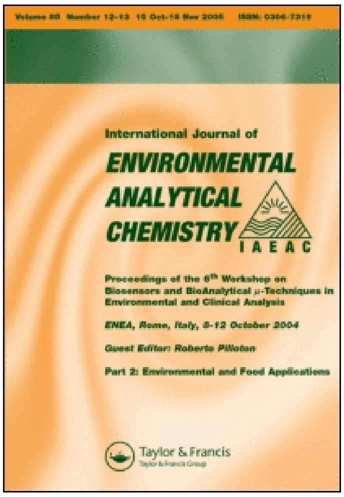

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Synthesis, characterisation and application of two new lariat crown ethers in construction of PVC membrane, coated wire and coated graphite electrodes: application to flow injection potentiometry

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Two lariat crown ethers, 7-(2-Hydroxy-5-methylbenzyl)-5,6,7,8,9,10-hexahydro-2*H*-benzo[*b*][1,4,7,10,13]pentadecine-3,11(4*H*,12*H*)dione, **L1** and, (7-(5-tert-buthyl-2-hydroxybenzyl)-5,6,7,8,9,10-hexahydro-2H-benzo[b][1,4,7,10,13]dioatriazacyclopentadecine-3,11 (4h, 12, H) dione, **L2** was synthesised, characterised and used as active components for fabrication of PVC membrane electrode (PME), coated graphite electrode (CGE) and coated wire electrodes (CWE) for sensing Co^{2+} ion. Potassium tetrakis(p-cholorophenyl) borate(KTpClPB) and o-nitrophenyloctyl ether (o-NPOE) were used as anion excluder and plasticiser, respectively, in a PVC matrix. The two lariat ethers were tested, **L1** has shown better electrode characteristics than the other. The electrodes exhibited linear Nernstian responses to Co^{2+} ion in the linear concentration range of 3.3×10^{-6}–1.9×10^{-2} M (for PME), 2.3×10^{-7}–7.9×10^{-2} M (for CWE), and 5.0×10^{-8}–1.2×10^{-2} M (for CGE). The CGE was used as a proper detection system in flow-injection potentiometry (FIP) with a linear Nernstian range of 2.3×10^{-7}–1.2×10^{-2} M. Over a pH range of 3.2 to 8.0, the limit of detection for PME, CWE, CGE, and CGE-FIP systems were found to be 1.2×10^{-6}, 2.5×10^{-7}, 3.5×10^{-8} and 1.0×10^{-7} M, respectively. The electrodes revealed fairly good discriminating ability towards Co^{2+} in comparison with a large number of alkali, alkaline earth, transition and heavy metal ions. The electrodes were found to be chemically inert, showing fast response time of <5 s, and could be used practically over a period of 1 month. CGE has also been used for measurement of Co^{2+} in binary mixtures.

Keywords: cobalt ion-selective electrodes; lariat crown ethers; PVC membrane; coated graphite and coated wire; potentiometry

1. Introduction

A variety of chemically, clinically or environmentally important analytes are now routinely monitored using ion-selective electrodes based on an impregnated polymeric membrane [1]. In recent decades many intensive studies on the design and synthesis of highly selective and sensitive ion carriers as sensory molecules for ion-selective electrodes have been reported. Recently, much interest has been focused on crown ethers. Crown ethers have been found

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as highly selective complexing agents for many metal ions. They can be applied in separation and determination of metal ions based on molecular recognition [2]. Generally, crown ether forms a stable complex with a metal ion that fits well in its cavity. Lariat crown ethers (LCEs) are designed to enhance the cation-binding ability of crown ethers through the co-operative ligation of additional donor atom(s) introduced in a side arm. Thus, LCEs often exhibit different cation-binding properties from the parent crown ethers [3]. Some of these compounds form selective and ideal complexes with some transition and heavy metal ions and were successfully used as neutral carriers in the ion-selective electrodes.

Pollution caused by heavy metals is a major environmental problem in the world. Mining and industrial operations discharge large quantities of effluents into water bodies. Thus, rivers, lakes and estuaries are polluted with heavy metals to different degrees. Cobalt is one of such type of metals. Cobalt is widespread in nature in meteorites, fresh waters, soils, plants and animals. Cobalt deficiency in animals may lead to retarded growth, loss of appetite and anaemia, and rapid recovery from these symptoms occurs upon feeding them with a cobalt supplementary diet. However, despite the urgent need for ion-selective electrodes for the potentiometric monitoring of Co^{2+} ions, there have been only limited reports on Co^{2+}-ion selective electrodes in literature [4–13]. Thus, the fast, simple and accurate determination of cobalt in different samples is very important. Moreover, most reported potentiometric cobalt sensors suffer from lack of stability and selectivity, limited concentration range, long response time, short lifetime, and significant interferences from many cations.

The advantages of flow injection potentiometry (FIP) by ion selective electrodes, such as low cost, simple instrumentation, rapid response, high sampling rate, wide linear response and high selectivity, have been well recognised over the last two decades [14–19]. Moreover, the transient nature of the signal in flow injection analysis (FIA) may help to overcome the effects of interfering ions if the electrode's response to these ions is slower than that to the target analyte [16], and the lifetime of electrodes may be extended, as the surface is predominantly exposed to carrier solution. However, selectivity and fabrication/packaging are still seen as two of the key aspects in the design of potentiometric sensors [20].

In recent years, we have used a variety of ligands as ion carriers in the preparation of new ion-selective electrodes [10,11,18,19,21–34]. In this paper, we report a highly selective, sensitive PVC membrane electrode for Co^{2+} ions based on two recently synthesised lariat crown ethers (**L1**, **L2**) as neutral carriers [35,36].

