

Synthesis, Complexation and Use of Calix[4]crown-6 as a Novel Neutral Ionophore for the Preparation of a Selective and Sensitive PVC-Membrane Potentiometric Sensor for Ba²⁺ Ion

S. Sahari^a, M. Taghdiri^b, K. Alizadeh^d, Z. Asfari^c and M. Shamsipur^{a,*}

^a*Department of Chemistry, Razi University, Kermanshah, Iran*

^b*Department of Chemistry, Payame Noor University (PNU), Ardakan, Iran*

^c*Department of Chemistry, Lorestan University, Khorramabad, Iran*

^d*Laboratoire de Chimie Analytique et Minerale, UMR 778, ULP/CNRS/IN2P3(LC4), ECPM, 25 Rue Becquerel, F-67087, Strasbourg Cedex, France*

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Calix[4]crown-6 (**L**) was synthesized and the stoichiometry and stability of its complexes with alkali, alkaline earth, Ag⁺, Tl⁺ and NH₄⁺ ions were studied conductometrically in acetonitrile solution. The resulting 1:1 Ba²⁺-**L** complex was found to be the most stable one among all cation complexes studied. The optimized structures of the ligand and its Ba²⁺ complex are also reported. Based on the findings, **L** was used as a suitable ionophore to prepare a PVC-membrane selective electrode for Ba²⁺ ion. The electrode revealed a Nernstian behavior over wide barium ion concentration 1.0 × 10⁻⁶ to 1.0 × 10⁻³ M with only little trace of 7.1 × 10⁻⁷ M. The potentiometric responses were found to be independent of the pH of test solutions in the range of 4.0-10.0. The proposed electrode response time of about 10 s proved to be highly selective for Ba²⁺ ion over a wide variety of cations including alkali, alkaline earth, transition and heavy metal ions. The sensor could be used for at least three months without any noticeable deviation. The practical utility of the proposed electrode was also examined.

Keywords: Calix[4]crown-6, Complexation studies, Conductance, Ba²⁺ ion, PVC-membrane, Potentiometric sensor

INTRODUCTION

Elemental barium is often used in barium-nickel alloys for spark-plug electrodes, in vacuum tubes as drying and oxygen-removing agent and in fluorescent lamps. Barium compounds are extensively used in oil and gas industries to make drilling mud, and have wide applications in medical tests and X-ray photography. They are also used to make paint, bricks, tiles, glass, jet fuels, electronic components and rubber [1,2].

Some barium compounds released during industrial

processes can dissolve easily in water and are found in lakes, rivers, and streams. Because of their water-solubility, these barium compounds spread over vast distances. Discharges of barium compounds from corresponding industrial plants and those from medical tests and X-ray applications also pollute the environment [2].

A small amount of water-soluble barium may cause a person to experience breathing difficulties, increased blood pressures, heart rhythm changes, stomach irritation, muscle weakness, gastrointestinal disorders, changes in nerve reflexes, swelling of brain and liver, as well as kidney and heart damage. Extended exposure to high levels of barium has

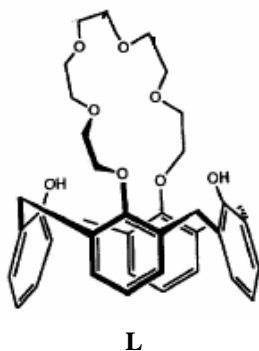
*Corresponding author. E-mail: mshamsipur@yahoo.com

been found to cause changes in heart rhythm, kidney problems, significant weight loss, paralysis and death [2,3].

Thus, due to the critical importance of barium in industry and in many biological samples and urgent need for new barium-sensors for potentiometric monitoring of Ba^{2+} ion in different industrial, biological and environmental samples, a number of Ba^{2+} -selective membrane electrodes have been introduced during the past decade [2,4-7].

