



Lead-selective poly(vinyl chloride) electrodes based on some synthesized benzo-substituted macrocyclic diamides

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ABSTRACT

A series of recently synthesized benzo- and pyridine-substituted macrocyclic diamides were studied to characterize their abilities as lead ion carriers in PVC membrane electrodes. The electrode based on 3,15,21-triaza-4,5;13,14-dibenzo-6,9,12-trioxabicycloheneicosa-1,17,19-triene-2,16-dione exhibits a Nernstian response for Pb²⁺ ions over a wide concentration range (1.3×10^{-2} to 3.6×10^{-6} mol L⁻¹) with a limit of detection of 2.0×10^{-6} mol L⁻¹ (0.4 ppm). The response time of the sensor is ~16 s, and the membrane can be used for more than two months without observing any deviation. The electrode revealed comparatively good selectivities with respect to many cations including alkali earth, transition and heavy metal ions. The proposed sensor could be used in pH range of 3.7–6.5. It was used as an indicator electrode in potentiometric titration of chromate ions with a lead ion solution.

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1. Introduction

In recent years, the importance of controlling the level of environmental pollutant in natural waterways, portable water and soils has increased interest in the development of chemical sensors for heavy metal ions. Ion-selective electrodes are studied because they permit the potentiometric measurement of the activity of a given ion in the presence of other ions. It also offers interesting advantages such as fast response, high selectivity, sensitivity, good precision, simplicity, low cost and wide linearity range. These characteristics have inevitably led to sensors for ionic species [1]. Specific metal–ligand interactions are among the most important of potentiometric sensors [2]. Such interactions have been used in the development of cation- and anion-selective electrodes based on different ionophores.

Due to increased industrial use of lead and its serious hazardous effect to human health [3], the electrochemical properties and preparation of lead ion-selective membrane electrodes have been extensively studied [4–21]. Because macrocyclic ligands can form selective and stable complexes with metal ions of compatible dimensions [22,23], and can potentially be applied to their selective separation and determination [1,24,25] continuous interest has been focused on the design and synthesis of new functional-

ized macrocycles for specific application [26]. Several macrocyclic diamides prepared from salicylaldehyde derivatives and appropriate diamino compounds [27] have been reported to have successful use as ion carriers in the construction of PVC-based ion-selective electrodes for Ag⁺ [28] Ca²⁺ [29], Cs⁺ [30] and Sr²⁺ ions [31].

In this work we report PVC membrane sensors for lead ion based on five recently synthesized benzo-substituted macrocyclic diamides (Fig. 1), which exhibited significantly high selectivity to Pb²⁺ ion over alkali, alkaline earth, and several transition metal ions.

2. Experimental

2.1. Reagents

Reagent-grade dimethyl sebacate (DMS), tetrahydrofuran (THF), potassium perchlorotetraphenyl borate (KpCITPB) and high relative molecular weight PVC were purchased from Fluka Chemical Company (Buchs, Switzerland) and used as received. Reagent-grade nitrate salts of all cations used from Merck Chemical Company (Darmstadt, Germany) were of the highest purity available and used without any further purification except for vacuum drying over P₂O₅. Triply distilled deionized water was used throughout. Macrocyclic diamides L1–L5 were synthesized and purified as described before [32]. Purity of the macrocyclic diamides was carefully checked by NMR, IR, and GC/MS methods. Structures of the macrocyclic diamides derivatives used are given in Fig. 1.