2. Experimental

2.1 *Reagents*

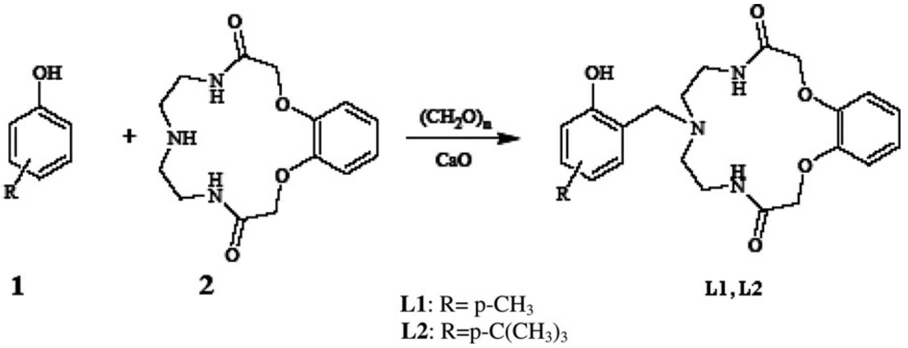
Reagent grade o-nitrophenyloctyl ether (o-NPOE), dimethylsebacate (DMS), diethylsebacate (DES), dibuthylphthalate (DBP), potassium tetrakis(p-cholorophenyl) borate (KTpClPB), tetrahydrofuran (THF) and powdered PVC were purchased from Merck and Fluka, respectively, used as received. Cobalt nitrate and the nitrate salts of other cations used were of the highest purity available (all from Merck) and used without any further purification except for vacuum-drying over P_2O_5. Triply distilled de-ionised water was used.

2.2 *General procedure for synthesising the two lariat ethers, L1 and L2*

Azacrown ether **2** (1 mmol) was synthesised during a convinent procedure [37], phenol (1.2 mmol), paraformaldehide (1.2 mmol), and CaO (1 g) were thoroughly mixed. The resulting fine powder was transferred to a round-bottom flask and stirred in an oil bath at 100°C for 20–30 min. After cooling, acetone was added to the mixture and CaO was removed by filteration. Evaporation of the solvent under reduced pressure gave the crude products, which were purified by flash column chromathography (eluent: *n*-hexane/EtOAc; 1/1) or recrystallised from EtOAc.

NMR spectra were recorded on a Bruker Avance DP spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. Infrared spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instruments at 70 or 20 ev. Melting points determined in open capillary tubes in a Büchi-535 circulating oil melting point apparatus. UV/Vis. spectra was obtained with an Ultrospec 3000 UV/Vis. spectrometer. Elemental analyses were performed at the National Oil Co. of Iran, Tehran Research Center. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. Column chromatography was carried out on short columns of silica gel 60 (70–230 mesh) in glass columns (2–3 cm diameter) using 15–30 gram of silica gel per one gram of crude mixture. Chemical materials were either prepared in our laboratories or were purchased from Fluka, Aldrich and Merck Companies. M.P., IR, 1H NMR, and UV data of the two lariate ethers are given below:

Lariat ether L1, 7-(2-Hydroxy-5-methylbenzyl)-5,6,7,8,9,10-hexahydro-2H-benzo[b][1,4,7,10,13]dioxatriazacyclopentadecine-3,11(4H,12H)dione, (Scheme 1) was obtained as a white powder in 85% yield, M.P. 206°C, IR (KBr): 3400(s), 3200(br), 2900(m), 2860(m), 2680(vs), 1662(vs), 1598(m), 1540(s), 1506(s), 1438(m), 1259(s), 1215(s), 1128(s), 1047(s), 815(s), 740(s) cm. 1H NMR ($CDCl_3$): δ 2.22(s, 3H), 2.75(t, 4H, $J = 5.3$ Hz), 3.54(t, 4H, $J = 5.3$ Hz), 3.73(s, 2H), 4.51(s, 4H), 6.64(d, 1H, $J = 8.0$ Hz), 6.87–7.07(m, 6H), 7.56(s, 2H), 8.14(s, 1H). 13C NMR ($CDCl_3$): δ 20.8, 36.2, 53.3, 56.0, 68.7, 114.9, 116.1, 122.4, 123.2, 129.5, 130.0, 131.0, 147.6, 154.0, 168.3. MS *m*/*z* (%): 415(M++2, 1.2), 414(M++1, 4.2), 413(M+, 10.0), 396(2.4), 341(16.5), 292(37.7), 225(41.9), 206(15.5), 180(12.3), 176(23.2), 162(27.5), 121(93.3), 91(85.4), 85(60.8), 69(60.0), 56(86.6), 43(100.0). Anal. Calcd. for $C_{22}H_{27}N_3O_5$ (413.467): C, 63.91; H, 6.58; N, 10.16. Found: C, 63.75; H, 6.43; N, 9.87. UV($CHCl_3$): $\lambda_{max}(\log \varepsilon)$244(3.04), and 271(3.33) nm.



Scheme 1.

Lariate ether L2, (7-(5-tert-buthyl-2-hydroxybenzyl)-5,6,7,8,9,10-hexahydro-2H-benzo[b][1,4,7,10,13]dioatriazacyclopentadecine-3,11(4H,12,H)dione (Scheme 1), was obtained as white powder in 75% yield. M.P. 214°C. IR (KBr): 3377(s), 3281(br), 2955(m), 2906(m), 1676(vs), 1597(m), 1539(s), 1506(s), 1439(m), 1346(s), 1263(s), 1225(m), 1128(s), 1051(s), 820(m), 725(s) cm^{-1}. 1H NMR ($CDCl_3$): δ 1.23(s, 9H), 2.74(t, 4H, $J = 5.3$ Hz), 3.52(t, 4H, $J = 5.3$ Hz), 3.73(s, 2H), 4.44(s, 4H), 6.68(d, 1H, $J = 8.4$ Hz), 6.84–7.01(m, 4H), 7.04(s, 1H), 7.11(d, 1H, $J = 8.4$ Hz), 7.62(s, 2H), 8.44(s, 1H). 13C NMR ($CDCl_3$): δ 31.5, 33.9, 35.7, 52.8, 54.4, 68.0, 114.1, 115.2, 121.4, 122.6, 125.8, 127.1, 142.5, 147.0, 153.6, 167.9. MS *m/z* (%): 456(M++1, 0.6), 455(M+, 2.8), 384(1.7), 383(6.7), 294(1.7), 293(3.9), 292(28.7), 225(30.9), 204(21.9), 163(48.9), 147(36.5), 119(37.1), 85(72.5), 69(71.3), 56(100). Anal. Calcd for $C_{25}H_{33}N_3O_5$ (455.547): C, 65.91; H, 7.30; N, 9.22. Found: C, 66.07; H, 7.41; N, 9.05. UV($CHCl_3$): $\lambda_{max}(\log \varepsilon)$245(2.96),267(3.23), and 282(3.19)nm.

