lanthanum and related metals in mixtures^{8–10} require a pre-separation step, which is time-consuming and introduces lower accuracy and higher costs. On the other hand, the azo-substituted dyes that are usually employed for the spectrophotometric determination of lanthanum are shown to be nonspecific reagents for this purpose.^{11–14} More sophisticated analytical techniques such as atomic absorption spectrometry and inductively coupled plasma spectroscopy are not sufficiently sensitive for the determination of lanthanum at low concentration.¹⁵

A few ion-selective electrodes have also been developed for the potentiometric determination of La³⁺.^{16–19} However, these efforts have not been very fruitful as the developed electrodes possess narrow working concentration ranges and suffer serious interferences from various cations including Cu²⁺, Ni²⁺, and Ce³⁺. In recent years, we have employed some thia-substituted macrocycles as suitable ionophores for the preparation of ion-selective electrodes for silver,²⁰ mercury,^{21,22} cadmium,²³ and cerium ions.²⁴ In this work, we report highly selective and sensitive plasticized polymeric membrane (PPME) and membrane-coated graphite electrodes (MCGE) for La³⁺ ion based on 1,3,5-trithiacyclohexane (TTCH) as an excellent neutral ionophore. It should be noted that we have recently used this ionophore for the preparation of a Ce³⁺.

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selective PVC membrane sensor, under different experimental conditions.²⁴

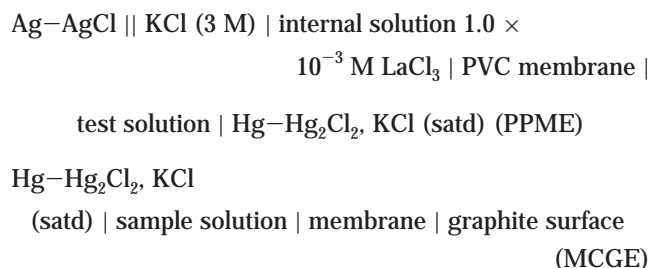
EXPERIMENTAL SECTION

Reagents. Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), acetophenone (AP), sodium tetraphenylborate (NaTPB), oleic acid (OA), 1,3,5-trithiacyclohexane (TTCH), 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 P₂O₅. Triply distilled deionized water was used throughout.

Electrode Preparation. The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of PVC, 53 mg of plasticizer AP, 15 mg of additive OA, and 2 mg of ionophore TTCH 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, at room temperature, until an oily concentrated mixture was obtained. A Pyrex tube (5-mm o.d.) was dipped into the mixture for ~5 s so that a nontransparent membrane of ~0.3-mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for ~1 h. The tube was then filled with internal filling solution (1.0×10^{-3} M LaCl₃). The electrode was finally conditioned for 4 h by soaking in a 5.0×10^{-3} M lanthanum chloride. A silver/silver chloride electrode was used as an internal reference electrode.

To prepare the coated graphite membrane electrodes, spectroscopic grade graphite rods of 3-mm diameter and 15-mm length 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 48 h by soaking in a 5.0×10^{-3} M solution of LaCl₃.

emf Measurements. The emf measurement with the plasticized polymeric membrane electrodes and the membrane-coated graphite electrodes were carried out with the following cell assemblies:



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.²⁰⁻²⁴

Water Solubility and Partition Coefficient of TTCH. The water solubility of TTCH was examined as follows.¹⁵⁻²⁵ Milligram

amounts of TTCH were shaken with 50.0 mL of water overnight at 25 °C. Then the mixture was centrifuged, and the remaining ligand was weighed after vacuum drying.

The experimental procedure for obtaining the partition coefficient of TTCH was as follows. A 20.0-mL 1-octanol solution of 1.38 mg of TTCH and an equal volume of water in a stoppered glass tube (volume of 50.0 mL) was shaken in a thermostatted water bath at 25 °C for 12 h. The TTCH concentration in organic phase was then measured spectrophotometrically at 240.5 nm after separation of the two phases. The partition coefficient was then determined using the equilibrium concentrations of TTCH in water and 1-octanol.

Fluoride Ion Determination in Pharmaceutical Samples.

