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A Co^{2+}-Selective Poly(vinyl chloride) Membrane Electrode Based on a Newly Synthesized 3,3′-(Dodecylazanediyl)bis(*N*-(2-(2-aminoethylamino)ethyl)propanamide) Compound

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A Co^{2+} ion-selective membrane sensor has been fabricated in a poly(vinyl chloride) matrix based on a recently synthesized 3,3′-(dodecylazanediyl)bis(*N*-(2-(2-aminoethylamino)ethyl)propanamide) (DAEP) as a neutral carrier, sodium tetraphenylborate (NaTPB) as an anionic excluder, and dioctylphthalate (DOP) as a solvent mediator. The electrode exhibits a Nernstian response over a wide concentration range [$(6.58 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1})$ M] between pH 2.5 and 8.5, and the limit of detection is $6.82 \cdot 10^{-8}$ M. The response time of the sensor is about 5 s, and it can be used over a period of 5 months without any divergence in potential. The proposed membrane sensor revealed good selectivity for Co^{2+} over a wide variety of other metal ions. The electrode has been used as an indicator electrode in the potentiometric titration of Co^{2+} with ethylenediaminetetraacetic acid (EDTA) and the direct determination of Co^{2+} in wastewater from the electroplating industry.

Introduction

Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals. There are nonradioactive and radioactive forms of cobalt. Nonradioactive cobalt, referred to as stable cobalt, is used to produce alloys (mixtures of metals) used in the manufacturing of aircraft engines, magnets, grinding and cutting tools, and artificial hip and knee joints. Cobalt compounds are also used to color glass, ceramics, and paints and as a drier for porcelain enamel and paints. Cobalt is widely used in the paint and varnish industries, in ink as a drying agent, in the preparation of pigments like cobalt blue and cobalt green, in ground coats for porcelain enamels, in lithium ion battery electrodes, and as a catalyst in the petroleum and chemical industries and in the electroplating industry.[1]

Natural sources and the burning of coal or oil or the production of cobalt alloys are methods for entering cobalt into the environment. Cobalt might be associated with particles in the air which will settle to the ground within a few days. Cobalt cannot be destroyed in the environment. It can only change its form or become attached or separated from particles. Radioactive decay is the only way of decreasing the amount of radioactive cobalt in the environment.[2]

Cobalt has both beneficial and harmful effects on human health. Cobalt is beneficial for humans because it is part of vitamin B_{12}. For common livestock species, the maximum dietary tolerable level of cobalt is $10\ mg \cdot L^{-1}$, and if consumed in large doses it could result in lung and heart effects and dermatitis. Liver and kidney effects have also been observed in animals exposed to high levels of cobalt. Exposure to large amounts of radioactive cobalt or the radiation it emits can damage cells in the human body. It may also cause acute radiation syndrome which includes nausea, diarrhea, irritation of the gastrointestinal tract, and vomiting. In the International Agency for Research on Cancer, cobalt has been classified as a possible human carcinogen. A dose of 500 mg can be toxic, and the maximum tolerable limit of cobalt in diet is $10\ mg \cdot L^{-1}$.[3]

Several analytical techniques such as atomic absorption spectrometry,[4] cyclic voltammetry,[5] spectrophotometry,[6] and spectrofluorimetry have been extensively used for the quantification of cobalt.[7] Maintenance and operational cost of these techniques are expensive and require adequate expertise. Therefore, these methods of analysis could not be used at the industrial level. Ion sensors are reliable, low-cost, quick, and portable analytical techniques, and such requirements are the needs of today.

Various ionophores, such as chelates,[8] extractants,[9] macrocycles,[10–15] mercapto compounds,[16] cobalt phenanthroline complexes,[17] OXCDD (diamide),[18] a Schiff base,[19,20] isothiazole,[21] and a variety of other ligands,[22,23] have been reported for cobalt selective sensors, and different ionophores, such as crown,[24–27] macrocycles,[28–30] organic resins,[31,32] 4-tert-butylcalix[6]arene,[33] di-(2-ethylhexyl)phosphoric acid (DEHPA) and dibutyl(butyl)phosphonate (DBBP),[34] a Schiff base,[35,36] and neutral carriers and organic exchangers,[37] have been used for other heavy metals. Selective analytical methodologies, which are easily operated and involve harmless reagents, have therefore been proposed as alternatives to standard methods. Potentiometric sensors based on ion-selective electrodes are especially suited for such determination because they offer advantages such as selectivity, sensitivity, good precision, simplicity, and low cost.[38] This method has some disadvantages such as a working concentration range with a near or non-Nernstian response, which exhibits high response times and poor reproducibility.