2.3 *Electromotive force measurements*

All electromotive force (emf) measurements were carried out with the following cell assemblies:

Ag–AgCl|1.0×10^{-2} M $Co(NO_3)_2$|PVC membrane|test solution||Hg–Hg_2Cl_2, KCl (saturated), (for PME);
Spectroscopic grade graphite|PVC membrane|test solution||Hg–Hg_2Cl_2, KCl (saturated), (for CGE and FIP-CGE);
Pt-wire|PVC membrane|test solution||Hg–Hg_2Cl_2, KCl (saturated), (for CWE).

A Hioki multimeter was used for the potential measurements at 25.1 ± 0.1°C. The emf observations were made relative to a double-junction saturated calomel electrode (Metrohm) with the chamber filled with an ammonium nitrate solution. Activities were calculated according to the Debye–Hückel procedure.

3. Results and discussion

3.1 *Preliminary experiment*

In preliminary experiments, spectra of **L1** and **L2** were recorded upon gradual addition of cobalt nitrate solutions in acetonitrile (Figure 1A and B). As it is shown, a stronger interaction of **L1** through complexation with Co^{2+} was observed showing strong interaction of the ligand with cobalt ion in acetonitrile.

Meanwhile, complexation of **L1**, and **L2** with some potential metal ions including Cd^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}, Ag^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Mg^{2+} and Pb^{2+} ions were investigated conductometrically [38,39] in acetonitrile solution at 25.00 ± 0.01°C. The stability constants of the resulting complexes were evaluated from molar conductance-mole ratio data using a non-linear program written in MATLAB, and the formation constant results are summarised in Table 1. It is observed from Figure 1C and D, in all cases, addition of the neutral ligands to the cation solution (1.0×10^{-4} M) caused a rather large and continuous increase in the conductivity of solution, indicating the higher mobility of the complexed cations compared to the solvated ones [38]. The increased conductivity of the metal nitrates in acetonitrile solution upon addition of the ligand can also be related to some extent to the dissociation of some ion-paired species usually present in acetonitrile as

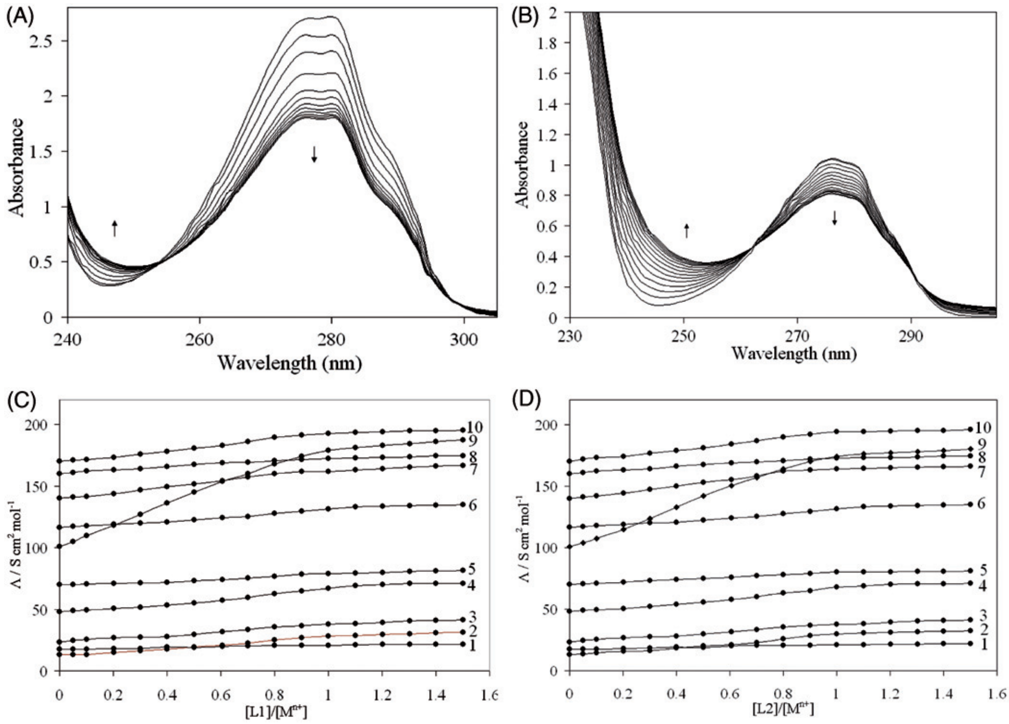


Figure 1. Spectrophotometric (Absorbance) and conductometric (Λ) studies of **L1** and **L2** in acetonitrile: **A** and **B** represent spectra of **L1**, and **L2** upon addition of Co^{2+} ion in acetonitrile solution, respectively, the arrows indicate increase and decrease of absorbance, **C** and **D** represent molar conductance-mole ratio plots of **L1** and **L2**, respectively, **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, represent the plots for Al^{3+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, and Ag^{+}, respectively.

Table 1. Formation constant measurements ($\log K_f$) for complexation of **L1** and **L2** with the different metal ions in acetonitril solution.