Two sodium fluoride tablets (1.0 mg/tablet) were placed in a 100-mL beaker, 25 mL of water was added, and the solution was mixed thoroughly. Then the undissolved components were separated on a filter paper, and the clear filtrate was titrated with a 0.10 M solution of lanthanum nitrate solution using the proposed MCGE as an indicator electrode.

An appropriate volume of the sodium fluoride mouthwash solutions (i.e., 0.10 mL of the 2% solution or 0.50 mL of the 0.2% solution) was diluted to 25.0 mL, and the pH was adjusted to 7.0 (using a concentrated NaOH solution). The resulting solutions were then titrated with a 0.10 M solution of lanthanum nitrate solution using the proposed MCGE as an indicator electrode.

RESULTS AND DISCUSSION

1,3,5-Trithiacyclohexane (TTCH) with three donating sulfur atoms in its structure, negligible water solubility, low molecular weight, and flexible structure was expected to act as a suitable ionophore in the preparation of PVC membrane sensors for given transitional and heavy metal ions of proper size and charge. It should be noted that the solubility of TTCH, obtained by shaking an excess of ligand with water overnight at 25 °C and developing the results gravimetrically, was found to be $(1.3 \pm 0.4) \times 10^{-4}$ M. Moreover, the partition coefficient of TTCH between water and 1-octanol was determined by using various ligand concentrations in equal phase volumes and equilibrating for 12 h. The equilibrium concentrations of TTCH in both phases were determined spectrophotometrically, as described in the Experimental Section. The resulting partition coefficient value was $K = [\text{TTCH}]_{\text{aq}}/[\text{TTCH}]_{\text{org}} = (4.8 \pm 0.2) \times 10^{-3}$. It is interesting to note that the successful use of a variety of acyclic and macrocyclic ligands with K values of $>4 \times 10^{-3}$ as suitable ionophores in the PVC membrane sensors for different cations has been reported in the literature.²⁵

Thus, in preliminary experiments, it was used as a neutral carrier to prepare PVC MCGEs for a variety of transition and heavy metal ions. The potential responses of some of the most sensitive electrodes based on TTCH are shown in Figure 1. It is interesting to note that, in the case of each cation tested, the electrode was conditioned for 48 h by soaking in a 5.0×10^{-3} M solution of the chloride (for La³⁺ ion) or nitrate (for other cations tested) salts of the corresponding cation, to obtain thermodynamically meaningful potential responses and selectivity behaviors. As is obvious from Figure 1, among different cations tested, La³⁺ with the most sensitive response seems to be suitably determined with the electrode in the concentration range of 1.0×10^{-2} – 1.0×10^{-7}

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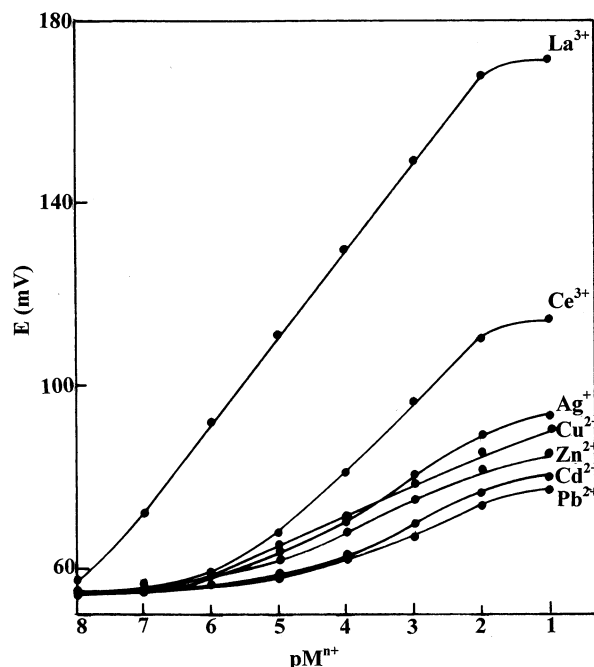


Figure 1. Potential response of various MCGEs based on TTCH. Conditions: membrane ingredients, 30% PVC, 53% AP, 2% TTCH, and 15% OA. Each electrode has been conditioned in 5.0×10^{-3} M concentration of the corresponding cation for 48 h.