In this communication we report a highly selective and high lifetime poly(vinyl chloride) (PVC) membrane for the cobalt ion based on 3,3′-(dodecylazanediyl)bis(*N*-(2-(2-aminoethylamino)ethyl)propanamide) (DAEP). Moreover, this ionophore molecule (DAEP) has a hydrophobic (C_{12}) and a hydrophilic

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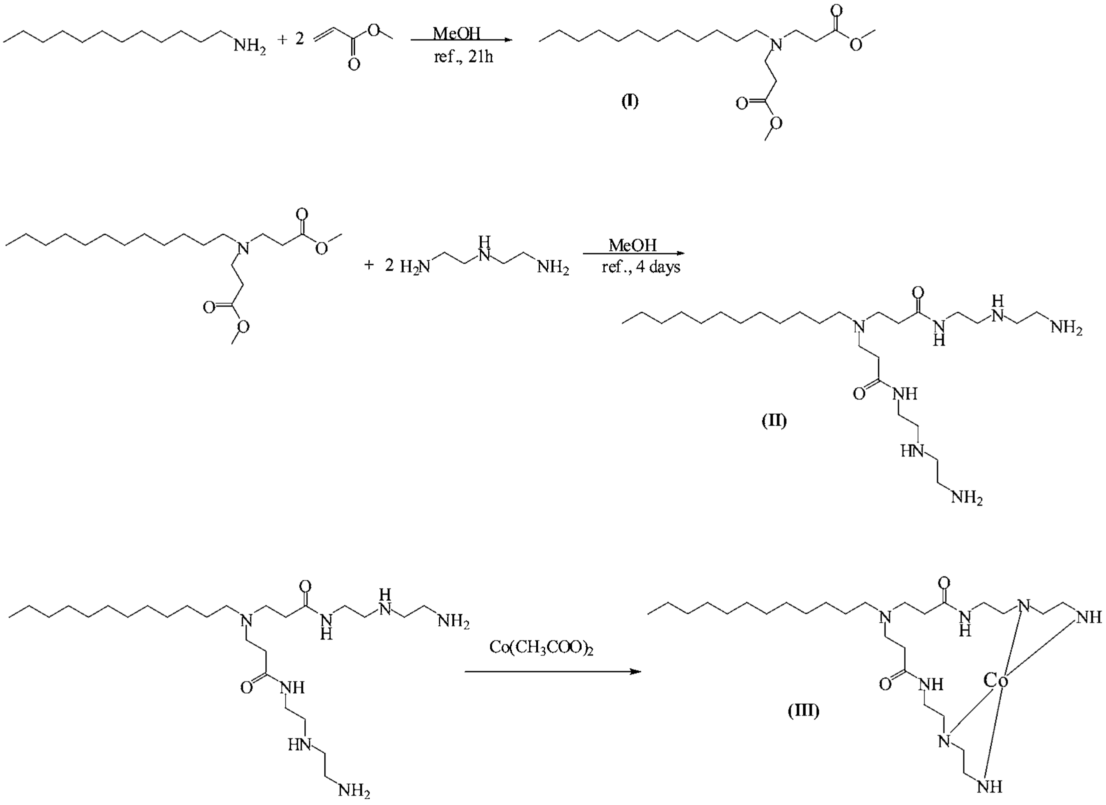
Scheme 1. Synthesis of DAEP



segment. The hydrophilic part contains two oxygen and seven nitrogen-donating atoms. These heteroatoms are easily able to coordinate with cobalt ions in solution and in the solid state by attractive $n-\pi^*$ stacking interactions. The feature of this ionophore is its geometric and cavity control of host−guest complexation and modulation of its hydrophobic ability to produce remarkable selectivity, sensitivity, and stability for a specific ion.

Experimental Section

Reagents. Reagent grade sodium tetraphenylborate (NaTPB), dibutylphthalate (DBP), dioctylphthalate (DOP), tetrahydrofuran (THF), high molecular weight PVC, dodecylamine, methyl acrylate, and diethylenetriamine (DETA) were purchased from Merck and used as received. Cobalt acetate (from Merck) was used without any further purification, except for vacuum drying over P_2O_5, as a cobalt salt for the study of the membrane sensor. Doubly distilled water was used for the preparation of solutions of metal salts of different concentrations by diluting stock standard solution (0.1 M).