	$\log K_f(\pm 0.1)$			$\log K_f(\pm 0.1)$	
M^{n+}	**L1**	**L2**	M^{n+}	**L1**	**L2**
Co^{2+}	4.9	4.6	Hg^{2+}	1.2	1.6
Cu^{2+}	1.4	1.6	Pb^{2+}	<1	<1
Ag^{+}	1.1	1.3	Al^{3+}	<1	<1
Cd^{2+}	1.4	1.5	Ni^{2+}	1.3	1.7
Mn^{2+}	1.3	1.4	Mg^{2+}	1.1	1.2

a solvent of intermediate dielectric constant and relatively low solvating ability, as a result of the metal ion complexation with **L1** or **L2** [39]. It is interesting to note that, in the case of Co^{2+} ion, the slope of the corresponding molar conductance-[**L1** and/or **L2**]/[Co^{2+}] mole ratio plot for both of the ligand changed sharply at the point where the ligand-to-cation mole ratio was about 1, indicating the formation of a stable 1 : 1 complex in solution (Table 1). However, in the case of other metal ions tested, the relatively large increase in solution conductivity upon addition of **L1** and/or **L2** did not show a significant tendency of levelling off even at mole ratios greater than 3, emphasising the formation of weaker complexes.

3.2 *Electrode preparation*

The general procedure to prepare the PVC membrane was to mix thoroughly 65.3 mg of plasticiser o-NPOE, 32.7 mg of powdered PVC, 1.0 mg of ionophore (**L1**), and 1.0 mg of additive KTpClPB in a glass dish of 2 cm diameter. The mixture was then completely dissolved in 4 mL of THF. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm i.d. on tip) was dipped into the mixture for 2 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 6 h. The tube was then filled with an internal solution (1.0×10^{-2} M Co^{2+}). The electrode was finally conditioned for 24 h in a 1.0×10^{-2} M Co^{2+} solution. A silver/silver chloride electrode was used as an internal reference electrode. To prepare the coated graphite electrodes, spectroscopic grade graphite rods 10 mm long and 3 mm diameter were used. A shielded copper wire was glued at one end of the graphite rod and the electrode was sealed into the end of a PVC tube of about the same diameter with 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 stabilise overnight. The electrode was finally conditioned by soaking in a 1.0×10^{-2} M cobalt nitrate solution for 48 h. A spectroscopic grade Pt-wire of 20 mm length and 2 mm diameter was mounted and glued at the end of a PVC tube with the same diameter and a shielded copper wire was glued at the end of the Pt-wire. The working surface of the wire was polished with an appropriate abrasive, then with alumina slurries on a polishing cloth, sonicated in distilled water and dried in air. The polished wire was dipped into the membrane mentioned above and the solvent was evaporated. A membrane was formed at the surface of the Pt-wire and the electrode was allowed to be dried for 6 h and then conditioned in a 1.0×10^{-2} M cobalt nitrate solution for 36 h.

3.3 *Optimisation of potentiometric response of the PME, CWE, and CGE*

Several parameters were investigated in order to evaluate the performance of the cobalt ion-selective electrodes based on ionophores **L1** and **L2** (using CGE system) in terms of membrane composition, calibration curve slopes, reproducibility, linear concentration range, limit of detection, response time, selectivity, and sample analysis. The performance characteristics of the ionophore-incorporated PVC membrane may also be dependent on electrode composition and the nature of the solution of which the electrodes are composed [22–33,40–47]. Thus, different aspects of composition of membranes based on **L1** and **L2** for Co^{2+} ion were optimised and the results were summarised in Table 2. Besides the critical role of the nature of the ionophore in preparing PVC membrane electrodes, it is well understood from Figure 2, the incorporation of **L1** in the optimised polymeric membrane give pronounced selectivity toward Co^{2+} ion compared to the other metal ions.

Table 2. Optimisation of membrane components for membrane coated graphite electrode.

Electrode no.	Components (%) Plasticiser	PVC	Ionophore	Additive (KTpClPB)	Slope (mV/decade of activity)	Linear range (M)
1	66.0(o–NPOE)	33.0	1.0(**L1**)	Without	15.0	3.0×10^{-5} to 1.0×10^{-2}
2	65.7(o–NPOE)	32.8	1.0(**L1**)	0.5	17.1	3.3×10^{-7} to 3.0×1^{-2}
3	65.3(o–NPOE)	32.7	1.0(**L1**)	1.0	29.4	5.0×10^{-8} to 1.2×10^{-2}
4	65.0(o–NPOE)	32.5	1.0(**L1**)	1.5	21.3	3.3×10^{-6} to 3.0×10^{-2}
5	64.7(o–NPOE)	32.3	1.0(**L1**)	2.0	19.7	3.3×10^{-6} to 3.0×10^{-2}
6	66.0(o–NPOE)	33.0	Without	1.0	2.80	5.1×10^{-4} to 3.0×10^{-2}
7	65.7(o–NPOE)	32.8	0.5(**L1**)	1.0	12.3	3.3×10^{-6} to 3.0×10^{-2}
8	65.0(o–NPOE)	32.5	1.5(**L1**)	1.0	25.0	2.7×10^{-6} to 7.0×10^{-3}
9	64.7(o–NPOE)	32.3	2.0(**L1**)	1.0	24.3	3.3×10^{-6} to 3.0×10^{-2}
10	65.3(DBP)	32.7	1.0(**L1**)	1.0	11.8	2.0×10^{-5} to 7.0×10^{-3}
11	65.3(DMS)	32.7	1.0(**L1**)	1.0	21.9	3.3×10^{-5} to 1.7×10^{-2}
12	65.3(DES)	32.7	1.0(**L1**)	1.0	22.6	1.0×10^{-6} to 3.0×10^{-2}
13	66.0(o–NPOE)	33.0	1.0(**L2**)	Without	10.5	3.0×10^{-5} to 1.0×10^{-2}
14	65.7(o–NPOE)	32.8	1.0(**L2**)	0.5	14.6	3.3×10^{-6} to 6.9×10^{-2}
15	65.3(o–NPOE)	32.7	1.0(**L2**)	1.0	22.4	7.9×10^{-7} to 1.2×10^{-2}
16	65.0(o–NPOE)	32.5	1.0(**L2**)	1.5	24.7	3.3×10^{-6} to 1.0×10^{-2}
17	64.7(o–NPOE)	32.3	0.5(**L2**)	2.0	10.5	2.3×10^{-6} to 3.0×10^{-2}
18	65.3(o–NPOE)	32.7	1.0(**L2**)	1.0	11.7	3.3×10^{-6} to 1.0×10^{-2}
19	65.0(o–NPOE)	32.5	1.5(**L2**)	1.0	22.3	1.2×10^{-6} to 1.2×10^{-3}
20	64.7(o–NPOE)	32.3	2.0(**L2**)	1.0	16.4	3.3×10^{-6} to 3.0×10^{-2}
21	65.3(DBP)	32.7	1.0(**L2**)	1.0	8.90	3.3×10^{-5} to 1.2×10^{-4}
22	65.3(DMS)	32.7	1.0(**L2**)	1.0	15.5	3.3×10^{-5} to 7.9×10^{-3}
23	65.3(DES)	32.7	1.0(**L2**)	1.0	19.3	3.3×10^{-6} to 1.9×10^{-2}

