

Full Paper

Quantitative Monitoring of Cobalt Ions by a Co²⁺ Selective Electrode Based on a calix[4]arene Derivative

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Abstract- A highly Co²⁺ ion-selective polyvinyl chloride (PVC) membrane sensor based on a derivative of calix[4]arene (L) as an excellent sensing material is successfully developed. The electrodes display a Nernstian behavior (29.7±0.4 mV decade⁻¹) over wide Co²⁺ ion concentration ranges from 1.9×10⁻⁷ to 1.0×10⁻¹ M with very low limits of detection (8.4×10⁻⁸ M). The electrodes have a relatively fast response time (<50 s), a satisfactory reproducibility and relatively long life time. The proposed sensor shows a fairly good selectivity toward Co²⁺ ion in comparison with other common cations. The potentiometric responses are independent of the pH of the test solutions in the range of 2.5–8.4. The practical utility of the proposed electrodes have been demonstrated by their use in potentiometric titration of cobalt with EDTA. It was also successfully applied in determination of cobalt ions in some aqueous samples.

Keywords- Co²⁺ Ion-Selective Electrode, PVC Membrane, Calix[4]arene, Potentiometry, Sensors

1. INTRODUCTION

During the last decades, many intensive studies have been reported on the design and synthesis of highly selective carriers as sensory molecules for ion-selective electrodes (ISEs) [1–3].

The increase use of ion sensors in the fields of environmental, agricultural and medicinal analysis is stimulating analytical chemists to develop new sensors for the fast, accurate, reproducible and selective determination of various species. In the past few decades, considerable efforts have led to the development of selective sensors for alkali, alkaline earth, and heavy metals [4].

Cobalt is an essential micronutrient for man, animals and plants for a range of metabolic process or some biochemical metalloenzyme reactions [5,6]. Cobalt acts as the central atom of vitamin B12 (cyanocobalamin), which is widely responsible for the production of red blood cells (4.35%) and the prevention of pernicious anemia [7]. Insufficient natural levels of cobalt in feed causes co-deficiency diseases characterized by pernicious anemia, loss of weight or retarded growth and is one of the main risk factors for cardiovascular diseases [8,9]. However, at high concentrations, cobalt is toxic and has been reported to produce pulmonary disorders, dermatitis, nausea, vomiting, diarrhea, blood pressure, slowed respiration, giddiness cardiomyopathy, hyperglycemia and so on [9].

Thus, due to the need for specific monitoring of Co^{2+} ion in many industrial, environmental, medicinal and food samples, a number of potentiometric cobalt ion-selective electrodes have been reported in the literature [10–21]. However, most of these electrodes possess either one, two or, in some cases, all of the following drawbacks: (1) narrow working concentration range, (2) high limit of detection and (3) significant interferences from many cations.

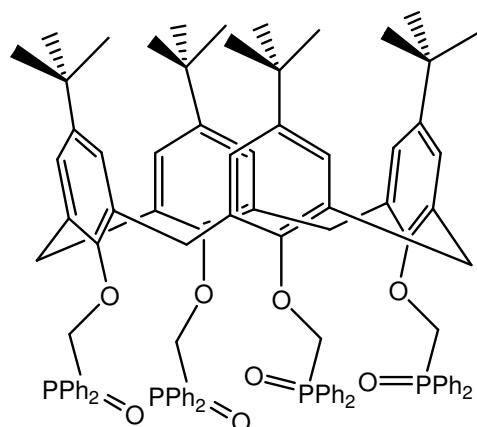


Fig. 1. Structure of the used selectophore (L)

In this work, investigations on the preparation of PVC membranes based on a derivatives of Calix[4]arene (L) and their utilization as Co^{2+} selective sensor were done (Fig. 1). The results is reported in the present work, show that these membranes exhibit high selectivity towards Co^{2+} ions over a large number of cations and could, therefore, be used as a selective sensor for its quantification.

2. EXPERIMENTAL

2.1. Reagents

Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight poly vinyl chloride (PVC) were purchased from Merck and Aldrich, and used as received. The nitrate and chloride salts of all cations used (all from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Triply distilled de-ionized water was used throughout. The calix[4]arene derivatives (L) was synthesized according to a procedure which has been previously reported [22].