Synthesis of DAEP. Methyl acrylate (3 mmol) was slowly added to a stirred solution of the appropriate amount of dodecylamine (1 mmol) in dry CH_3OH (20 mL). After stirring for 21 h at reflux temperature under nitrogen atmosphere, the solution was evaporated, giving dimethyl-3,3′-(dodecylazanediyl-)dipropanoate (I), which was used in the subsequent step without need for purification. This product was characterized using IR, ^1H NMR, CHN, and mass spectrometry. Yield 83 %, mp 32 °C. IR (KBr): ν_{max}/cm^{-1}, 1742 (s), 1589 (s). ^1H NMR ($CDCl_3$): δ (ppm): 0.67 (CH_3, 3H), 1.05 (CH_2, 20H), 2.18 (CH_2, 2H), 2.45 (CH_2, 4H), 2.55 (CH_2, 4H), 3.46 (CH_3, 6H). Elemental analysis. Calculated (%) for $C_{20}H_{39}NO_4$: C = 67.19, H = 10.99, N = 3.92; observed (%): C = 67.14, H = 11.06, N = 4.05. Mass (m/z): 357.

In the next step, DETA (5.25 mmol) was slowly added to dimethyl-3,3′-(dodecylazanediyl)dipropanoate (I) (1.75 mmol) in dry CH_3OH (20 mL), and the mixture was left stirring under N_2 at reflux temperature for 4 days. The solution was poured into water, the solid residue dissolved in chloroform, and the organic extract dried ($MgSO_4$) and evaporated, affording DAEP (II) (Scheme 1). The product was characterized using IR, ^1H NMR, CHN, and mass spectroscopy. Yield 78 %, mp 38 °C. IR (KBr): ν_{max}/cm^{-1}, 3553 (m), 3413 (w), 1657 (m), 1589 (s). ^1H NMR ($CDCl_3$): δ (ppm), 0.60 (CH_3, 3H), 0.98 (CH_2, 20H), 1.20 (NH_2, NH, 6H), 1.53 (CH_2, 12H), 2.05 (CH_2, 2H), 2.42 (CH_2, 4H), 2.44 (CH_2, 2H), 2.53 (CH_2, 4H), 2.57 (CH_2, 2H), 4.65 (NH, 2H). Elemental analysis. Calculated (%) for $C_{26}H_{57}N_7O_2$: C = 62.48, H = 11.50, N = 19.62; observed (%): C = 62.43, H = 11. 57, N = 19.70. Mass (m/z): 499.

Preparation of the Membrane. Homogeneous membranes of the ligand were prepared using PVC (binder) and NaTPB (anion excluder). The membrane components (Table 1) were mixed and dissolved in tetrahydrofuran. The resulting homogeneous syrup was vigorously stirred. A Pyrex funnel with a narrow opening diameter of 3 mm was dipped into the mixture for about 10 s, so that a nontransparent membrane of about 0.3 mm thickness was formed. The solvent was evaporated at room temperature. After 24 h, a transparent membrane of about 0.3 mm thickness was obtained. The funnel was then filled with an internal filling solution ($1.0 \cdot 10^{-2}$ M cobalt acetate). The electrode was finally conditioned by soaking for 24 h in a $1.0 \cdot 10^{-2}$ M solution of cobalt acetate.

Potential Measurement. The potential measurements were carried out at (25 ± 0.1) °C by using a saturated calomel electrode (SCE) as a reference electrode and a DAEP-based membrane electrode with an Ag/AgCl internal reference as the indicating electrode. The emf measurements were carried out with a pH meter model 162 (Fanavary Tajhizat Sanjesh). An