The host-guest chemistry and metal ion complexation of calixarenes and the related macrocyclic ligands have recently received considerable attention [8-13]. These are actually useful building blocks for the construction of relatively rigid lipophilic cation receptors and carriers with interesting properties [8-11]. Among different calixarene derivatives, calix[4]crown ethers have attracted the attention of many researchers [12-19]. Calix[4]crowns and calix[4]biscrowns can form a series of 1:1 and 2:1 metal-to-ligand complexes with alkali metal ions and Tl^+ ion [19-25]. Calixarenes and their crown ether derivatives have also been used as very suitable ionophores and chromo ionophores in the preparation of potentiometric and optical chemical sensors for a variety of metal ions [26-35].

This work reports the results of conductometric and theoretical studies of complexation of calix[4]crown-6 (**L**) with alkali and alkaline earth cations and Ag^+ , Tl^+ and NH_4^+ ions. Based on the selectivity order obtained from solution studies, the ligand was used as a suitable lipophilic ionophore for the construction of a new PVC-membrane electrode for the selective and sensitive determination of Ba^{2+} ions. To the best of our knowledge, there is no report in literature on the use of a calixarene crown derivative in the preparation of barium ion-selective electrodes.



EXPERIMENTAL

Reagents

All reagents used were analytical grade chemicals. Doubly distilled water was used for preparing all aqueous solutions. High molecular weight poly(vinyl chloride) (PVC), potassium tetrakis(4-chlorophenyl) borate (KTCIPB), sodium tetraphenyl borate (NaTPB) *o*-nitrophenyl octyl ether (*o*-NPOE), bis(2-ethylhexyl) phthalate (DOP), acetonitrile (AN) and tetrahydrofuran (THF) were obtained from Fluka. Reagent-grade $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, KClO_4 , $\text{AgClO}_4 \cdot \text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2$, $\text{Ba}(\text{ClO}_4)_2$, LiClO_4 and NH_4ClO_4 (all from Fluka) were of the highest purity available and used as received. Perchlorate salts of Sr^{2+} , Ca^{2+} , Tl^+ , Rb^+ and Cs^+ were prepared from the 1:1 reaction of perchloric acid with the corresponding carbonate salts (all from Merck). The resulting perchlorate salts were recrystallized three times from doubly distilled water and vacuum dried for 24 h and stored over P_2O_5 . Calix[4]crown-6 (**L**) was synthesized and purified as described in literature [16,36,37].

Conductance Measurements

Conductance measurements were carried out with a CMD 500 WPA conductivity meter. A dip-type conductivity cell made of platinum black with a cell constant of 0.8310 cm^{-1} was used. In all the measurements, the cell was thermostated at the desired temperature using a JULABO model F12-ED Refrigerated/Heating circulator with temperature stability $\pm 0.03 \text{ }^\circ\text{C}$.

In a typical experiment, 10 ml of a metal perchlorate solution in AN ($5.0 \times 10^{-5} \text{ M}$) was placed in a water-jacketed cell equipped with a magnetic stirrer and connected to the thermostat circulating water at $25.00 \pm 0.03 \text{ }^\circ\text{C}$. Then, a known amount of the ligand solution in AN ($1.0 \times 10^{-2} \text{ M}$) was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the ligand was continued until the desired ligand-to-cation mole ratio was achieved.

Electrode Preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 32 mg of powdered PVC, 60 mg of plasticizer NPOE and 3 mg of the additive in 3 ml of THF. To

this mixture was added 5 mg of ionophore **L** mixing the solution well. The resulting mixture was transferred into a 2-cm-diameter glass dish. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-mm o.d.) was dipped into the mixture for about 30 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 barium perchlorate). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M solution of Ba^{2+} ion. A silver/silver chloride electrode was used as an internal reference electrode.

Emf Measurements

Sample solutions were prepared in distilled water. All emf measurements with the polymeric membrane electrodes were carried out with the following cell assembly:

$\text{Ag-AgCl, KCl (satd)}|\text{internal solution, } 1.0 \times 10^{-3} \text{ M Ba}^{2+}|\text{PVC membrane}|\text{sample solution}|\text{Ag-AgCl, KCl (satd)}$

Activity coefficients were calculated according to the Deby-Huckel procedure [38]. A Metrohm analyzer was used for the potential measurements.