M with the MCGE. This is due to the selective behavior of the PVC membrane system against La^{3+} in comparison to other metal ions. Examination of the chemical structure of TTCH suggests that the electronic or spatial topography of the ligand should not be primarily responsible for the observed selectivity order. But, in fact, other parameters such as the nature of the plasticizer and additive as well as the charge density of metal ions can also influence the selectivity behavior of the PVC membrane over other cations.²⁶

In fact, a recent liquid–liquid extraction study clearly demonstrated that the presence of a fatty acid like lauric acid can have a strong synergistic effect on the selective extraction of lanthanide ions with a thia-substituted crown ether.²⁷ Thus, as is clear from the results obtained in this work and in the case of a previously reported Ce^{3+} ion-selective electrode based on TTCH,²⁴ the presence of OA as a lipophilic additive plays a key role in the selective behavior of the PVC membrane system for lanthanide ions. Likewise, some selectivity can be introduced by the nature of plasticizers used, as will be mentioned later.

It is well known that the selectivity and sensitivity obtained for a given ionophore depend significantly on the membrane composition and the nature of the solvent mediator and additives used.^{20–27} Thus, the influences of the membrane composition, nature and amount of plasticizer, and amount of oleic acid or sodium tetraphenylborate as lipophilic additives on the potential response of the lanthanum electrodes were investigated, and the results are summarized in Table 1.

A plasticizer/PVC ratio (w/w) of ~ 2 was used as an optimum value in construction of the membrane sensor. It has been shown that polymeric films with such a plasticizer/PVC ratio usually have

Table 1. Optimization of Membrane Ingredients

no.	composition (%)				slope (mV decade ⁻¹)
	PVC	plasticizer	TTCH	additive	
1	30	AP, 70			2
2	30	AP, 69	1		7.0
3	30	AP, 68	2		10.1
4	30	AP, 67	3		9.8
5	30	DBP, 68	2		7.3
6	30	BA, 68	2		8.9
7	30	AP, 67	2	NaTPB, 1	13.7
8	30	AP, 66	2	NaTPB, 2	17.9
9	30	AP, 65	2	NaTPB, 3	17.7
10	30	AP, 63	2	OA, 5	13.1
11	30	AP, 58	2	OA, 10	17.8
12	30	AP, 53	2	OA, 15	19.8
13	30	AP, 50	2	OA, 18	19.2
14	30	DBP, 53	2	OA, 15	15.7
15	30	BA, 53	2	OA, 15	16.3
16	30	AP, 55	—	OA, 15	<2

optimum physical properties and ensure high enough mobilities of their constituents;^{27–30} 2% TTCH was chosen as the optimal amount of ionophore in the PVC membranes.

Since the nature of the plasticizer influences the dielectric constant of membrane phase, the mobility of ionophore molecules, and the state of ligands,^{27,31} it is expected to play an important role in determining the ISE characteristics. Thus, two sets of membranes of similar composition (i.e., nos. 3, 5, and 6 and nos. 12, 14, and 15) but with three different plasticizers having different dielectric constants, namely, DBP ($\epsilon = 8.5$), BA ($\epsilon = 5.1$), and AP ($\epsilon = 17.4$), were prepared and tested. As shown in Table 1, AP with the highest dielectric constant in the series resulted in the best sensitivity of the potential responses. It is interesting to note that the use of AP as a plasticizer not only resulted in improved potentiometry of the electrode with respect to DBP and BA but also caused 2–10 times improvement in the selectivity coefficients of the electrode.

A comparison between our previously reported Ce^{3+} ion-selective electrode²⁴ and the proposed La^{3+} membrane sensors clearly revealed that, in the presence of the same ionophore (TTCH), a change in the nature of plasticizer will result in altering selectivity of the membrane system toward Ce^{3+} and La^{3+} ions. Interestingly, while the use of AP with a dielectric constant of 17.4 results in selective behavior of the TTCH-incorporated membrane toward La^{3+} ion, the use of BA with a lower dielectric constant of 5.1 as plasticizer altered the selectivity of membrane toward Ce^{3+} ions.²⁴ This is most probably due to the decreased solvation energy of La^{3+} with respect to Ce^{3+} ion by some 50 kJ mol⁻¹.³²