Table 1. Composition of PVC-Based Membranes of DAEP and Their Performance as a Co(II)-Selective Electrode

	composition of membrane (% w/w) (ratio of components)					linear range	slope of activity	response time
membrane no.	ionophore	PVC	NaTPB	DOP	DBP	M	mV/decade	s
1	4.5	30	4.5	61		$1.5 \cdot 10^{-5}$ to $1.0 \cdot 10^{-1}$	22.6	< 15
2	5	30	5	60		$2.1 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$	25.5	< 10
3	5	31	3	61		$8.6 \cdot 10^{-5}$ to$1.0 \cdot 10^{-1}$	22	< 15
4	10	30	3	57		$2.4 \cdot 10^{-6}$ to $1.0 \cdot 10^{-1}$	25	< 10
5	10	30	5	55		$3.9 \cdot 10^{-6}$ to $1.0 \cdot 10^{-1}$	26.4	< 5
6	10	32	3	55		$7.4 \cdot 10^{-6}$ to $1.0 \cdot 10^{-1}$	26.5	< 5
7	20	30	5	45		$8.0 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$	29.5	< 10
8	20	32	3	45		$6.1 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$	28	< 10
9	20	20	5	55		$6.58 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$	30.5	< 5
10	5	30	5		60	$3.2 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$	23	< 10
11	20	30	5		45	$4.7 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$	27	< 10

electrode cell assembly of the following type was used: Ag/AgCl | internal solution, ($1.0 \cdot 10^{-2}$ M, Co^{2+}) | membrane | test solutions || SCE.

The concentration of the metal ion in the test solutions varied from ($1.0 \cdot 10^{-8}$ to $1.0 \cdot 10^{-1}$) M. Each solution was stirred, and the potential reading was recorded when it became stable and then plotted as a logarithmic function of Co^{2+} cation activity. The activities of metal ions were calculated according to the Debye−Hückel procedure. The response time was defined as the time taken to reach a potential of 90 % of the potential difference in two measurements. Reproducibility was defined by the deviation from the average potential value in the same four dips to read measurements.

The activities of metal ions were based on the activity coefficient γ data calculated from the modified form of the Debye−Hückel equation, eq 1,[39] which is applicable to any ion:

$$\log y = -0.511Z^2\left[\left(\frac{\mu^{1/2}}{(1 + 1.5\mu^{1/2})}\right) - 0.2\mu\right] \qquad (1)$$

where μ is the ionic strength and Z is the charge of the ion.

Results and Discussion

Preliminary Potentiometry Studies. The ligand (DAEP) was used as a suitable ion carrier in constructing PVC-membrane electrodes for a number of transition metal ions and heavy metal ions of proper size and charge. The potential response of the present electrode to different metal ions based on the ligand (DAEP) is shown in Figure 1. As can be seen, among different tested cations, Co^{2+} with the most sensitive response seems to be suitably determined by the PVC membrane based on the ligand (DAEP). The emf responses obtained for all other cations are much lower than those expected by the Nernstian equation. This is due to the selective behavior of the ionophore toward Co^{2+} in comparison with some other metal ions.

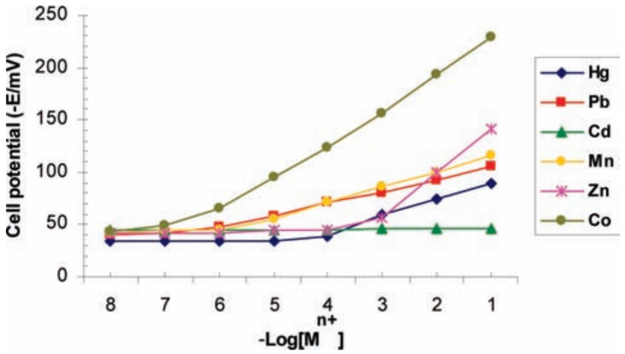


Figure 1. Potential response of the selective electrodes based on DAEP to various metal ions.

DAEP has a N_7O_2 moiety that can play as a nonadentate ligand. This part of the molecule is flexible enough to provide the optimum structure for selective interaction with Co^{2+}. Moreover, it should be mentioned that in the interaction between the ligand and the metal ion, the membrane composition is very important. Also, to obtain an efficient membrane with an acceptable response, the nature and amount of plasticizer are critical because they affect the dielectric constant of the membrane phase, the state of ligands, and the mobility of the ionophore molecules.[40,41]

Influence of Membrane Composition. Besides the importance of the nature of the ionophore in preparing membrane selective sensors, some other important features of the PVC membrane are known to significantly influence the linearity range, sensitivity, and selectivity of ion-selective electrodes. Thus, several membrane compositions were investigated, and the membrane having a composition of 20:20:5:55 of ionophore (DAEP)/PVC/NaTPB/DOP gave the best response characteristics, as shown in Table 1.