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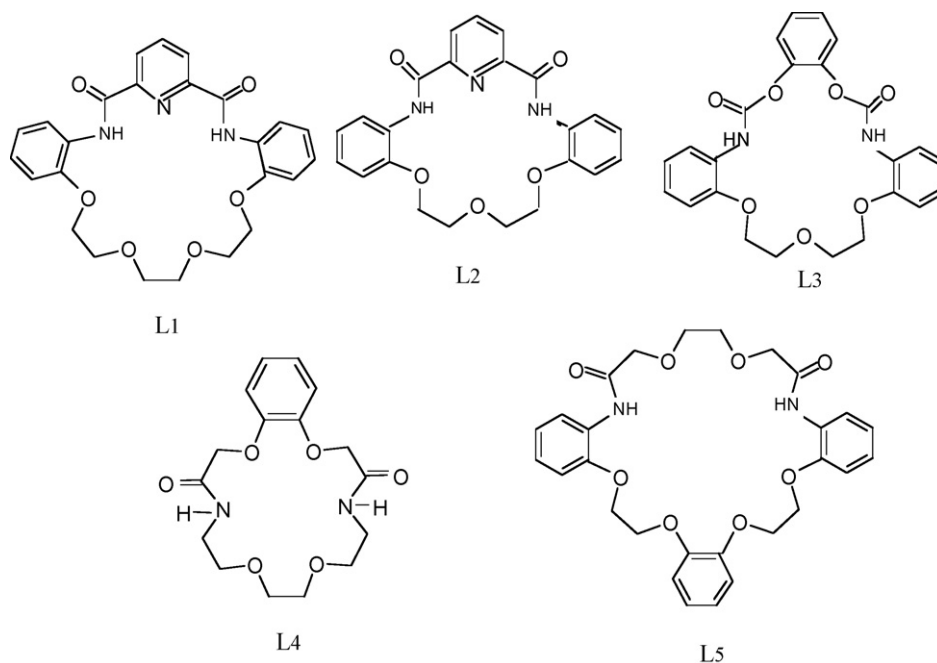


Fig. 1. Structures of ion carriers.

2.2. Electrode preparation

The general procedure to prepare the PVC membrane was mixed thoroughly 61.4 mg of plasticizer DMS, 30 mg of powdered PVC and 7 mg of ionophore and 1.6 mg of KpCITPB in 5 mL of 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 (4–5 mm diameter at the top) was dipped into the oily mixture for about 10 s so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and at room temperature for about 1 h. The tube was then filled with internal filling solution ($1.5 \times 10^{-2} \text{ mol L}^{-1}$ lead nitrate). The electrode was finally conditioned for 20 h by soaking in a $1.0 \times 10^{-3} \text{ mol L}^{-1}$ solution of $\text{Pb}(\text{NO}_3)_2$. A silver/silver chloride electrode was used as an internal reference electrode.

2.3. EMF measurements

All EMF measurements were carried out the following assembly: $\text{Ag}-\text{AgCl} | 3.0 \text{ mol L}^{-1} \text{ KCl} | \text{internal solution}, 0.1 \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2 | \text{PVC membrane} | \text{test solution} | \text{Ag}-\text{AgCl}, \text{KCl} (0.1 \text{ mol L}^{-1})$.

A Metrohm ion analyzer pH/mV meter was used for the potential measurements at $25.0 \pm 0.1 \text{ }^\circ\text{C}$. Activities were calculated according to Debye–Hückel procedure [33].

3. Results and discussion

The selectivity of ordinary crown ethers for alkaline earth metal ions is much lower than that for alkali cations [23,34]. However, increased selectivity toward alkaline earth cations were observed with some polyoxalactones [35]. Amide substitution in the cavity of benzocrown ethers may not only contribute to their cation selectivity toward some alkaline earth and transition metal ions but also allow the macrocycles to have properties more closely resembling those of naturally occurring ionophores [36]. The enhanced selectivity behavior of macrocyclic diamides L1–L5 as well as their water insolubility led us to examine their abilities as potential ion carriers in the PVC membrane sensors selective to Pb^{2+} ions.

As described by the HSAB concept, a so-called “soft” acid such as a transition metal ion and a nitrogen atom as a “soft” base often form a strong coordination bond [37]. For this reason, nitrogen atom-containing molecules often form a stable complex with a transition metal ion. In addition, a reversible potentiometric response to the metal ion is needed for an ion-selective electrode. Thus, in the case where the crown ethers are used as ionophores in the preparation of ion-selective electrodes, the number and position of donor atoms and the ring size of ligand molecule must be carefully considered in the design of the ionophore chemical structure.

3.1. Complexation of macrocyclic diamides with different cations in dimethylsulfoxide solutions

In preliminary experiments, complexation of some alkali, alkaline earth and heavy metal ions with macrocyclic diamides L1–L5 were studied in dimethylsulfoxide solution by means of a competitive spectrophotometric technique using murexide as a metal ion indicator. It was found that, in all cases, the lead complexes were more stable than other cations used. The complex formation constant, K_f , of metal ion–murexide (as colored ligand) and metal ion–ionophore (L1–L5, as buffer ligand) were determined by absorbance measurements at λ_{max} of the metal ion–murexide complex in DMSO solutions in which constant concentrations of both ligands were titrated with a concentrated metal ion solution in DMSO. The results revealed that the ligand L2 forms a relatively more stable complex with Pb^{2+} ion than other macrocyclic diamides L1 and L3–L5.