It is well known that the presence of lipophilic anionic sites in cation-selective membrane electrodes not only improves the response behavior and selectivity^{27,33–35} but also may catalyze the exchange kinetics at the sample–membrane interface.³⁶

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Thus, Table 1 shows that the addition of 2% NaTPB (no. 8) and 15% OA (no. 12) will result in a considerable increase in the slope of the corresponding potential responses of the membrane electrodes. However, the presence of OA resulted in a Nernstian slope of $19.8 \text{ mV decade}^{-1}$, while the use of NaTPB as an additive showed a sub-Nernstian slope of $17.9 \text{ mV decade}^{-1}$. We recently reported the first use of OA as a very suitable lipophilic additive in inducing permselectivity to some PVC-based cation-selective electrodes.^{21,22,24,37–40} To further support the fundamental role of TTCH as a suitable ionophore for La^{3+} ions, a TTCH-free membrane containing PBV, AP, and OA was also prepared (no. 16) and its potential response toward varying concentration of La^{3+} ion was measured. As is obvious from Table 1, no measurable emf pLa^{3+} response was obtained for this membrane. As can be seen from Table 1, membrane no. 12 with a PVC/AP/TTCH/OA percent ratio of 30:53:2:15 shows a potential response with a nice Nernstian slope.

The influence of the concentration of internal solution in the PPME on its potential response was studied. The LaCl_3 concentration was changed from 1.0×10^{-4} to $1.0 \times 10^{-2} \text{ M}$, and the emf pLa^{3+} plots were obtained. It was found that the variation of the concentration of the internal La^{3+} solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. A $1.0 \times 10^{-3} \text{ M}$ concentration of the reference solution is quite appropriate for smooth functioning of the system.

The optimum equilibration time, in a $5.0 \times 10^{-3} \text{ M}$ solution of LaCl_3 , for the PPME and MCGE are 4 and 48 h, respectively, after which they generate stable potentials when placed in contact with La^{3+} solutions. The critical response characteristics of both La^{3+} electrodes were assessed according to the IUPAC recommendations.⁴¹ The emf responses of the PPME and MCGE at varying concentration of lanthanum ions (Figure 2) show linear ranges from 8.0×10^{-6} to $5.0 \times 10^{-2} \text{ M}$ for PPME (slope, $19.6 \pm 0.5 \text{ mV decade}^{-1}$) and from 4.0×10^{-8} to $1.0 \times 10^{-2} \text{ M}$ for MCGE (slope, $19.8 \pm 0.3 \text{ mV decade}^{-1}$). The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration of the calibration graphs (Figure 2), was $5.0 \times 10^{-6} \text{ M}$ for PPME and $2.0 \times 10^{-8} \text{ M}$ for MCGE.

The average time required for the electrodes to reach a potential response within $\pm 1 \text{ mV}$ of the final equilibrium value after successive immersion in a series of La^{3+} solutions, each having a 10-fold difference in concentration, was studied. The static response time of the electrodes thus obtained for concentrations

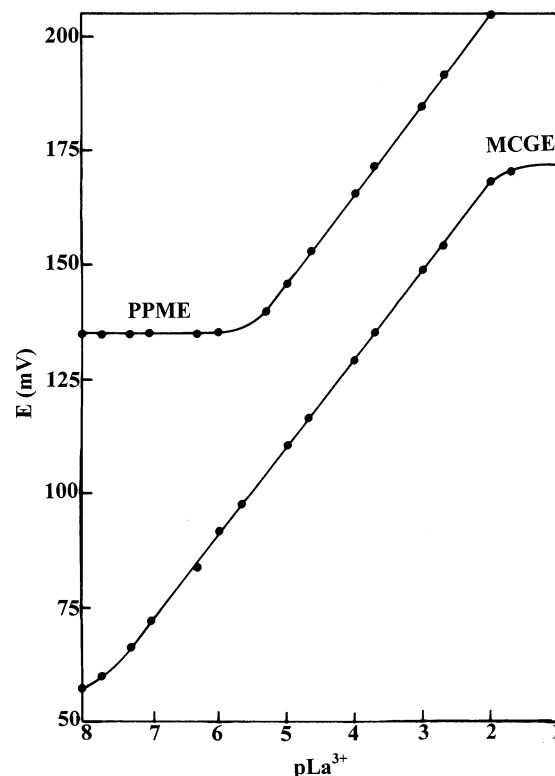


Figure 2. Calibration graphs for the proposed PPME and MCGE at pH 5.

of $\leq 1.0 \times 10^{-3} \text{ M}$ was found to be $< 10 \text{ s}$. Such a fast response time is most probably due to the fast exchange kinetics of complexation–decomplexation of La^{3+} with TTCH at the test solution–membrane interface.