The PVC-based membrane of ligand DAEP as an ion-selective electrode for Co^{2+} ions generated a stable potential response in a solution containing $1 \cdot 10^{-2}$ M Co^{2+} ion concentration. The Nernstian response and slope remained constant over a wide concentration range [($6.58 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$) M] between pH 2.5 and 8.5. The properties of the membranes, namely, the response time, lifetime, and selectivity were dependent on the ratio of the electroactive phase and the binder materials.

The DAEP-based membrane showed good linearity with the addition of a solvent mediator (DBP or DOP), and it was observed that the addition of DOP, in comparison with DBP, led to a significant improvement in the working concentration range of ($6.58 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$) M; the slope was 30.5 mV per decade of concentration. The results showed that the addition of DOP gave the highest possible selectivity and sensitivity. The role of DOP is to make the membrane more flexible and improve both the membrane permittivity and the mobility of the ion-exchanger sites. In fact, DOP is a fairly polar plasticizer and can coordinate with most cations. The polarity of the media affects deeply on the electrode detection limits and can lower ion-pair formation.

The effect of plasticizers (DBP and DOP), NaTPB, and the amounts of PVC and ion carrier on the performance of the membranes was also studied. The results are given in Table 1. The working concentration ranges and slopes for all of the membrane electrodes (nos. 1 to 11) are given in Table 1. Hence, on the basis of the data presented in Table 1, membrane no. 9 was chosen and studied in detail as a Co^{2+}-selective electrode for all further investigations.

To measure the ability of the ionophore to act as an ion carrier, we modified a polymeric membrane based on PVC with

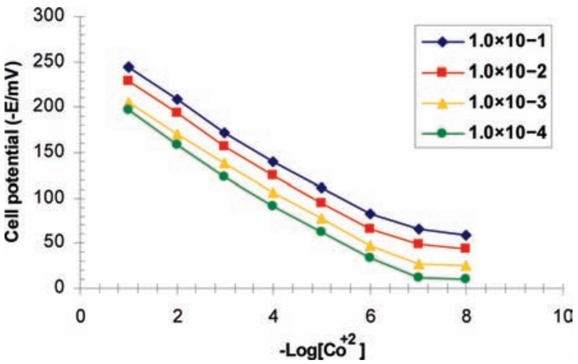


Figure 2. Effect of the concentration of an internal reference solution on electrode response at various concentrations of ($1.0 \cdot 10^{-1}$, $1.0 \cdot 10^{-2}$, $1.0 \cdot 10^{-3}$, and $1.0 \cdot 10^{-4}$) M Co^{2+} solutions on the potential.

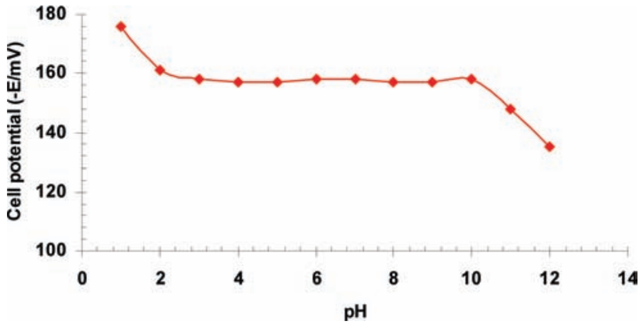


Figure 3. Influence of pH of $1.0 \cdot 10^{-3}$ M Co^{2+} solutions on the potential response of the optimized Co^{2+}-selective electrode.

different amounts of this new ionophore. In the absence of the ionophore, the response of the membrane in regards to sensitivity was poor. Also, the existence of hydrophilic charged additives, such as NaTPB, improves response behavior and selectivity[42] and the potentiometric behavior of ion-selective electrodes.[43] Thus, several membrane compositions were investigated, and as mentioned previously, the membrane having a composition of 20:20:5:55 of ionophore DAEP/PVC/NaTPB/DOP gave the best response characteristics.

Effect of Internal Reference Solution. The influence of the concentration of the Co^{2+} ion in the internal solution of the membrane selective electrode on the potential response was also studied. The cobalt acetate solution concentration was varied from ($1.0 \cdot 10^{-1}$ to $1.0 \cdot 10^{-4}$) M, and the potential values were recorded (Figure 2). The variation of the concentration of the internal cobalt acetate solution did not cause any significant difference in the potential response except for an expected change in the intercept of the resulting Nernstian plots. However, the internal cobalt acetate solution with a $1.0 \cdot 10^{-2}$ M concentration of the reference solution was found quite appropriate for smooth functioning of the sensor system, and it was used for all further investigations.