RESULTS AND DISCUSSION

Preliminary Complexation Studies

Conductometric studies. In order to find a clue about the stoichiometry and stability of the alkali, alkaline earth, Ag^+ , Tl^+ and NH_4^+ ion complexes with calix[4]crown-6 (**L**), the complexation of metal ions with **L** was studied in acetonitrile solution conductometrically. To evaluate the influence of adding **L** on the molar conductance of the metal ions used in acetonitrile solution, the conductivity at a constant salt concentration (5.0×10^{-5} M) was monitored while increasing the ligand concentration at 25.00 ± 0.03 °C. The resulting [ligand]/[metal ion] mole ratio plots are shown in Fig. 1. As can be seen, in all the cases studied, the addition of the crown ether to the metal ion solutions causes a continuous decrease in the molar conductance of the solutions, indicating the lower mobility of the metal ion complexes compared to the solvated cations.

From Fig. 1, it is seen that, in the case of Ba^{2+} and Tl^+ ions, the slopes of the corresponding molar conductance-mole ratio

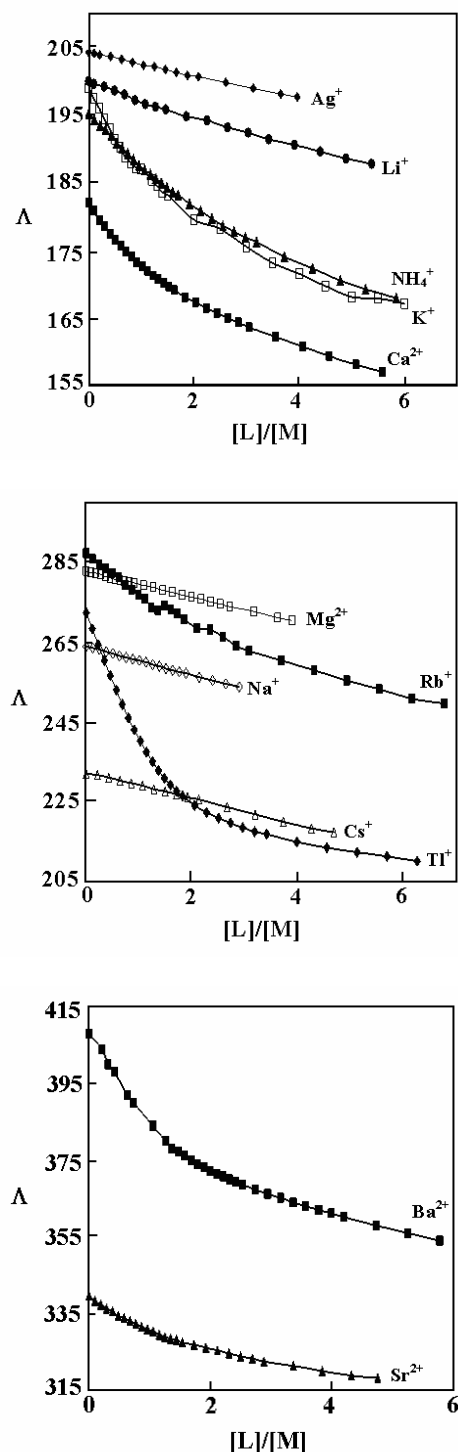


Fig. 1. Molar conductance ($\text{S cm}^2 \text{ mol}^{-1}$) vs. $[\text{L}]/[\text{M}]$ for various cations in AN at 25 °C.

plots change sharply at the point where the ligand to cation mole ratio is about one, emphasizing the formation of relatively stable 1:1 complexes between **L** and the cations used. However, in other cases, the relatively large decrease in molar conductance of the cations upon addition of the ligand does not show any tendency of leveling off, even at mole ratios of > 3-5, indicating the formation of weaker complexes.