2.2. Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 60 mg of plasticizer NPOE, 3 mg of additive NaTPB, and 7 mg of ionophore L in 4 mL of fresh THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm o.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at the room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M of $\text{Co}(\text{NO}_3)_2$). The electrode was finally conditioned by soaking in a 1.0×10^{-2} M $\text{Co}(\text{NO}_3)_2$ solution for 24 h [10,11]. A silver/silver chloride wire was used as an internal reference electrode.

2.3. The emf measurements

The emf measurements with the polymeric membrane electrodes were carried out with the following cell assembly:

$\text{Ag}-\text{AgCl} \parallel 3 \text{ M KCl} \parallel \text{internal solution}, 1.0 \times 10^{-3} \text{ M Co}(\text{NO}_3)_2 \parallel \text{PVC membrane} \parallel \text{test solution} \parallel \text{Hg}-\text{Hg}_2\text{Cl}_2, \text{KCl (satd)}$.

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 °C. Activities were calculated according to the Debye–Hückel procedure [23].

3. RESULTS AND DISCUSSION

3.1. Preliminary Studies

In preliminary experiment, the complexation of L with several metal ions, including Cd²⁺, Co²⁺, Hg²⁺, Ca²⁺, Zn²⁺, Cu²⁺, Pb²⁺, Sn²⁺, K⁺, Mg²⁺, Cr³⁺, Fe²⁺, Mn²⁺ and Ag⁺ was studied conductometrically in acetonitrile solution at 25.00±0.05 °C [24-27], in order to obtain a clue about the stoichiometry and stability of resulting complexes. For evaluation of the stability constants from the conductivity versus [L]/[Mn⁺] mole ratio data, a nonlinear least-squares curve-fitting program KINFIT was used [28]. The resulting K values, obtained from computer are summarized in Table 1. As it is obvious from Table 1, in the case of other metal ions examined, the change in conductivity of the corresponding acetonitrile solutions upon addition of L is negligible, emphasizing the formation of very weak complexes between these cations and the ligand. The results thus obtained revealed the much higher selectivity of L for cobalt ion over other cationic species studied except with cadmium ion, which is expected to have some minor competition with Cobalt ion for the ligand.

Table 1. Formation constants of different cations complexes with L in acetonitrile at 25 °C

Cation	LogK _f	Cation	LogK _f
Co ²⁺	4.69±0.05	K ⁺	2.25±0.04
Cd ²⁺	3.81±0.15	Ca ²⁺	2.22±0.09
Ag ⁺	2.53±0.09	Cu ²⁺	2.20±0.07
Na ⁺	2.49±0.04	Ce ⁺	2.11±0.07
Fe ²⁺	2.41±0.05	Mn ²⁺	2.08±0.09
Tl ⁺	2.37±0.08	Al ³⁺	2.03±0.04
Ba ²⁺	2.33±0.11	Mg ²⁺	1.96±0.03
Sr ²⁺	2.27±0.08	Zn ²⁺	1.81±0.17

Lipophilic character of the ligand was expected to act as a suitable ionophore for Co²⁺ ion in a PVC membrane electrode. In preliminary experiments, it was found that, while the use of an ionophore-free PVC membrane resulted in no measurable response with respect to Co²⁺, the addition of L shows a Nernstian response for the cation in the range of 1.9×10⁻¹-1.0×10⁻⁷ M (Fig. 2). Meanwhile, the ligand L was also used as a neutral carrier to prepare PVC membrane electrodes for a variety of metal ions other than Co²⁺. The potential responses of some of the most sensitive electrodes based on L are also shown in Fig. 3. As is obvious from Fig. 3, among different cations tested, Co²⁺ with the most sensitive response seems to be suitably determined with the electrode. This is due to the selective behavior of the PVC membrane system against Co²⁺ in comparison to the metal ions tested.