Influence of pH. The pH dependence of the electrode potential was tested for $1.0 \cdot 10^{-2}$ M of Co^{2+} ions (Figure 3). The pH of the solution was investigated by adding a nitric acid (0.1 M) or ammonia (0.1 M) solution in the range of 1.0 to 12.0. The potentials remained constant from pH 2.5 to 10.0. The results showed that the decrease of the potential at higher pH values might be due to the formation of some hydroxyl complexes of Co^{2+} in the solution and the decrease in concentration of Co^{2+}. On the other hand, the deviation of the response potential at lower pH values is probably due to simultaneous response of the electrode to H_3O^+ and Co^{2+} ions.[44] The sensitivity change of the membrane at low pH values could be related to the deactivation of the membrane by protonation of the nitrogen atoms in the ionophore structure, and this behavior at high pH values should be related to high concentrations of hydroxide ions in solution.

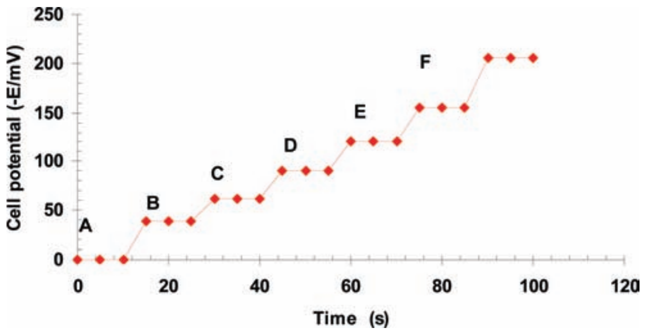


Figure 4. Dynamic response of (DAEP) membrane electrode for stepwise changes in the concentration of Co^{2+}: A, $1.0 \cdot 10^{-6}$ M; B, $1.0 \cdot 10^{-5}$ M; C, $1.0 \cdot 10^{-4}$ M; D, $1.0 \cdot 10^{-3}$ M; E, $1.0 \cdot 10^{-2}$ M; F, $1.0 \cdot 10^{-1}$ M.

Response Characteristics. The electrode exhibits a linear response to the activity of the Co^{2+} ion in the range of ($1.0 \cdot 10^{-7}$ to $1.0 \cdot 10^{-1}$) M. The response time of the electrode was tested by measuring the time required to achieve a steady potential within ± 1 mV fluctuation by a rapid increase in the Co^{2+} ion concentration. The response time of the electrode based on the proposed ligand demonstrated a steady potential within less than 5 s. In this study, the practical response time was recorded by changing the Co^{2+} ion concentration in solution, over a concentration range of ($1.0 \cdot 10^{-1}$ to $6.58 \cdot 10^{-7}$) M (Figure 4). The final equilibrium value was measured after the successive immersion of a series of cobalt ion solutions, each having a 10-fold difference in concentration. As can be seen, in the whole concentration range, the electrode reached its equilibrium response in a very short time (< 5 s).

The slopes of the calibration plots were 30.5 ± 1.0 mV per decade of cobalt ion activity change at (25 ± 0.1) °C. The detection limit was $6.82 \cdot 10^{-8}$ M, as determined from the intersection of the two extrapolated segments of the calibration graph. The standard deviation of 10 replicate measurements was ± 0.5 mV.

The membranes were used over a period of 5 months without any measurable divergence. During this time, the detection limit and the slope of the electrode remained almost constant. The membranes were stored in 0.1 M Co^{2+} when not in use, and the detection limit and the slope of the electrode remained almost constant. Subsequently, the electrochemical behavior of the electrode gradually deteriorated, which may be due to aging of the membrane matrix while contacting aqueous solution.

Potentiometric Selectivity. Selectivity coefficient ($K^{\mathrm{pot}}_{\mathrm{Co,M}}$) values describing the performance of the sensor in the presence of interfering ions was determined by using a fixed primary ion method (FPI), using eq 2.[45] These values ($K^{\mathrm{pot}}_{\mathrm{Co,M}}$) have been evaluated from the potential measurements of the solutions containing a fixed concentration of Co^{2+} (0.01 M) and titration with M^{n+} solution of ($1.0 \cdot 10^{-4}$ M). The selectivity coefficient values (Table 2) are considerably smaller than unity, which indicate that the sensor under consideration is sufficiently selective toward Co^{2+} over alkali, alkaline earth metals, and several common transition ions. It can be seen from the selectivity coefficient data that the present sensor is significantly selective to cobalt over all of the interfering ions. In view of the good selectivity of the sensor, it can be used for Co^{2+} determination by direct potentiometry in the presence of many foreign ions.