The formation constants, K_f , and the limiting molar conductances, Λ_o , of the resulting 1:1 complexes between **L** and the cations used in acetonitrile were evaluated by computer fitting of the observed molar conductances, Λ , at various ligand/metal ion mole ratios to the previously derived equations [39,40] which express the Λ as a function of the free and complexed metal ions and the formation constant by using a nonlinear least-squares program KINFIT [41]. The details are described elsewhere [42].

The formation constants of cations-**L** complexes in acetonitrile, obtained by computer fitting of the molar conductance-mole ratio data, are listed in Table 1. As it can be seen from Table 1, the stability order of the univalent and bivalent metal ions with **L** decreases in the order $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{Ti}^+ > \text{K}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{Li}^+ > \text{Na}^+ > \text{Cs}^+$, respectively. Obviously, Ba^{2+} and Ti^+ ions (with about the same ionic radius of 1.43 and 1.49 Å [43]) form the most stable complexes in the series, most probably due to the best fitting of these cations inside the crown ether cavity [12-19], the Ba^{2+} complex being more stable because of its higher charge density. It is note worthy that the increased stability of the **L** complex of Ti^+ over that of Rb^+ ion with the same ionic radii of 1.49 Å [43] is most probably due to the contribution of a strong cation- π interaction in the former complex [25].

Theoretical studies. To obtain more information about the optimized structures of ligand **L** and its selective 1:1 complex with barium ion, the molecular structures of the uncomplexed ligand and its complex with barium ion were built using the Hyperchem program version 7.0, run on a Pentium(IV) personal computer [44]. The structure of the free ligand was optimized using the 6-31G* basis set at the restricted Hartree-Fock (RHF) level of theory. The optimized structure of the ligand was then used to detect the initial structure of its Ba^{2+} complex. Finally, the structure of the resulting 1:1 complex was optimized using the Lan12mb basis set at the RHF level of theory. No molecular symmetry constraint was applied;

Table 1. Formation Constants of Different Cation-**L** Complexes in AN at 25 °C

Cation ^a	log K_f
Ba^{2+} (1.43 Å)	4.36 ± 0.04
Sr^{2+} (1.27 Å)	4.01 ± 0.03
Ca^{2+} (1.06 Å)	3.86 ± 0.07
Mg^{2+} (0.78 Å)	2.52 ± 0.03
Ti^+ (1.49 Å)	4.24 ± 0.04
K^+ (1.33 Å)	4.00 ± 0.06
NH_4^+ (-)	3.66 ± 0.03
Rb^+ (1.49 Å)	3.61 ± 0.06
Li^+ (0.78 Å)	3.16 ± 0.04
Ag^+ (1.13 Å)	2.85 ± 0.02
Na^+ (0.98 Å)	2.80 ± 0.07
Cs^+ (1.65 Å)	2.04 ± 0.04

^aValues in parentheses are the ionic radii of cations [43].

rather, all bond lengths, bond angles, and torsion angles were fully optimized using the Gaussian 98 program [45]. The optimized molecular structures of the free ligand **L** and its 1:1 complex with Ba^{2+} ion are shown in Fig. 2. It should be noted that, in the foregoing calculations, the vibrational frequencies were calculated for both ligand **L** and its complex with Ba^{2+} to check that the optimized geometries of the molecular systems correspond to the true energy minima. All the calculated frequencies were found to be positive, so that it can be concluded that the geometric structures shown in Fig. 2 are correct [46,47].

As is obvious from Fig. 2, in the case of the free ligand, the six ether oxygens of the crown ring located in a more or less planar situation, is located almost perpendicular to the plane of the upper rim of the calix[4]arene backbone, so that the two -OH groups of the calix molecule are situated symmetrically on the two sides of the crown cavity. In the optimized structures of the 1:1 (Ba.L)²⁺ complex, the cation is well incorporated inside the twisted ligand cavity and coordinated not only to all six donating oxygen atoms of the crown moiety, but also to the two upper rim -OH groups of the calix[4]arene, in a more or less spherical geometry. In our recent proton NMR study of the complexation of **L** with Ti^+ ion [24], a large