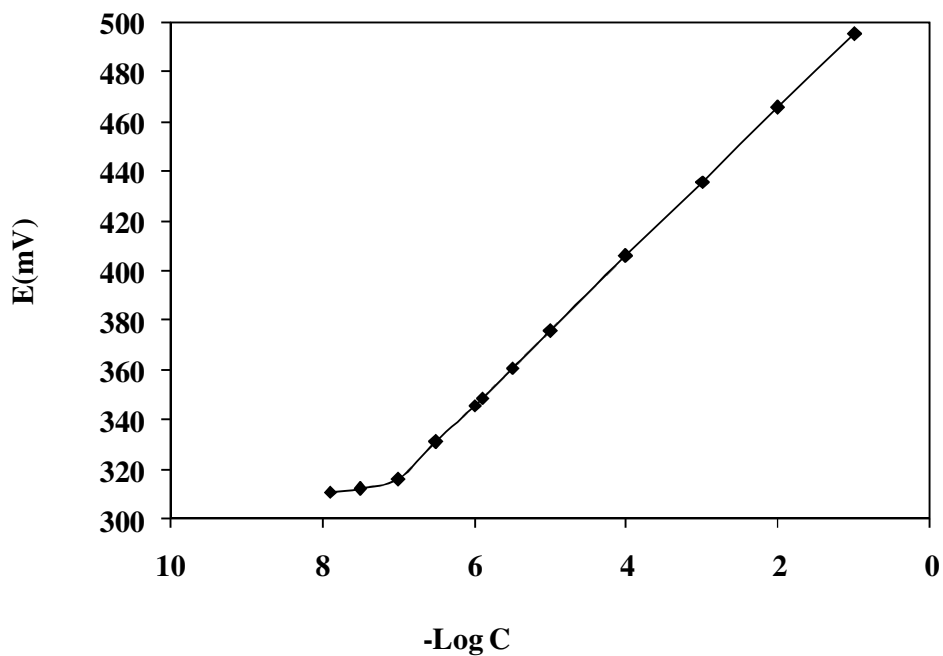


Fig. 2. Calibration graph for cobalt ISE

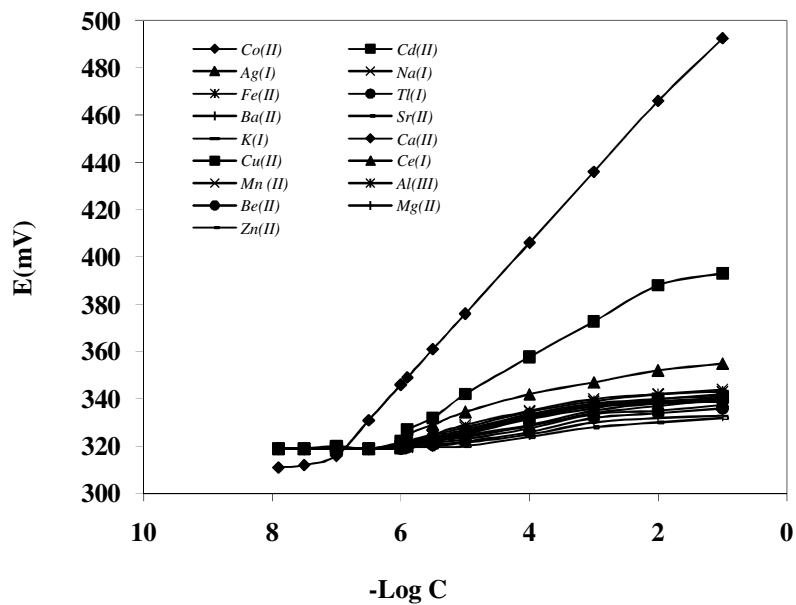


Fig. 3. Potential responses of various cation-selective electrodes based on L

3.2. Membrane Composition

Besides of the critical role of the ionophore in preparing of membrane electrodes, it is well understood that the performance characteristics for the ionophore-incorporated PVC membrane may also be very dependent on electrode composition and the nature of the solution of which the electrodes are composed [29-40]. Thus, different aspects of the composition of membranes based on L for Co^{2+} ion were optimized, and the results are summarized in Table 2.