A comparison of the foregoing data revealed that, while both electrodes show nice Nernstian behaviors with fast responses, the linear range and limit of detection of the MCGE are greatly improved relative to those of the PPME. The improved performance characteristics of the MCGE over those of the PPME presumably originate from the coated graphite technology, where an internal $1.0 \times 10^{-3} \text{ M}$ LaCl_3 solution, in the case of PPME, has been replaced by a copper wire of much higher electrical conductivity, in the case of MCGE. Furthermore, the membrane electrodes prepared were used practically for at least 6 months without any measurable change in lifetime, slope, or detection limit, the lifetime of the MCGE being longer than that of the PPME. It should be noted that the reuse of the dried electrode required further conditioning. The standard deviation of the slope of the calibration graphs at a range 1.0×10^{-5} – $1.0 \times 10^{-2} \text{ M}$ for the PPME during a long time period of > 6 months was at the most ± 0.5 (see Table 2).

The influence of pH of the test solution ($1.0 \times 10^{-4} \text{ M}$ LaCl_3) on the potential responses of the both electrodes was examined over the pH range 2.0–10.0. The pH was adjusted by introducing small drops of 0.1 M solutions of nitric acid or sodium hydroxide, and the results are shown in Figure 3. As seen, the potentials remained constant over a pH range of 5.0–8.0 for both sensors, beyond which the potentials change considerably. The observed drifts at higher pH values could be due to the formation of some hydroxy complexes of La^{3+} ion in solutions. The observed

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Table 2. Slope of a PPME Working for a Long Period of Time

date	slope (mV decade ⁻¹)			
	no. 1	no. 2	no. 3	average
April 21, 2000	19.5	19.1	20.4	19.7 ± 0.7
May 3, 2000	20.9	21.1	19.7	20.6 ± 0.8
May 7, 2000	19.2	19.0	18.7	19.0 ± 0.3
May 10, 2000	19.7	19.0	19.1	19.3 ± 0.4
May 12, 2000	19.2	18.9	18.7	18.9 ± 0.3
May 19, 2000	19.7	19.2	20.1	19.7 ± 0.5
May 31, 2000	19.7	20.1	19.5	19.8 ± 0.3
June 15, 2000	20.0	19.7	19.3	19.7 ± 0.4
June 23, 2000	19.7	19.2	18.7	19.2 ± 0.5
July 6, 2000	19.5	19.0	18.7	19.1 ± 0.4
July 23, 2000	19.3	18.7	18.9	19.0 ± 0.3
August 7, 2000	19.5	19.1	18.7	19.1 ± 0.4
August 26, 2000	19.8	19.2	18.9	19.3 ± 0.5
September 19, 2000	18.9	19.2	19.1	19.1 ± 0.2
October 6, 2000	19.3	19.5	18.9	19.2 ± 0.3
October 19, 2000	19.1	18.9	18.6	18.9 ± 0.3
November 3, 2000	18.7	19.2	18.9	18.9 ± 0.3
total average	19.3 ± 0.5			

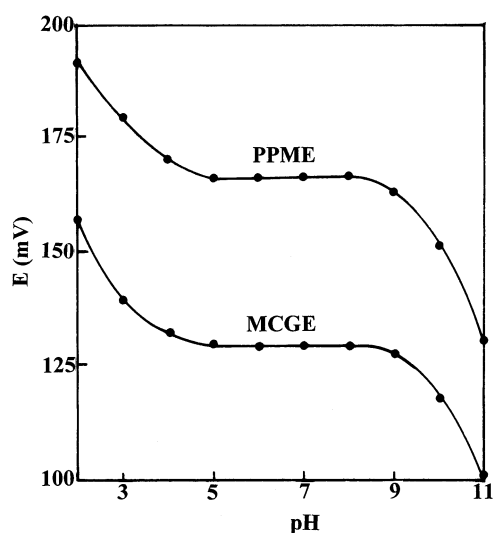


Figure 3. Effect of pH of the test solution on the potential response of the PPME and MCGE, at a lanthanum concentration of 1.0×10^{-4} M.

increases at low-pH values indicate that the membrane sensors respond to hydrogen ions.