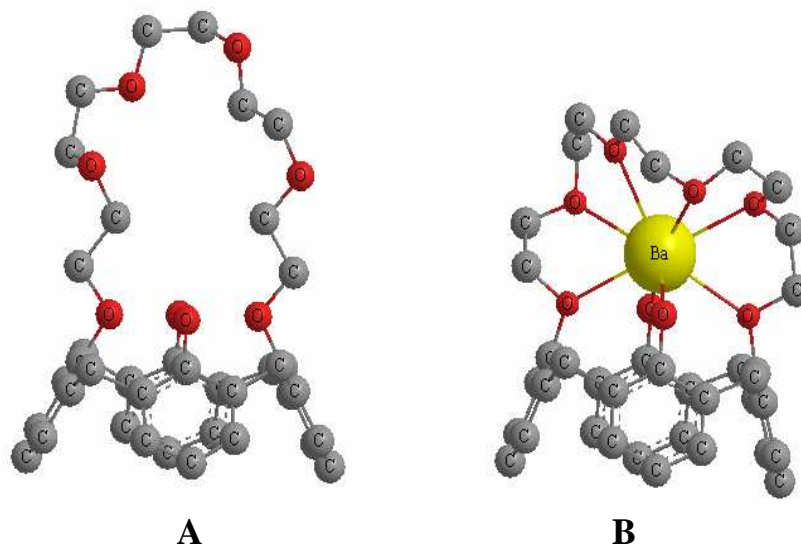


Fig. 2. Optimized structures of free ligand **L** (A) and its 1:1 complex with Ba^{2+} ion (B).

chemical shift observed for the OH-bearing phenyl signals of the ligand upon complexation with the metal ion, clearly supported the relatively strong interaction of the two hydroxyl groups with the Tl^+ ion.

Accordingly, based on the above preliminary results, the increased selectivity of **L** for Ba^{2+} over other metal ions tested, as well as its high lipophilic character, the ligand was expected to act as a suitable ionophore for Ba^{2+} ion in a PVC membrane electrode. During the preliminary experiments, it was found that, while the use of an ionophore-free PVC membrane resulted in no measurable response with respect to Ba^{2+} ion, the addition of **L** showed a Nernstian response for the cation in the range of 1.0×10^{-6} - 1.0×10^{-3} M (Fig. 3). Meanwhile, ligand **L** was also used as a neutral carrier to prepare PVC membrane electrodes for a variety of metal ions. The potential responses of various ion selective electrodes based on **L** also included in Fig. 3. As seen, except for the Ba^{2+} ion-selective electrode, in all other cases, the slope of the corresponding potential-pM plots was much lower than the expected Nernstian slopes of 59.0 and 29.5 mV per decade for uni- and bivalent cations, respectively.

PVC Polymeric Membrane Ion-Selective Electrode Studies

Based on the results of the complexation of different metal

ions with **L**, in the next step, the ligand was used as a potential ionophore for the preparation of a new PVC-membrane Ba^{2+} ion-selective electrode. Thus, several parameters were investigated in order to evaluate the performance of the ion-selective electrodes based on ionophore **L** in terms of membrane composition, calibration curve slopes, reproducibility, linear range, limit of detection, response time, selectivity and sample analysis, as described below.

Membrane composition. It is well known that the sensitivity and selectivity obtained for a given ionophore depend significantly on the membrane composition, the nature of solvent mediator and the additives used [48-51]. Thus, the influences of the membrane composition, the nature and amount of the plasticizer and additive on the potential response of the Ba^{2+} sensor were investigated with the results summarized in Table 2.

Since the nature of the plasticizer affects the dielectric constant and the state of ligands [48-52], it is expected to play an important role in determining the ion-selective electrode characteristics. As it is seen from Table 2, among the four plasticizers tested, NPOE resulted in a better sensitivity and wider linear calibration range. The plasticizer/PVC ratios of 1-2 were examined. The membrane prepared with a plasticizer/PVC ratio of about 1.9 was found to yield the best results.