Table 2. Potentiometric Selectivity Coefficient Values of Various Interfering Ions (0.01 M)

M^{n+}	$K^{pot}_{Co^{2+},M}$	M^{n+}	$K^{pot}_{Co^{2+},M}$
Na^+	$2.3 \cdot 10^{-3}$	Ni^{2+}	$3.5 \cdot 10^{-3}$
K^+	$1.5 \cdot 10^{-3}$	Mn^{2+}	$2.9 \cdot 10^{-3}$
Mg^{2+}	$0.7 \cdot 10^{-3}$	Pb^{2+}	$5.6 \cdot 10^{-3}$
Ca^{2+}	$0.5 \cdot 10^{-3}$	Cd^{2+}	$2.3 \cdot 10^{-3}$
Li^+	$1.1 \cdot 10^{-3}$	Zn^{2+}	$7.4 \cdot 10^{-3}$
Ag^+	$4.8 \cdot 10^{-3}$	Cr^{3+}	$3.7 \cdot 10^{-3}$
Cu^{2+}	$4.1 \cdot 10^{-3}$	Hg^{2+}	$6.7 \cdot 10^{-3}$

Table 3. Potentiometric Determination of the Co^{2+} Ion in Water and Wastewater Samples

added to sample	found by analysis by the AAS	recovery by the sensor	
ppm	ppm	ppm	%
Wastewater Industry, 24 h			
0.0	0.14 ± 0.01	0.13 ± 0.01	93
0.5	0.64 ± 0.01	0.63 ± 0.01	98
1.0	1.14 ± 0.01	1.14 ± 0.01	100
1.5	1.62 ± 0.01	1.60 ± 0.01	99
2.0	2.11 ± 0.01	2.11 ± 0.01	100
Wastewater Industry, Galvanized			
0.0	0.28 ± 0.01	0.27 ± 0.01	96
0.5	0.78 ± 0.01	0.78 ± 0.01	100
1.0	1.28 ± 0.01	1.26 ± 0.01	99
1.5	1.75 ± 0.01	1.75 ± 0.01	100
2.0	2.27 ± 0.01	2.27 ± 0.01	100
Drink Water			
0.0	0.12 ± 0.01	0.11 ± 0.01	92
0.5	0.62 ± 0.01	0.61 ± 0.01	98
1.0	1.14 ± 0.01	1.12 ± 0.01	99
1.5	1.62 ± 0.01	1.62 ± 0.01	100
2.0	2.11 ± 0.01	2.11 ± 0.01	100

$$K^{pot}_{ij} = a_i[10^{\Delta E Z_i F/2.303RT} - 1]a_j^{Z_i/Z_j} \tag{2}$$

where $\Delta E = E_{i+j} - E_i$.

Analytical Application. Wastewater Analysis. This electrode has been successfully applied to the direct determination of cobalt in different water samples. Samples of industrial wastewater over a 24 h period, wastewater from a galvanization factory, and drink water were collected, filtered, and stored. To each one of these samples we have added a cobalt solution with concentrations in the range of (0.5, 1.0, 1.5, and 2.0) $mg \cdot L^{-1}$ as a standard. The concentrations of cobalt in the samples, obtained by the proposed sensor, were in close agreement with those determined by the atomic absorption spectrophotometry (Table 3).

Potentiometric Titration. The electrode was also applied as an indicator electrode to determine the end point in the potentiometric titration of Co^{2+} with ethylenediaminetetraacetic acid (EDTA). Twenty-five mL of $1.0 \cdot 10^{-3}$ M Co^{2+} solution was titrated against $1.0 \cdot 10^{-1}$ M EDTA solution.

Comparison with Other Co^{2+} Selective Electrodes. The analytical performance of this membrane electrode has been compared with other membranes employing different neutral ionophores that have been studied previously. The response characteristics and the main analytical features of some of the reported Co^{2+} ion selective electrodes are represented in Table 4. As seen, the proposed electrode is superior to the previously reported sensors in terms of selectivity, working concentration range, pH range, slope, and detection limit and comparable with regards to parameters such as lifetime, response time, and reproducibility.