3.2. Effect of ligand structure on electrode potential

To investigate the suitability of the purified macrocyclic diamides L1–L5 as lead ion carriers in the PVC membranes, five different membrane electrodes (with the same composition) with these ionophores were prepared and their potential responses were obtained (Fig. 2). As can be seen, under similar experimental conditions, the efficiency of the macrocyclic diamides as Pb^{2+} carrier in the membrane decreases in the order $\text{L2} > \text{L1} \sim \text{L3} > \text{L4} > \text{L5}$.

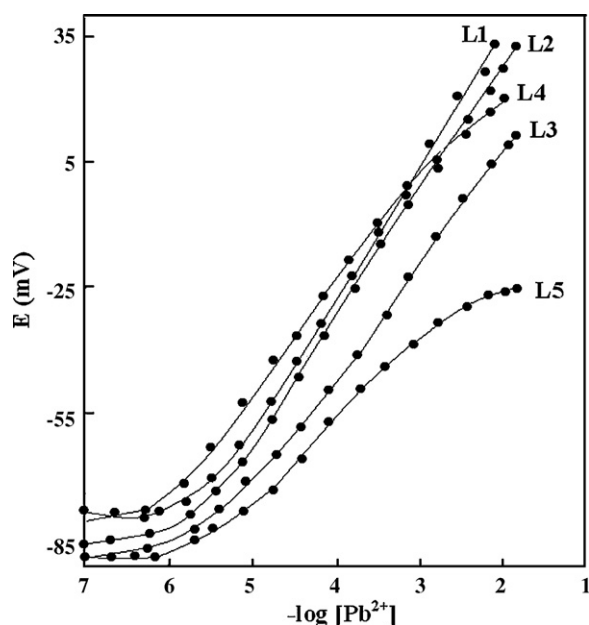


Fig. 2. Potentiometric response of the lead ion-selective electrodes based on different macrocyclic diamides L1–L5.

It is immediately obvious that both the types of donor groups and the cavity size influence considerably the complexing ability of the ligands toward Pb^{2+} ion and consequently the potential response of the resulting membrane sensor. Membrane based on L1 and L3 showed linear ranges from ca. $pPb = 4.44$ – 1.89 and ca. $pPb = 4.76$ – 1.89 with super Nernstian slope of 31.2 ($r^2 = 0.999$) and near Nernstian slope of 27.2 ($r^2 = 0.999$) mV decade $^{-1}$, respectively (see Fig. 2). The large slope for L1 seems to be mainly due to the existence of a pyridine ring between two amide groups in the macrocyclic ring as well as the cavity size which can considerably influence the ion exchange. As can be noted from Fig. 2, the membrane based on L4 and L5 showed linear ranges from ca. $pPb = 4.44$ – 2 and $pPb = 5.44$ – 3.16 with slopes of 22 ($r^2 = 0.995$) and 20.5 ($r^2 = 0.996$) mV decade $^{-1}$, respectively. The largely decreased efficiency of macrocycles L4 and L5 compared with L1–L3 seems to be mainly due to the existence of three benzo groups on the macrocyclic ring which results in the enhanced configuration rigidity of ligand L5 [38–40].

On the other hand, among the macrocyclic diamides L1 and L2, with more sensitive potentiometric response, the 18-membered macrocycle L2 with a pyridine group in ligand ring is the most suitable ion carrier in the PVC membrane sensor. It should be noted that the use of 18-membered macrocycle as ion carrier in the preparation of lead ion-selective electrode has already been reported in the literature [10,11]. However a further increase in cavity size from L2 to L1, will affect complexing ability of the ligands for lead ion.