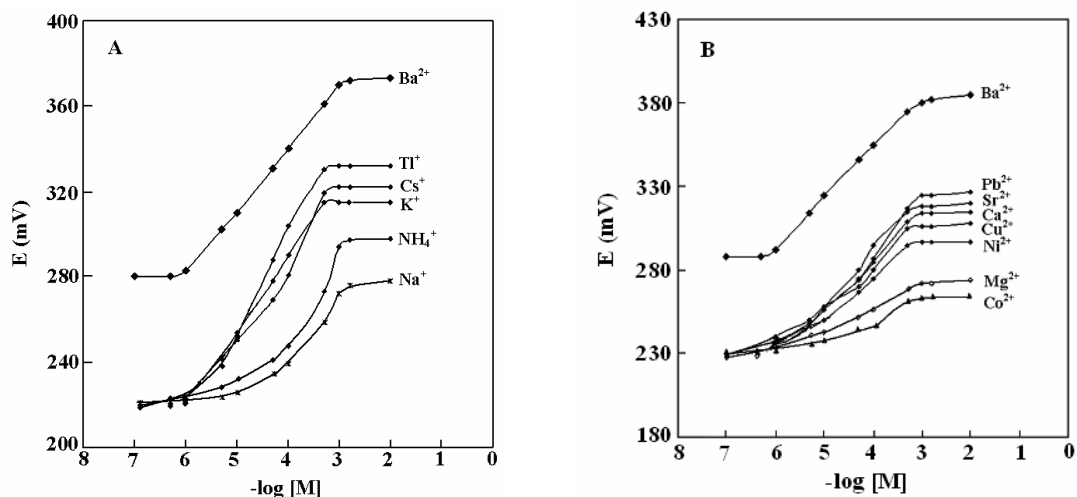


Fig. 3. Potential responses of various ion-selective electrodes based on L.

Table 2. Optimization of Membrane Ingredients

No.	Composition (%)				Slope (mV decade ⁻¹)	Linear range (M)
	PVC	Plasticizer	L	Additive		
1	32.5	NPOE, 63	4.5	-	22	1×10^{-6} - 1×10^{-4}
2	30.0	NPOE, 53.5	5.0	OA, 11.5	18	1×10^{-6} - 1×10^{-4}
3	32.0	NPOE, 60	5.0	NaTPB, 3	29	1×10^{-6} - 1×10^{-3}
4	30.5	NPOE, 59	7.0	NaTPB, 3.5	25	1×10^{-6} - 1×10^{-4}
5	32.5	NPOE, 61	3.0	NaTPB, 3.5	22	1×10^{-6} - 1×10^{-4}
6	29.5	NPOE, 60.5	5.0	NaTPB, 5	21	1×10^{-6} - 1×10^{-4}
7	30.5	NPOE, 59.5	3.0	NaTPB, 7	24	1×10^{-6} - 1×10^{-4}
8	31.0	AP, 60.5	5.0	NaTPB, 3.5	25	1×10^{-6} - 1×10^{-5}
9	30.5	BA, 61	5.0	NaTPB, 3.5	20	1×10^{-6} - 1×10^{-4}
10	31.5	DOP, 60	5.0	NaTPB, 3.5	18	1×10^{-5} - 1×10^{-3}

Research has revealed that the presence of lipophilic anionic sites in a cation-selective membrane electrode not only improves the response behavior and selectivity [48,53,54], but also may catalyze the exchange kinetics at the sample-membrane interface [55]. Table 2 indicates that the presence of 3% NaTPB as a proper lipophilic additive enhances the sensitivity of the electrode significantly.

As it is obvious from Table 2, the optimization of the amount of ionophore L in the membrane was performed in the range of 3%-7%, and the best calibration slope was found to be 5%. Thus, as it is clear from Table 2 (no. 3), the use of 60% NPOE in the presence of 32% PVC, 5% ionophore L and 3% NaTPB (No. 3) resulted in the best sensitivity, with a Nernstian slope over a wide dynamic range of 1.0×10^{-6} - $1.0 \times$

10^{-3} M.