The potentiometric response of membrane ion-selective electrodes based on neutral ionophores is greatly influenced by polarity of the membrane medium, which is defined by dielectric constants of the major membrane components [48–51]. The influence of the nature of the plasticiser on the electrode response was studied. Four kinds of plasticisers with different dielectric constants, namely DMS, DES, DBP and o-NPOE, were checked. As shown in Table 2, o-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 plasticiser affects not only the dielectric constant of membrane phase but also the mobility of ionophore molecules and the state of the ligands [48,50,51]. As expected, the amount of ionophore was found to affect the PVC membrane sensitivity (nos. 6–9 and 17–20). The calibration slope increased with increasing **L1** content until a value of 1% was reached. However, further increase in the amount of ionophore resulted in a diminished response slope of the electrode, most probably due to some inhomogeneity and possible saturation of the membrane [52]. It is well known that incorporation of lipophilic additives can significantly influence the performance characteristics of a membrane sensor [34,53–65]. The presence of the lipophilic additive not only improves the response characteristics and selectivity [48,49], but also may catalyse the exchange kinetics at the sample-membrane interface [63]. In this work, we examined the influence KTpClPB, as a suitable lipophilic additive on the response characteristics of the proposed membrane coated graphite

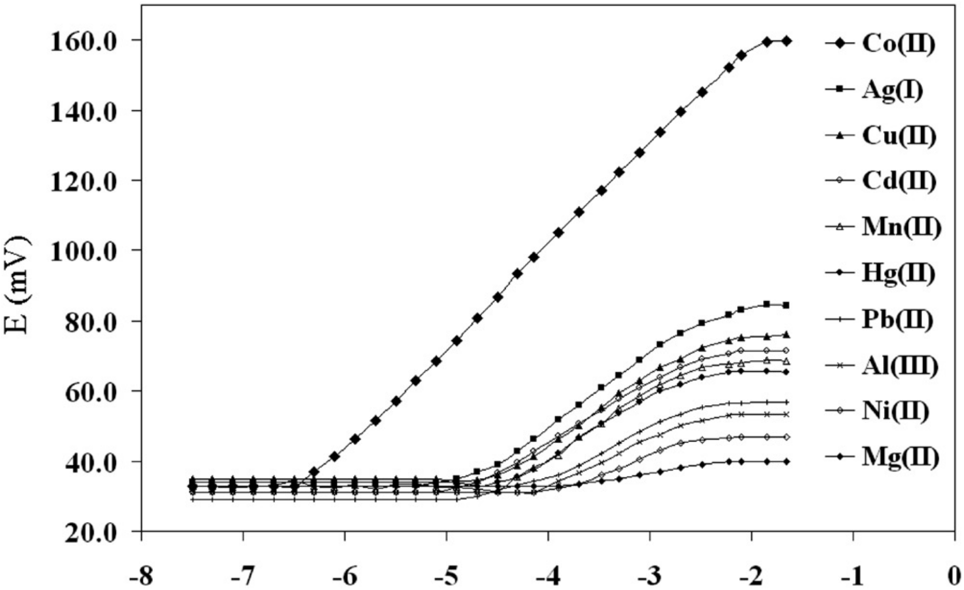


Figure 2. Response of different potential cation to the PME based on **L1.**

electrode (CGE). The data given in Table 1 indicate that, in the absence of a proper additive, the sensitivity of the PVC membrane based on **L1** and **L2** is quite low (nos. 1 and 13), with a slope of 15 and 10.5 mV/decade, respectively. However, the presence of either 1% KTpClPB (no. 3), will improve the sensitivity of the PME. Besides, electrode no. 15 with **L2**, as ionophore and the same additive content, gives lower slope and shorter linear range. As is obvious from Table 2, electrode no. 3 with a PVC/o-NPOE/KTpClPB/**L1** mass per cent ratio of 32.7 : 65.3 : 1 : 1 resulted in a Nernstian behaviour of the membrane electrode over a wide concentration range. Hence the composition of the electrode no. 3 was selected as an optimal composition for construction of PME, CWE and CGE through the next studies in the current work.

The practical response time required for the Co^{2+} ion selective electrodes to reach a potential within ±1 mV of the final equilibrium value after successive immersion of each electrode in a series of Co^{2+} ion solutions, each having a 10-fold difference in concentration, was measured. The standard deviation of 10 replicate measurements was ±0.5 mV. The dynamic response of the CGE was found to be <5 s over the entire linear concentration range. The response time for the PME and CWE system were about 15 and 10 s, respectively. This is most probably due to the fast exchange kinetics of complexation decomplexation of the ligand (**L1**) with Co^{2+} ion at the test solution and membrane interface. So the CGE system was applied in the FIP as a detection system, as it needs a response time as fast as possible to work.