Table 2. Optimization of membrane ingredients

No.	Composition					Slope(mV/decade)
	PVC	Plasticizer	Ligand	OA	NaTPB	
1	30	70,DBP	0	-	-	≈0
2	30	67,DBP	3	-	-	12.2±0.5
3	30	65,DBP	5	-	-	14.6±0.4
4	30	63,DBP	7	-	-	13.3±0.9
5	30	65,BA	5	-	-	14.1±0.5
6	30	65,NPOE	5	-	-	18.5±0.5
7	20	75,NPOE	5	-	-	12.1±0.6
8	40	55,NPOE	5	-	-	16.2±0.4
9	30	60,NPOE	5	5	-	19.5±0.8
10	30	55,NPOE	5	10	-	20.9±0.6
11	30	50,NPOE	5	15	-	18.3±0.8
12	30	64,NPOE	5	-	1	25.6±0.3
13	30	63,NPOE	5	-	2	29.7±0.4
14	30	62,NPOE	5	-	3	27.4±0.5

As expected, the amount of the ionophore was found to affect the PVC membrane sensitivity (nos. 1-4). The calibration slope increased with increasing L content until a value of 5% was reached. However, further addition of the ionophore resulted in a diminished response slope of the electrode, most probably due to some in homogeneity and possible saturation of the membrane [41].

The potentiometric response of the membrane ion-selective electrodes based on neutral ionophores is greatly influenced by the polarity of the membrane medium, which is defined by the dielectric constants of the major membrane components. [41-43] the influence of the nature of plasticizer on the Co^{2+} response was studied on electrodes containing three types of plasticizers having different dielectric constants, namely, DBP, BA and NPOE. As shown in

Table 2, NPOE with the highest dielectric constant in the series resulted in the best sensitivity of the potential responses.

It should be noted that the nature of the plasticizer affects not only the dielectric constant of the membrane phase but also the mobility of the ionophore molecules and the state of the ligands [42, 44]. Also amount of plasticizer in membrane was tested. The calibration slope increased with increasing NPOE content until a value of 65 % was reached. However, further addition of the NPOE resulted in a diminished response slope of the electrode.

It is well known that the incorporation of lipophilic additives can significantly influence the performance characteristics of a membrane sensor [45-48]. The presence of additives not only improves the response characteristics and selectivity [45] but also may catalyze the exchange kinetics at the sample-membrane interface [49]. In this work, we examined the influence of both OA and NaTPB, as suitable lipophilic additives, on the response characteristics of the proposed PVC membrane, and the results are also included in Table 2. The data given in Table 2 indicate that, in the absence of a proper additive, the sensitivity of the PVC membrane based on L is quite low (nos. 1-8, with slopes of $< 18.5 \text{ mV decade}^{-1}$). However, the presence of 2% NaTPB (no. 13), as suitable lipophilic additive, will improve the sensitivity of the Co^{2+} sensor considerably (with a slope $29.7 \text{ mV decade}^{-1}$). It is interesting to note that, in membrane 13, the molar ratio of the ionophore to NaTPB is 2.5, which implies that NaTPB is not primarily a phase transfer catalyst but also contributes to the complexation mechanism, as described by Eugster et. al [50]. Moreover, with a fraction of 2%wt, NaTPB is expected to contribute significantly to the dielectric constant of the the membrane in addition to the plasticizer.

As it is obvious from Table 2, the membrane 13 with a PVC/NPOE/NaTPB/L percent ratio of 30:63:2:5 resulted in Nernstian behavior of the membrane electrode over a wide concentration range.

3.3. Effect of Internal Solution

Based on the generally adopted ion-selective response formalism, [40] the internal solution may affect the electrode response when the membrane internal diffusion potential is appreciable. Thus, the proposed sensor was examined at different concentrations of inner reference solution, as it is described in the experimental section. It was found that the variation of the concentration of the internal solution (in the range of 1.0×10^{-2} - $1.0 \times 10^{-3} \text{ M Co}^{2+}$) does not cause any significant difference in the corresponding potential response, except for an expected change in the intercept of the resulting Nernstian plots (Fig. 4). A $1.0 \times 10^{-3} \text{ M}$ concentration of the reference solution is quite appropriate for smooth functioning of the electrode system.