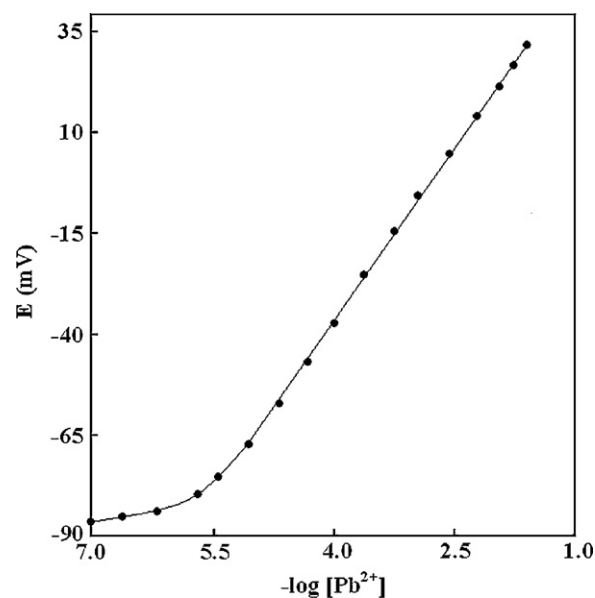


Fig. 3. Calibration graph for the Pb^{2+} ion-selective electrode.

Having the same cavity size, the increased tendency of L2 than that of L3 for Pb^{2+} ion may be explained on the basis of existence of a further nitrogen atom in the L2 structure by the substitution of a pyridine group in its macrocyclic ring. We noted, however, that the membrane electrode with L2 has the best linear range from ca. $pPb = 5.44$ – 1.88 with slope of 29.7 ($r^2 = 0.999$) mV decade $^{-1}$ (Fig. 3). Thus, the ligand L2 was chosen as the most suitable ionophore for the preparation of the lead PVC membrane lead ion-selective electrode. The potential response of the prepared electrode to lead ion was much more sensitive than that to the other ions tried (i.e., alkali, alkaline earth and some transition metal ions). This is most probably due to the highly selective behavior of ionophore for Pb^{2+} over other metal ion as well as the rapid exchange kinetics of the resulting Pb^{2+} –L2 complex.

3.3. Effect of membrane composition

It is well-known that sensitivities and selectivities obtained for a given ionophore depend significantly on the membrane ingredients and nature of solvent mediators and additives used [25–28]. Thus, we investigated the influence of membrane composition on the potential response for lead sensor. The results are summarized in Table 1. The potential response of the electrode is found to be dependent on the concentration of lipophilic anionic salts incorporated in the membranes (Nos. 1–5). The data indicates that membrane without lipophilic additive salts responded weakly to lead ion with a slope of 16.8 , but with a good limit of detection (No. 1). However, addition of KpCITPB as a lipophilic salt increased the

Table 1
Optimization of membrane ingredients.

No.	Composition (%)				Linear range (mol L $^{-1}$)	Slope (mV decade $^{-1}$)
	Carrier	PVC	DMS	KpCITPB		
1	L2, 5	31	64	0	3.6×10^{-6} to 1.6×10^{-3}	16.9
2	L2, 2	33	64	1	6.0×10^{-6} to 1.6×10^{-3}	23.2
3	L2, 5	31	63	1	6.0×10^{-6} to 1.2×10^{-2}	25.0
4	L2, 7	30	62	1	3.6×10^{-6} to 1.6×10^{-2}	26.7
5	L2, 7	30	61.4	1.6	3.6×10^{-6} to 1.6×10^{-2}	29.7
6	L1, 7	30	61.4	1.6	3.6×10^{-5} to 1.3×10^{-2}	31.2
7	L3, 7	30	61.4	1.6	1.7×10^{-5} to 1.3×10^{-2}	27.2
8	L4, 7	30	61.4	1.6	3.6×10^{-5} to 1.0×10^{-2}	23.0
9	L5, 7	30	61.4	1.6	3.6×10^{-6} to 6.9×10^{-4}	19.8

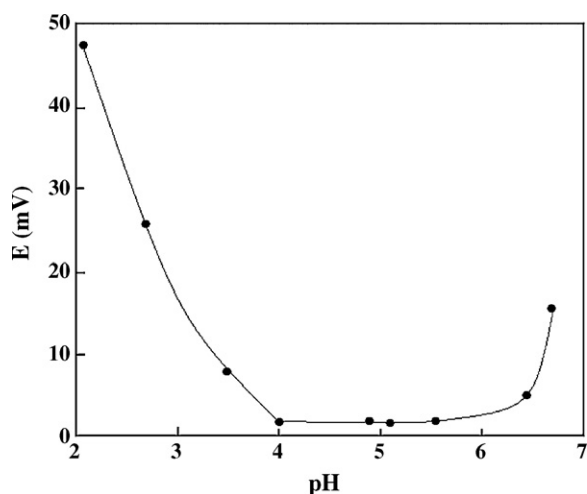


Fig. 4. Effect of pH of test solution on the potential response of the Pb^{2+} ion-selective electrode.