The influence of pH of the test solution on the potential response of the CGE at 5.0×10^{-4} M cobalt nitrate solution was tested in the pH range of 2–11, and the results are shown in Figure 3. As seen, the potential remained constant over the pH range of 3.2 to 8, beyond which the potential changed considerably. At low pH, the potential increased, indicating that the membrane sensor responds to hydrogen ions, while at higher pH values, a large decrease in potential could be due to the formation of some hydroxyl complexes of

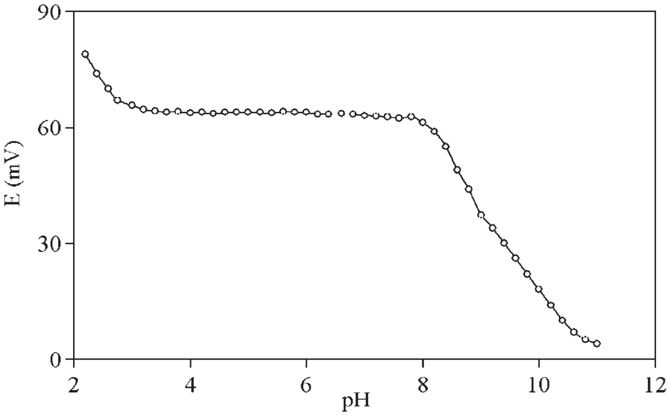


Figure 3. Effect of pH of test solution on response of the Co^{2+} ion-selective electrode based on **L1** in a 5.0×10^{-4} M cobalt nitrate solution.

Co^{2+} ion in the solution. It should be noted that, at lower Co^{2+} concentration (say 1.0×10^{-5} M), the optimum working pH can be extended to about 9.3.

The stability and lifetime of the Co^{2+} ion-CGE were tested over a period of 1 month. During this period, the electrode was in use over the extended period of time (3 days per week). A slight gradual decrease in the slope, from 29.4 to 26.1 ± 0.1 mV/decade of activity, was observed.

The influence of several common cationic species on the potential response of the Co^{2+} ion-CGE were investigated by examining selectivity coefficients of the electrodes for the different cationic species. In this work, the selectivity coefficients of the electrodes were evaluated by using the fixed interference method (FIM) [66]. In the FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} M) and varying amount of Co^{2+} ions. The selectivity coefficient is calculated from the following equation:

$$\log K^{pot}_{co,M} = \frac{a_{Co^{2+}}}{a_B^{z_A/z_B}}$$

where $a_{Co^{2+}}$ is the activity of the primary ion (Co^{2+}) at the lower detection limit in the presence of interfering ion B with activity of a_B, having z_A and z_B their respective charges.

The resulting $\log k^{pot}_{Co,M}$ values are summarised in Table 3. It is seen that, in all cases, the selectivity coefficients are in the order of 10^{-2} and lower, indicating negligible interference in the performance of the membrane sensor assemblies. Meanwhile, the results obtained in the current study are compared with that of the best Co^{2+} ion selective electrodes reported earlier [9–12,67–71]. The results are summarised in Table 4.

3.4 *Flow-injection potentiometry with the CGE*

In the next step, the proposed Co^{2+}-selective CGE was successfully used as a suitable indicator electrode in the flow injection system shown in Figure 4. In order to achieve the best FIP response, several flow injection parameters including tubing length, flow rate,

Table 3. Selectivity coefficients measurements ($\log K^{Pot}_{Co,M}$) based on FIM, for the three kinds of cobalt selective electrode systems.

	$\log K^{Pot}_{Co,M}$		
M^{n+}	PME	CWE	CGE
Ni^{2+}	−2.6	−3.1	−2.6
Cu^{2+}	−1.8	−2.6	−2.7
Ag^{+}	−2.2	−2.1	−3.2
Hg^{2+}	−2.7	−2.8	−2.9
Cd^{2+}	−3.1	−3.3	−3.3
La^{3+}	−4.7	−4.6	<−5
Pb^{2+}	−2.9	−3.1	−3.3
Fe^{3+}	−3.5	−3.7	−3.8
Zn^{2+}	−3.2	−3.3	−3.8
Al^{3+}	−3.5	−3.7	−4.0
Ce^{3+}	−3.9	−3.7	<−5
Na^{+}	<−5	<−5	<−5
Be^{2+}	<−5	<−5	<−5
Ba^{2+}	<−5	<−5	<−5

Table 4. Comparison of the present study with the previous works.

Response time(s)	Linear range (pCo)	Selectivity coefficient measurements ($\log K^{pot}_{Co,M}$)	Reference
20	5.09–1.00	Ni^{2+} (−1.29), Fe^{3+} (−1.0), Na^{+} (−0.23)	[9]
10	5.70–2.00	Ni^{2+} (−1.09)	[10]
10	6.15–2.00	Cu^{2+} (−2.250, Hg^{2+} (−2.23), Ag^{+} (−2.16), Cd^{2+} (−2.6)	[11]
>5	6.40–2.00	Cu^{2+} (−1.83), Ag^{+} (−1.76), Cd^{2+} (−1.98)	[12]
>25	6.00–1.00	Ni^{2+} (−1.15), Pb^{2+} (−1.05)	[13]
12	7.15–1.00	Ni^{2+} (−1.60), Cu^{2+} (−0.38), Hg^{2+} (−1.23)	[67]
12	6.20–1.00	Ni^{2+} (−0.25), Cu^{2+} (−1.16), Ag^{+} (−2.00)	[68]
15	5.20–1.00	Ni^{2+} (−1.22), Cu^{2+} (−1.16) Hg^{2+} (−2.03) Ag^{+} (−2.00)	[69]
15–20	5.20–1.00	Ni^{2+} (−2.22), Cu^{2+} (−1.20), Zn^{2+} (−2.64), Hg^{2+} (−2.04), Ag^{+} (−3.00), Na^{+} (−2.10), Pb^{2+} (−2.70), Cd^{2+} (−2.37), Al^{3+} (−3.65), Mg^{2+} (−2.2), Ba^{2+} (−2.7)	[70]
10	5.28–1.00	Ni^{2+} (−2.16), Cu^{2+} (−2.35), Zn^{2+} (−2.14), Hg^{2+} (−2.16), Ag^{+} (−2.31), Na^{+} (−2.79), Pb^{2+} (−2.18)	[71]
<5	7.30–1.90	Ni^{2+} (−2.60), Cu^{2+} (−2.70), Zn^{2+} (−3.80), Hg^{2+} (−2.90), Ag^{+} (−3.20), Fe^{3+} (−3.80), Cd^{2+} (−3.30) Pb^{2+} (−3.30), Al^{3+} (−4.00) Ce^{3+}, La^{3+}, Be^{2+}, Ba^{2+}, and Na^{+}, less than −5	This work