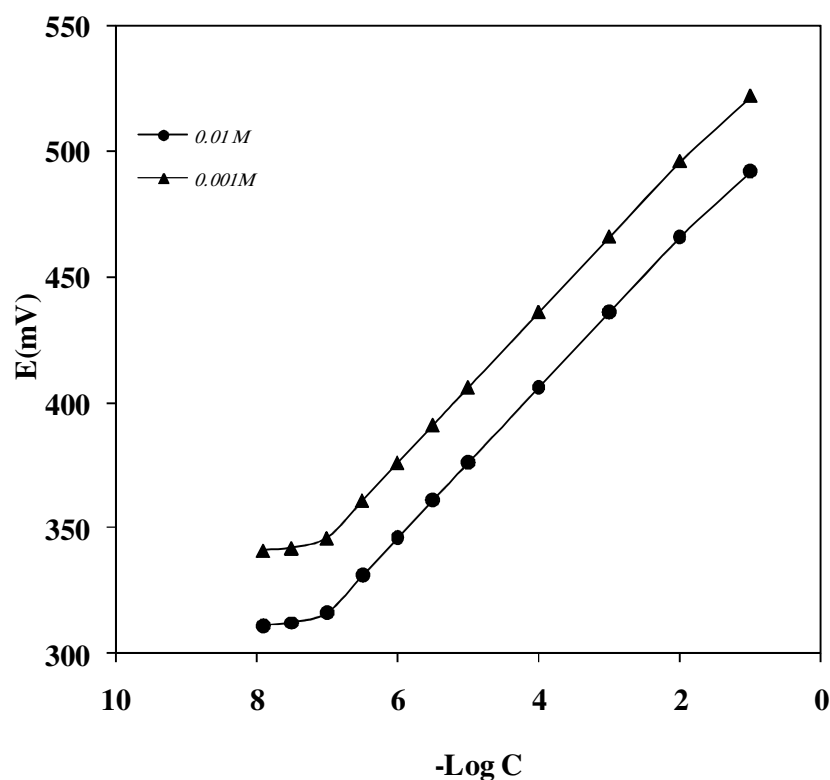


Fig. 4. Effect of internal solution on the membrane electrode

3.4. Response Characteristics of Co^{2+} - ISE

The critical response characteristics of the proposed Co^{2+} -selective electrode were investigated according to IUPAC recommendations [51]. The emf response of the polymeric membrane electrodes (Fig. 2) indicates their Nernstian behavior over a wide concentration range.

The emf response of the membrane electrode at varying Co^{2+} concentrations (Fig. 2) depicts a rectilinear range from 1.9×10^{-7} - 1.0×10^{-1} M with a Nernstian slope of 29.7 ± 0.4 mV decade⁻¹. The limit of detection was 8.4×10^{-8} M as determined from the intersection of the two extrapolated segments of the calibration plots.

According to the first IUPAC recommendation, [51] the practical response time is defined as “the length of time which elapses between the instant at which an ion-selective electrode and a reference electrode are brought into contact with a sample solution (or the instant at which the concentration of the ion of interest in a solution in contact with an ion-selective electrode and a reference electrode is changed) and the first instant at which the potential of the cell becomes equal to its steady-state value within 1 mV.”

While the 1994 IUPAC recommendation defines the response time as “the time which elapses between the instant at which an ion selective electrode and a reference electrode (ISE

cell) are brought into contact with a sample solution (or at which the activity of the ion of interest in a solution is changed) and the first instant at which the emf/time slope ($\Delta E/\Delta t$) becomes equal to a limiting value on the basis of the experimental conditions and/or requirements concerning the accuracy” [52,53]. Thus, the practical response time required for the Co^{2+} sensor to reach a potential within (1 mV of the final equilibrium value after successive immersion of a series of Cobalt ion solutions, each having a 10-fold difference in concentration, was measured. As is obvious from Fig. 6, the practical response time of the membrane electrode thus obtained was <50 s, over the entire concentration range.

The stability and lifetime of the sensor were tested over a period of 4 months. During this period, the electrode was in daily use over extended period of time (1 h per day).

3.5. pH effect of the Test Solution

The influence of pH of the test solution on the potential response of the membrane electrode was tested in the pH range of 2-10, and the results are shown in Fig. 5. As seen, the potential remained constant from pH 2.5 to 8.4, beyond which the potential changed considerably.