Effect of internal solution. The influence of the concentration of the internal solution on the potential response of the PME was investigated. The $\text{Ba}(\text{ClO}_4)_2$ concentrations were changed from 1.0×10^{-4} - 1.0×10^{-2} M and the emf-p Ba^{2+} 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 change in the intercept of the resulting plot. A 1.0×10^{-3} M concentration of the references solution is quite appropriate for a smooth functioning of the polymeric membrane system. It should be noted that a change in concentration of the internal solution is expected to change the potential difference on the internal solution/membrane interface and, consequently, the overall emf of the cell assembly.

Effect of pH of the test solution. The effect of pH range from 2 to 12 on the response of the Ba^{2+} -selective electrode was determined in a solution with 1.0×10^{-3} M of Ba^{2+} , the pH of the solution being adjusted using 0.1 M solution of either HCl or NaOH. The resulting emf-pH plot shown in Fig. 4 revealed that there is no significant variation in the values of the potential when the pH of the solution varies between 4.0 and 10.0. At pH values lower than 4, there is a decrease in the potential of the electrodes indicating that, in the membrane, the ionophore is protonated. The observed decrease in potential at $\text{pH} > 10$ could be due to the formation of some hydroxyl complexes of Ba^{2+} in solution.

Response characteristics of the membrane electrode. Optimum conditioning time for the membrane sensor in a 1.0×10^{-3} M barium perchlorate solution is 24 h. It then generates stable potentials when placed in contact with Ba^{2+} solutions. The membrane sensors thus prepared could be used under-stretch conditions for at least three months without any measurable divergence.

The PVC-membrane electrode, prepared as the optimized composition, was found to generate stable potentials when placed in contact with Ba^{2+} solutions. The critical response characteristic of the electrode was assessed according to IUPAC recommendations [56]. The average time required for the membrane sensor to reach a potential within 1 mV of the final equilibrium value after the successive immersion of a series of barium ion solutions, each having a 10-fold difference in concentrations, was measured. The static

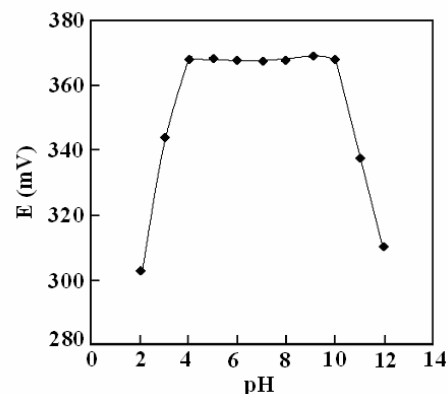


Fig. 4. Effect of pH of test solution on the electrode potential response in the presence of 1.0×10^{-3} M Ba^{2+} .

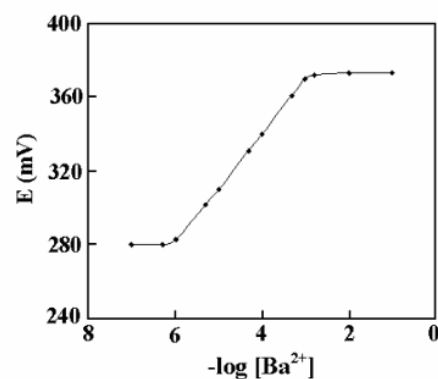


Fig. 5. Calibration graphs of Ba^{2+} ion-electrode with membrane no. 3.

response time thus obtained was 10 s for concentrations $\leq 1.0 \times 10^{-4}$ M, and potentials stayed constant for 5 min, after which only a very slow divergence was recorded. The sensing behavior of the membrane remained unchanged when the potentials recorded either from high to low concentrations or vice versa.