sample volume, composition of carrier solution and sampling rate were thoroughly investigated.

The length of tubing from injection valve port to cell was made as small as practical to minimise dispersion and dilution. For the proposed system, 10 cm was selected for tubing

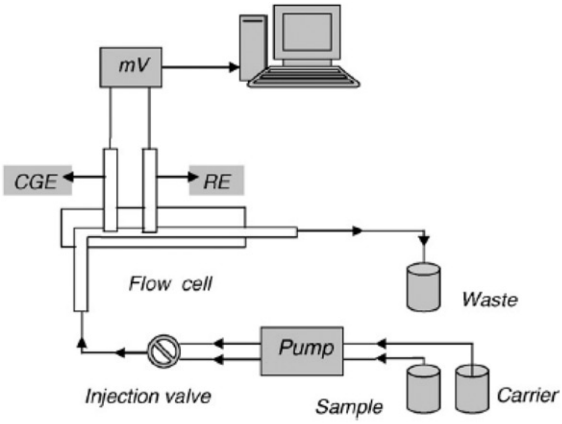


Figure 4. Manifold of the flow injection potentiometric system.

length with respect to peak heights of the FIP system. The dependency of the peak height and peak width (and time to recover the base line) with flow rate was studied by evaluation of the electrode response to a 1.0×10^{-2} M solution of cobalt ion. As the flow rate increased, the peaks became narrower and increased in height to a nearly plateau at a flow rate of 30 mL min^{-1}. However, the peak width increased considerably at flow rates higher than 30 mL min^{-1}. This large flow rate allows increase of sampling rate and decrease of the total time of analysis. In general, the peak height increases with increasing sample volume, although the effect was less marked at higher concentrations [72,73]. A flow rate of 30 mL min^{-1} was selected as an optimum value for further studies. In the proposed flow system, a 1.0×10^{-3} M HNO_3 solution was used as a carrier solution. For this system, different sample volumes from 100 to 600 µL were studied; the peak height reached nearly 100% of steady-state as 200 µL injected. Thus, this sample volume was selected as an optimum amount.

In the analytical flow systems, the sampling rate (sample throughput) is an important feature representing the capability of the system in online analysis. The proposed FIP system revealed sampling rates higher than 100 injections per hour.

In Figure 5 the different electrode system calibration curves are compared. As seen from this figure, the electrodes exhibited linear Nernstian responses to Co^{2+} ion in the concentration range of 3.3×10^{-6}–1.9×10^{-2} M (for PME), 2.3×10^{-7}–7.9×10^{-2} M (for CWE), and 5.0×10^{-8}–1.2×10^{-2} M (for CGE). The CGE was used as a proper detection system in flow-injection potentiometry (CGE-FIP) with a linear Nernstian range of 2.3×10^{-7}–1.2×10^{-2} M. Over a pH range of 3.2 to 8.0, the limit of detection for PME, CWE, CGE, and CGE-FIP systems were found to be 1.2×10^{-6}, 2.5×10^{-7}, 3.5×10^{-8} and 1.3×10^{-7} M, respectively. The CGE-FIP system obtained under optimal experimental conditions was used to evaluate repeatability of the FIP system. As seen from Figure 6, the CGE-FIP system is quite sensitive and applicable to the Co^{2+} ion concentration in the range of 1.0×10^{-7}–1.0×10^{-2} M Co^{2+} ion (A–F). The repeatability of the electrode response, as evaluated from the peak height relative standard deviation (%RSD) for 6 replicate injections of a solution, for example, 1.0×10^{-3} M Co^{2+} ion solution, was 1.0%. The standard deviation (pooled precision data) for 33 samples was estimated to be about 1.7 mV (Figure 6).

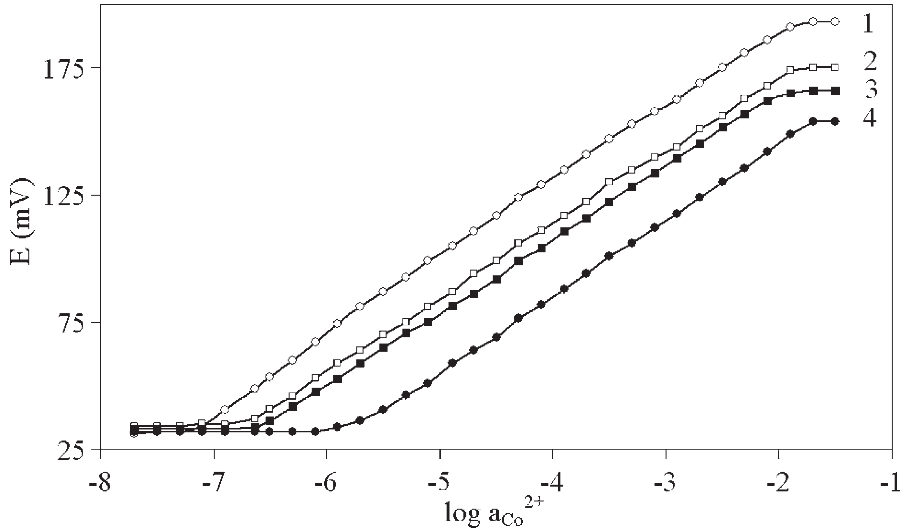


Figure 5. Calibration curves for different Co^{2+} ion-selective electrode systems, CGE, **1**; FIP-CGE, **2**; CWE, **3**; PME, **4**; based on **L1**.