At low pH, the potential increased, indicating that the membrane sensor responds to hydrogen ions, while the observed large decrease in potential at higher pH values could be due to the formation of some hydroxyl complexes of Co^{2+} in solution.

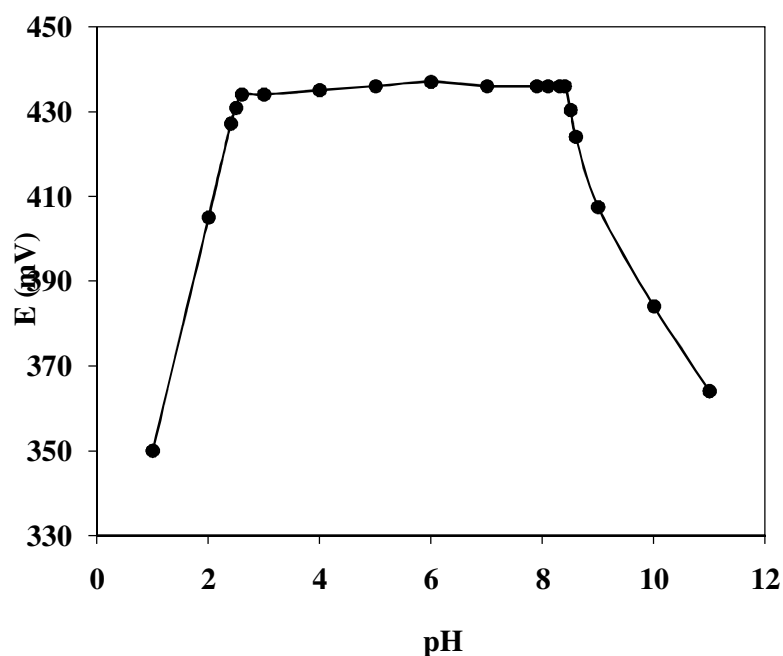


Fig. 5. Effect of pH test solution on the potential response of the uranyl selective electrode based on L. $[\text{Co}^{2+}] = 1.0 \times 10^{-3} \text{M}$

3.6. Selectivity Coefficients

The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients. In this work, the selectivity coefficients were evaluated by the IUPAC suggested separated solution (SSM) in Table 3.

From Table 3, it is readily seen that the proposed Co^{2+} ion-selective electrode is quite selective with respect to the common cations. Table 3 shows that, for all diverse ions used, the selectivity coefficients are in the order of 10^{-3} or smaller, indicating that they would not significantly disturb the functioning of the Co^{2+} ions-elective electrode.

3.7. Analytical application

The analytical applicability of the electrode was tested by using it as an indicator electrode, to determine the end point in the potentiometric titration of Co^{2+} with EDTA [54, 55]. 10 ml of 1.0×10^{-3} M Co^{2+} solution was titrated against 1.0×10^{-3} M EDTA solution after adjusting the pH of the solution at 6. Hexamine and nitric acid were used to adjust the pH of the solution. The potential data were plotted against the volume of EDTA (Fig. 7). The conventional sigmoid shape plot was obtained and the sharp break point corresponds to the stoichiometry of Co^{2+} -EDTA complex and indicates the end point of titration.