The emf response of the proposed Ba^{2+} sensor based on ionophore L (prepared under optimal membrane ingredients) indicated a rectilinear range from 1.0×10^{-6} to 1.0×10^{-3} M (Fig. 5). The slopes of the calibration curves showed a Nernstian slope of 29.1 ± 0.3 mV decade $^{-2}$ of activity change at 25 °C. The limit of detection was 7.1×10^{-7} M, as evaluated from the intersection of the two extrapolated segments of the

Table 3. Selectivity Coefficients ($K_{I,J}^{Pot}$) of Various Interfering Ions (M^{n+})

Ions	K_{pot}	Ions	K_{pot}
Li^+	6.5×10^{-3}	Sr^{2+}	6.1×10^{-3}
Na^+	9.0×10^{-3}	Co^{2+}	2.1×10^{-2}
K^+	2.7×10^{-1}	Ni^{2+}	3.3×10^{-2}
Cs^+	1.7×10^{-1}	Cu^{2+}	1.8×10^{-2}
Tl^+	5.5×10^{-1}	Zn^{2+}	1.4×10^{-2}
NH_4^+	4.0×10^{-2}	Fe^{2+}	4.1×10^{-3}
Mg^{2+}	8.6×10^{-3}	Pb^{2+}	2.2×10^{-2}
Ca^{2+}	8.0×10^{-3}		

calibration graph.

Selectivity coefficients. The influence of interfering ions on the potential response behavior of the ion-selective membrane electrodes is usually described in terms of the selectivity coefficient [57]. The potentiometric selectivity coefficient, K_{pot} , describing the preference by the membrane for an interfering ion M^{n+} relative to Ba^{2+} , was determined by the separated solutions method [57,58] as follows. The emf- pM^{n+} plots were obtained for the barium and the interfering ions (over a pM^{n+} range of 2-7), separately, using the proposed electrode systems. Then, by using a pair of values of primary (a_{Ba}) and interfering (a_{Mn}) ion concentrations at which the electrode takes the same potential in separate solutions (*i.e.*, isopotential concentrations) and equation $K_{pot} = \ln(a_{Ba}/a_{Mn}^{2/z})$, where z is the charge of interfering ion, the selectivity coefficient was determined. The resulting values are listed in Table 3. The obtained selectivity coefficients revealed the fact that the diverse ions listed in Table 3 would not cause any significant interference in the determination of Ba^{2+} ions by the proposed electrode, unless present in large amounts.

Applications. The proposed Ba^{2+} membrane sensor was found to work well under laboratory conditions. It was successfully applied to the titration of EDTA solution with Ba^{2+} ion solution, and the resulting titration curve is shown in Fig 6. As is obvious, the amount of Ba^{2+} ions solution can be accurately determined by the electrode.

The membrane sensor was also applied to the determination of Ba^{2+} in a mineral water sample from Damavand (Iran). While there was no indication of the

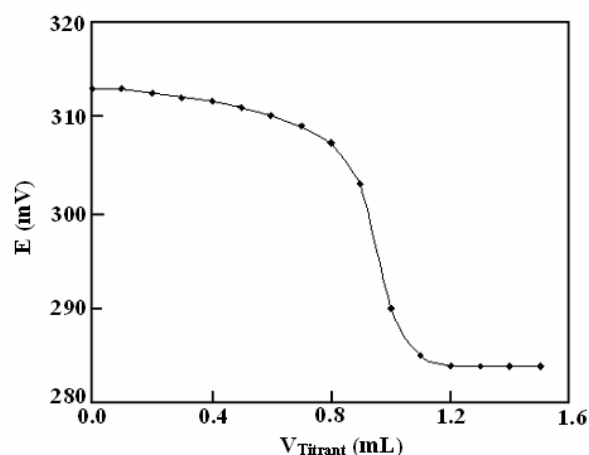


Fig. 6. Potentiometric titration curve of 100.0 ml of 1.0×10^{-5} M Ba^{2+} with 1.0×10^{-3} M EDTA, using the proposed PVC-membrane sensor as an indicator electrode.

presence of any barium ion in the water sample used, the average of three times recovery of a 2.50×10^{-6} M of Ba^{2+} ion added to the sample was quite promising, *i.e.*, $(2.54 \pm 0.07) \times 10^{-6}$ M.

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