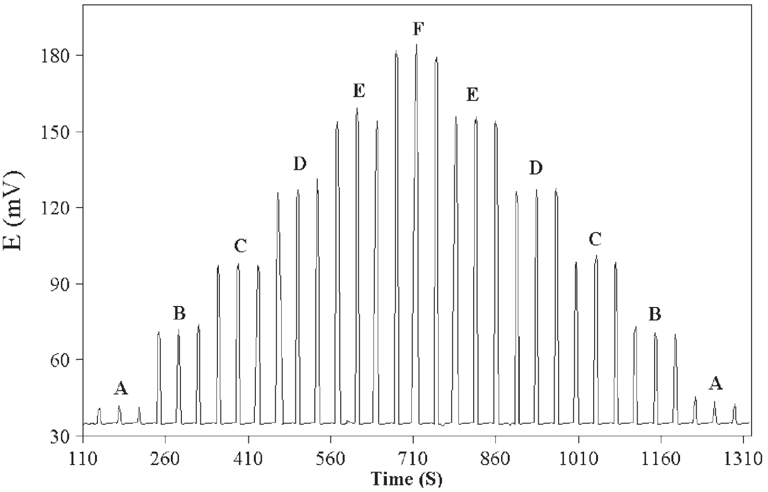


Figure 6. Repeatability of membrane coated graphite cobalt ion selective electrode using a flow system, **A–F** are 1.0×10^{-7} M, 1.0×10^{-6} M, 1.0×10^{-5} M, 1.0×10^{-4} M, 1.0×10^{-3} M, and 1.0×10^{-2} M cobalt nitrate solutions, respectively.

3.5 *Applications*

The proposed CGE-FIP system was used under laboratory conditions. The method was used for direct determination of Co^{2+} in synthetic binary mixtures of tap water samples. The results are summarised in Table 5. The three membrane electrodes, i.e. PME, CWE and CGE, were used for the complexometric titration of a 2.0×10^{-3} M of Co^{2+} ion solution with a 1.0×10^{-2} M EDTA (Figure 7). As seen from the figure, CGE shows the sharpest end point compared with the CWE and PME.

Table 5. Measurement of Co^{2+} ion concentration in binary mixtures.

Sample no.	Added ion concentration in tap water ($mg\,dm^{-3}$)	Co^{2+} added in tap water ($mg\,dm^{-3}$)	Co^{2+} as determined with ICP–AES	Co^{2+} as determined with Co^{2+}–CGE
1	10.0 (Cu^{2+})	7.00	7.16	7.23
2	10.0 (Hg^{2+})	11.0	11.3	11.4
3	10.0 (Pb^{2+})	10.0	9.71	10.6
4	10.0 (Cd^{2+})	13.0	10.5	11.1
5	10.0 (Ag^{+})	9.00	11.1	10.3

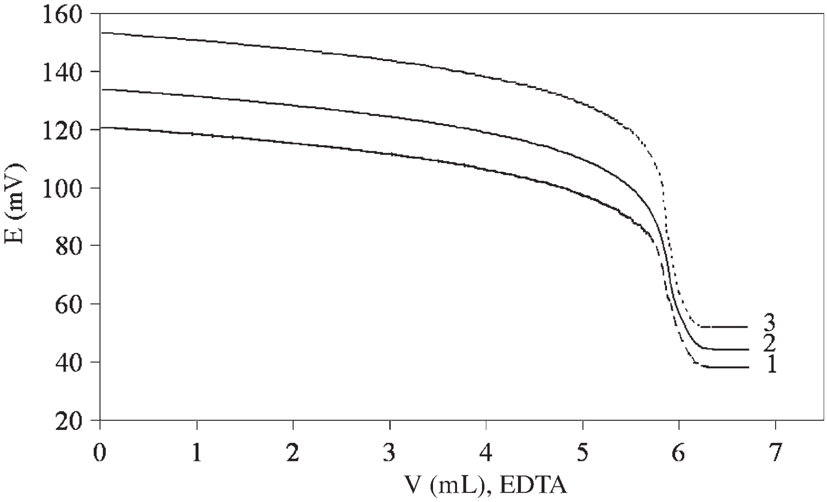


Figure 7. Titration of 30 mL Co^{2+} 2.0×10^{-3} M solution with EDTA 1.0×10^{-2} M solution using polymeric membrane electrode, **1** membrane coated wire electrode, **2** and coated graphite electrode, **3** as indicator electrodes.

4. Conclusion

Two lariat crown ethers, **L1** and **L2**, were synthesised, characterised and optimised to construct three kinds of potentiometric sensors (PME, CWE and CGE). Incorporation of **L1** in the membrane mixtures resulted in a wider linear range and much lower detection limit than in the case where **L2** was used, because of poorer solubility of L2 in the membrane mixtures.

CGE has shown the fastest response time, so it was used in the FIP system. Several important FIP system parameters have been optimised; the FIP system can be used under laboratory conditions, and it is stable and fast enough to analyse more than 33 samples in a short time with SD as small as 1.7 mV. The CGE sensor was successfully used in direct determination of cobalt ion in binary mixtures of some heavy metal ions. The potentiometric sensors were applied in the titration of cobalt nitrate solutions as well.

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