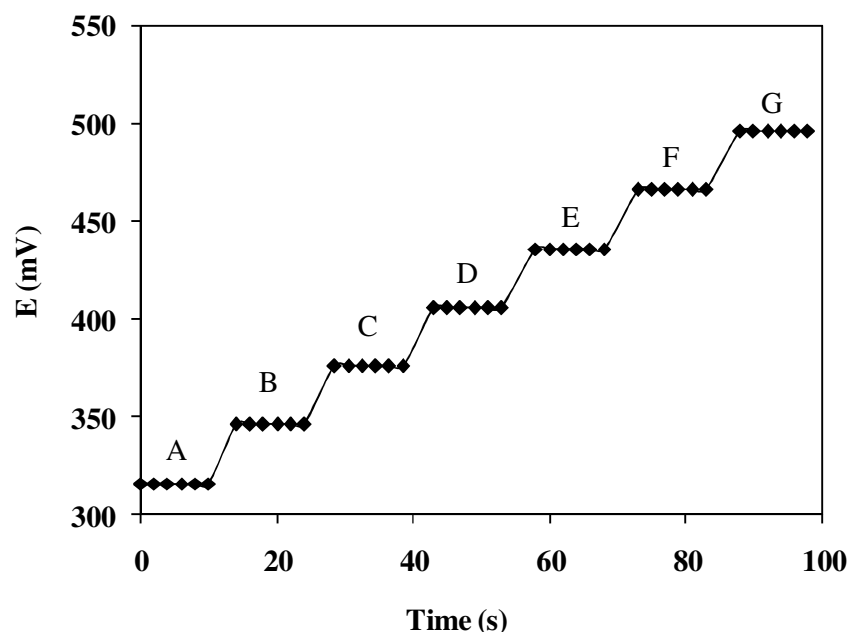
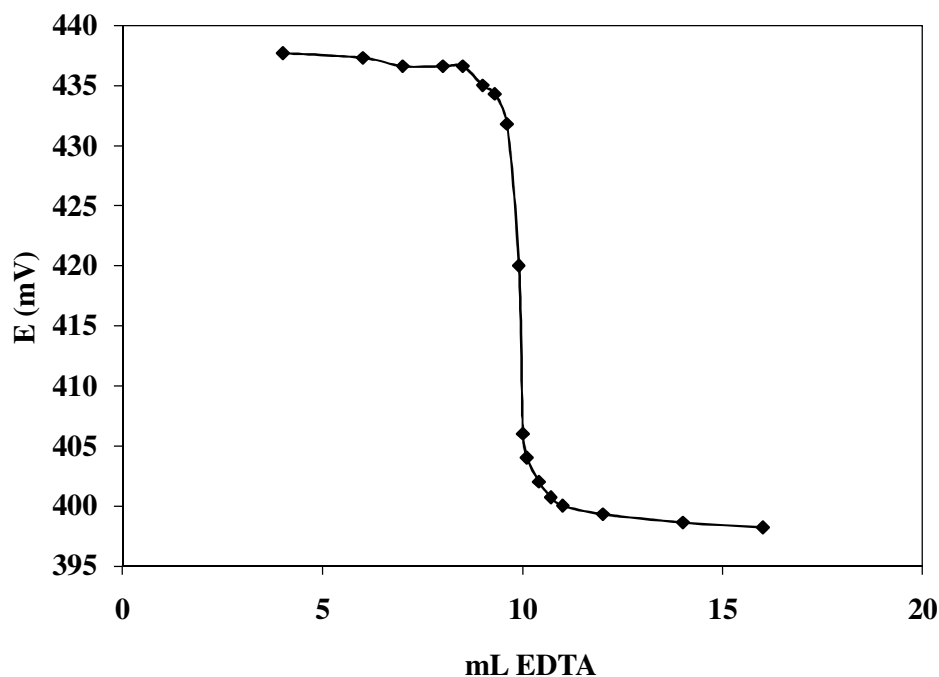


Fig. 6. Dynamic response of the proposed ion-selective electrode for step changes in concentration of Co^{2+} : (A) 1.0×10^{-7} , (B) 1.0×10^{-6} , (C) 1.0×10^{-5} , (D) 1.0×10^{-4} , (E) 1.0×10^{-3} , (F) 1.0×10^{-2} and (G) 1.0×10^{-1} M

Table 3. Selectivity coefficients ($K_{A,B}$) of Co^{2+} ion-selective electrode for different cations

<i>ion</i>	$K_{A,B}^{pot}$	<i>ion</i>	$K_{A,B}^{pot}$
Cd^{2+}	3.5×10^{-3}	Ca^{2+}	4.4×10^{-4}
Ag^+	9.1×10^{-4}	Cu^{2+}	3.8×10^{-4}
Na^+	8.5×10^{-4}	Ce^+	3.7×10^{-4}
Fe^{2+}	7.7×10^{-4}	Mn^{2+}	3.7×10^{-4}
Tl^+	5.9×10^{-4}	Al^{3+}	2.5×10^{-4}
Ba^{2+}	5.2×10^{-4}	Mg^{2+}	2.2×10^{-4}
Sr^{2+}	5.0×10^{-4}	Zn^{2+}	1.9×10^{-4}
K^+	4.6×10^{-4}		