Conclusion

Dendrites are unique synthetic macromolecules with a highly branched structure and cascade shape. Their interior has been

Table 4. Comparison of the Proposed Co^{2+}-Selective Electrode with the Reported Electrodes

		detection limit	slope		working concentration range	response time	
ref no.	ionophore	M	mV/decade of activity	pH range	M	s	real sample analysis
11	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacycloterradeca-4,11-dienediperchlorate	$8.0 \cdot 10^{-6}$	29.0	2.8−7.3	$1.0 \cdot 10^{-1}$ to $8.0 \cdot 10^{-6}$	20	not reported
13	benzosubstituted macrocyclic diamide	$6.0 \cdot 10^{-7}$	29.45 ± 0.5	3.0−8.0	$1.0 \cdot 10^{-2}$ to $2.0 \cdot 10^{-6}$	10	wastewater samples
19	5-((4-nitrophenyl)azo)-*N*-(2,4-dimethoxyphenyl)salicylaldimine	$8.0 \cdot 10^{-7}$	29.0 ± 1	3.5−6.0	$1.0 \cdot 10^{-2}$ to $9.0 \cdot 10^{-7}$	5−10	water samples
16	(2-mercapto-4-methylphenyl)-2-benzamido-3-phenylthiopropenolate	$1.0 \cdot 10^{-7}$	30.0 ± 1.0	5.0−8.0	$1.0 \cdot 10^{-2}$ to $4.0 \cdot 10^{-7}$	> 5	water samples
18	OXCCD	$9.0 \cdot 10^{-7}$	29.8	3.5−8.0	$1.0 \cdot 10^{-1}$ to $1.0 \cdot 10^{-6}$	> 25	water samples
12	dibenzopyridino-substituted macrocyclic diamide	$2.0 \cdot 10^{-7}$	29.1 ± 0.1	3.0−8.5	$1.0 \cdot 10^{-2}$ to $7.0 \cdot 10^{-7}$	10	wastewater samples
20	*N*,*N*-bis(salicylidene)-3,4-diaminotoluene	$5.0 \cdot 10^{-8}$	30 ± 0.2	2.0−9.0	$1.0 \cdot 10^{-1}$ to $7.9 \cdot 10^{-8}$	12	water
21	5-amino-3-methylisothiazole	$3.9 \cdot 10^{-7}$	29.5 ± 0.2	3.3−9.0	$1.0 \cdot 10^{-1}$ to $6.3 \cdot 10^{-7}$	12	water samples
15	2,3,4-pyridine-1,3,5,8,11,14-hexaazacyclohexadeca-2-ene	$8.5 \cdot 10^{-7}$	30.0	2.5−6.5	$1.0 \cdot 10^{-1}$ to $6.3 \cdot 10^{-6}$	15	wastewater of the electroplating industry
46	4-*tert*-butylthiacalix[4]arene	$3.0 \cdot 10^{-7}$	30.0 ± 0.5	2.5−6.0	$1.0 \cdot 10^{-1}$ to $5.3 \cdot 10^{-6}$	10	water and beer samples
this work	DAEP	$6.82 \cdot 10^{-8}$	30.5	2.5−10.0	$1.0 \cdot 10^{-1}$ to $6.58 \cdot 10^{-7}$	< 5	water and wastewater samples

shown to be capable of encapsulating various molecules. They can act as hosts for guest molecules capable of binding via noncovalent interactions such as van der Waals interaction or hydrogen bonding. Dendrites can be functionalized with various functional groups and hence allow the design of several novel applications, such as directional excitation energy transfer at the molecular level. In this work we demonstrated the applicability of the first generation of a new dendrite as an ionophore with a high ability for the adsorption of Co^{2+}.

The PVC-based membrane electrode with DOP as a solvent mediator (membrane no. 9) was the best among all of the membrane castings (nos. 1 to 11) prepared by using a polyamine ligand as a sensor material, DBP or DOP as a solvent mediator, and NaTPB as an anion excluder. The sensor exhibited good reproducibility over a period of 5 months. This electrode is superior to the existing electrodes with regard to the working concentration range, pH range, response time, and selectivity over a number of cations.

The response characteristics of the proposed PVC membrane electrode were compared with those of the best Co^{2+} ion-selective electrodes reported earlier (Table 4). It is apparent that the proposed electrode is superior to the existing electrodes with regard to working concentration range, pH range, and low detection limit.

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