The selectivity behavior is obviously one of the important characteristics of ion-selective electrodes, determining whether reliable measurement in the target sample is possible. To investigate the selectivity of the potentiometric electrodes proposed, their potential responses were investigated in the presence of a wide variety of interfering foreign cations using the matched potential method (MPM).^{42,43} This is a recently recommended procedure by IUPAC⁴² that gets rid of the limitations of the corresponding methods based on the Nicolsk–Eisenman equation for the determination of potentiometric selectivity coefficients.⁴⁴ These limitations include non-Nernstian behavior of interfering ions and inequality of charges of any primary interfering ions.

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Table 3. Selectivity Coefficients ($K_{A,B}^{Pot}$) of Various Interfering Cations

cation	PPME ^a			MCGE ^b
	AP	DBP	BA	AP
Li ⁺	3.5×10^{-4}	7.5×10^{-4}	8.5×10^{-4}	5.6×10^{-6}
Na ⁺	2.9×10^{-4}	8.4×10^{-4}	2.0×10^{-3}	5.1×10^{-6}
K ⁺	2.2×10^{-4}	1.5×10^{-3}	3.8×10^{-3}	3.9×10^{-6}
Mg ²⁺	1.7×10^{-4}	3.7×10^{-4}	5.5×10^{-4}	2.5×10^{-6}
Ca ²⁺	1.5×10^{-4}	4.9×10^{-4}	1.2×10^{-3}	2.2×10^{-6}
Sr ²⁺	1.3×10^{-4}	7.4×10^{-4}	3.1×10^{-3}	2.0×10^{-6}
Ba ²⁺	1.3×10^{-4}	9.6×10^{-4}	4.1×10^{-3}	2.0×10^{-6}
Ag ⁺	7.7×10^{-3}	2.1×10^{-2}	4.7×10^{-2}	5.2×10^{-4}
Tl ⁺	8.1×10^{-3}	2.3×10^{-2}	4.6×10^{-2}	6.6×10^{-4}
Co ²⁺	5.1×10^{-3}	7.3×10^{-3}	8.9×10^{-3}	3.5×10^{-4}
Ni ²⁺	5.6×10^{-3}	6.9×10^{-3}	8.7×10^{-3}	3.3×10^{-4}
Cu ²⁺	7.1×10^{-3}	7.4×10^{-3}	8.9×10^{-3}	5.2×10^{-4}
Zn ²⁺	3.5×10^{-3}	8.1×10^{-3}	1.6×10^{-2}	2.1×10^{-4}
Cd ²⁺	6.7×10^{-4}	3.5×10^{-3}	3.0×10^{-2}	5.2×10^{-5}
Pb ²⁺	2.7×10^{-4}	9.3×10^{-4}	4.6×10^{-3}	2.2×10^{-5}
Hg ²⁺	5.3×10^{-4}	3.8×10^{-3}	8.4×10^{-3}	3.6×10^{-5}
Ce ³⁺	3.5×10^{-2}	2.5×10^{-1}	>1	2.7×10^{-3}

^a Conditions: reference solution, 1.0×10^{-6} M LaCl₃; primary ion (A) 10^{-5} – 10^{-4} M La³⁺; interfering ions (B) 10^{-1} – 10^{-2} M. ^b Conditions: reference solution, 1.0×10^{-8} M LaCl₃; primary ion (A) 10^{-7} – 10^{-6} M La³⁺; interfering ions (B) 10^{-2} – 10^{-3} M.

According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion and the interfering ion that gives the same potential change in a reference solution.^{42,43} Thus, one should measure the change in potential upon changing the primary ion activity. Then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient, $K_{A,B}^{Pot}$, is determined as

$$K_{A,B}^{Pot} = \Delta a/a_B \quad (1)$$

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 resulting values obtained for the proposed La³⁺-selective PPME are summarized in Table 2. To investigate the influence of plasticizer on the selectivity behavior of the TTCH-based PVC membranes, the selectivity coefficients of membranes 14 and 15 (Table 1) having the same composition as the optimized membrane (i.e., no. 12), but with different plasticizers, were also obtained and the results are included in Table 3 for comparison.