**Fig. 7.** Titration plot of 10ml of 1.0×10^{-3} M Co^{2+} with 1.0×10^{-3} M EDTA solution at pH 6

3.8. Comparison of the Co^{2+} selective electrodes

The optimized formulation of the sensor no. 13 was compared in terms of analytical performance with membranes employing different neutral ionophores that had been studied previously. Table 4 represents the main analytical features of some Co^{2+} ion selective electrodes. The sensor is superior to existing sensors in terms of selectivity over a number of cations while comparable with regard to other parameters such as working concentration

range, Detection limit, and slope and pH range. Further, this sensor could be used in real sample analysis.

Table 4. Comparison of electrode performance with previous cobalt ion-selective electrodes

<i>Ref</i>	<i>Linearity range (mol L⁻¹)</i>	<i>Detection limit (mol L⁻¹)</i>	<i>Slope (mV decade⁻¹)</i>	<i>Serious interfering ions and - log K</i>	<i>pH range</i>
10	8.0×10 ⁻⁶ to 1.0×10 ⁻¹	8.0×10 ⁻⁶	29.0	Na ⁺ (0.23), Ni ²⁺ (1.29), Fe ³⁺ (1.05)	2.8-7.3
13	2.0×10 ⁻⁶ to 1.0×10 ⁻²	6.0×10 ⁻⁷	29.45±0.5	Ni ²⁺ (1.09)	3.0-8.0
11	9.0×10 ⁻⁷ to 1.0×10 ⁻²	8.0×10 ⁻⁷	29.0±1	Hg ²⁺ (2.12), Cu ²⁺ (2.46), Cd ²⁺ (2.41), Tl ⁺ (2.18)	3.5-6.0
15	4.0×10 ⁻⁷ to 1.0×10 ⁻²	1.0×10 ⁻⁷	30.0±1.0	Cu ²⁺ (1.83), Ag ⁺ (1.76), Tl ⁺ (1.95), Cd ²⁺ (1.98)	5.0-8.0
12	1.0×10 ⁻⁶ to 1.0×10 ⁻¹	9.0×10 ⁻⁷	29.8	Pb ²⁺ (1.05), Ni ²⁺ (1.15)	3.5-8.0
18	7.0×10 ⁻⁷ to 1.0×10 ⁻¹	5.0×10 ⁻⁸	30.0±0.2	Hg ²⁺ (1.23), Cu ²⁺ (0.38), Ni ²⁺ (1.60), Cd ²⁺ (2.97)	2.0-9.0
17	6.3×10 ⁻⁷ to 1.0×10 ⁻¹	3.9×10 ⁻⁷	29.5±0.2	Ni ²⁺ (0.25), Cu ²⁺ (1.34), Ag ⁺ (1.15)	3.3-9.0
19	6.3×10 ⁻⁶ to 1.0×10 ⁻¹	8.5×10 ⁻⁷	30.0	Ni ²⁺ (1.22), Cu ²⁺ (1.16), Ag ⁺ (2.0), Hg ²⁺ (2.03)	2.5-6.5
This work	1.9×10 ⁻⁷ to 1.0×10 ⁻¹	8.4×10 ⁻⁸	29.7±0.4	-	2.5-8.4

4. CONCLUSION

It was found that calix[4]arene derivatives (L) acts as an effective and selective ionophore agent for Co²⁺ ions. This affinity allowed us to prepare a new Co²⁺ ion-selective electrode based on this selectophore. The main advantages of the proposed potentiometric sensor are its simplicity of preparation, short conditioning time, fast response time (<50 s), wide dynamic range 1.9×10⁻⁷-1.0×10⁻¹ M, low detection limit 8.4×10⁻⁸ M, low cost, Nernstian behavior of 29.7±0.4 mV decade⁻¹. This sensor works nicely in the pH range of 2.5–8.4 and fairly good selectivity. It also displays a good stability and long lifetime.

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