As shown in Table 3, despite the much higher hydration energies of trivalent cations like La³⁺ over those of the bivalent and univalent cations, the selectivity coefficients obtained for lower charge cations is on the order of 10^{-3} or lower. This could only be due to the presence of TTCH in the PVC membrane and its highly selective complexation with lanthanide ions. Meanwhile, as was expected, the nature of the plasticizer was found to strongly influence the selectivity behavior of the membrane sensor. The data given in Table 3 clearly indicate that not only are the $K_{A,B}^{Pot}$ values significantly decreased upon changing the plasticizer from AP to DBP and BA but also, in the presence of BA, the selectivity of the membrane electrode toward La³⁺ and Ce³⁺ ions is altered. In this case, the resulting PVC membrane is actually a Ce³⁺ ion-selective electrode, rather than a La³⁺-selective electrode.²⁴

A comparison of the data given in Table 3 with the selectivity coefficients reported before^{16–19} revealed that the selectivity

Table 4. Results of Determination of Fluoride in Different Mouthwash Solutions

sample	labeled	found
sodium fluoride mouth wash solution (Chimia Daru Co., Tehran, Iran)	2.0%	$2.02 \pm 0.03\%$
sodium fluoride mouth wash solution (Shahre Daru Co., Tehran, Iran)	0.2%	$0.20 \pm 0.02\%$
sodium fluoride tablets (Loghman Pharmaceutical Co., Tehran, Iran)	1.0 mg tablet ⁻¹	0.999 ± 0.021 mg tablet ⁻¹

coefficients obtained by the proposed electrodes are significantly improved. In fact, in the case of both PPME and MCGE, the selectivity coefficients obtained for all 17 cations tested are on the order of 10^{-3} or lower, which indicate a negligible interference in the performance of the membrane sensor assemblies. It is interesting to note that, although the selectivity trend observed by both electrodes are more or less the same, the $K_{A,B}^{\text{Pot}}$ values obtained for MCGE are 1–2 orders of magnitude smaller than the corresponding values for PPME. This is actually one of the great advantages of the coated graphite electrodes, as has already been pointed out in the literature.^{45–49}

The proposed membrane electrodes were found to work well under laboratory conditions. The PPME was used as an indicator electrode in the successful titration of a La(III) ion solution (1.0×10^{-4} M) with an EDTA solution (1.0×10^{-2} M) at pH 7.0. The resulting titration curve is shown in Figure 4. It is seen that the amount of La(III) ion can be accurately determined with the electrode.

The MCGE was also successfully applied to the determination of F^- ion in three different pharmaceutical samples by the titration of fluoride ions present with a La^{3+} ion solution (0.100 M of $LaCl_3$). The exact amount of fluoride ion was then evaluated from the

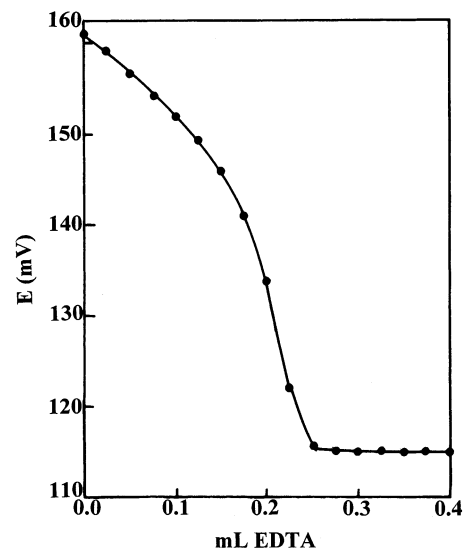


Figure 4. Potentiometric titration curve of 25.0 mL of 1.0×10^{-4} M $LaCl_3$ with 1.0×10^{-2} M EDTA at pH 7, using the PPME as an indicator electrode.

sharp inflection points of the resulting titration curve. The results of triplicate measurements are summarized in Table 4. As seen, there is a satisfactory agreement between the declared fluoride content and the determined values.

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