slope sharply. It is well-known that the presence of lipophilic anions in cation-selective membrane electrodes not only diminished the ohmic resistance [31] and enhanced the response behavior and selectivity, but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrode [17]. Thus, based on the results obtained, 1.6% of KpCITPB was chosen as the optimum amount of lipophilic salt in the PVC membrane. As is obvious from Table 1 the use of 7% amount of L2 along with 30% PVC 61.4% DMS and 1.6% KpCITPB resulted in the Nernstian behavior of the membrane sensor over a wide Pb^{2+} concentration range (No. 5). The electrode responded linearly to Pb^{2+} ion in a concentration range 3.6×10^{-6} to 1.6×10^{-2} mol L $^{-1}$ with a slope of 29.7 ± 0.6 mV per decade. The limit of detection, as determined from the intersection of the linear segments of the calibration graph, was 2.0×10^{-6} mol L $^{-1}$. The higher response obtained for membrane No. 5 with L2, in comparison with other ionophores (Table 1), emphasizes the role played by the ionophore and KpCITPB in controlling the membrane response behavior.

3.4. Influence of pH

The influence of pH of the test solution on the potential response of the lead sensor was tested at a 1.0×10^{-4} mol L $^{-1}$ Pb^{2+} concentration over the pH range 2–7, adjusted by using LiOH or HNO_3 , and the results are shown in Fig. 4. As seen, the potential remained constant from pH 3.7–6.5. The observed potential increases below and above this pH range may be due to the simultaneous response of the electrode to Pb^{2+} and H^+ , and Pb^{2+} and Li^+ , respectively [41].

Table 3
Comparison of selectivity coefficient Pb^{2+} ion-selective electrode.

Parameter	Ref. [7]	Ref. [8]	Ref. [9]	This work
$K_{\text{Pb,M}}^{\text{pot}}$				
Ni^{2+}	1.58×10^{-2}	5.6×10^{-3}	3.1×10^{-3}	8.6×10^{-3}
Sr^{2+}	–	7.7×10^{-3}	–	3.5×10^{-3}
Ba^{2+}	–	2.0×10^{-3}	4.8×10^{-3}	2.3×10^{-2}
Ca^{2+}	–	7.9×10^{-3}	–	4.5×10^{-3}
Co^{2+}	8.6×10^{-3}	7.0×10^{-3}	2.2×10^{-3}	4.0×10^{-4}
Cu^{2+}	8.6×10^{-3}	9.1×10^{-3}	5.2×10^{-3}	5.4×10^{-3}
Cd^{2+}	8.6×10^{-3}	3.6×10^{-3}	2.7×10^{-3}	4.0×10^{-3}
Linear range (mol L $^{-1}$)	2×10^{-5} to 5.0×10^{-2}	1.0×10^{-5} to 1.0×10^{-2}	1.0×10^{-5} to 1.0×10^{-2}	3.6×10^{-6} to 1.3×10^{-2}
LOD (mol L $^{-1}$)	1.0×10^{-5}	6.0×10^{-6}	6.0×10^{-6}	2.0×10^{-6}
pH range	–	5.0–7.5	4.5–7.0	3.7–6.7

Table 2
Selectivity coefficients of various interfering ions.

Interfering ion	$K_{\text{Pb,M}}^{\text{pot}}$	Interfering ion	$K_{\text{Pb,M}}^{\text{pot}}$
Ni^{2+}	8.6×10^{-3}	Co^{2+}	4.0×10^{-4}
Sr^{2+}	3.5×10^{-3}	Cu^{2+}	5.4×10^{-3}
Ba^{2+}	2.3×10^{-2}	Zn^{2+}	7.8×10^{-3}
Mg^{2+}	1.4×10^{-3}	Cd^{2+}	4.0×10^{-3}
Ca^{2+}	4.5×10^{-3}		

3.5. Optimization of equilibration time

Optimum conditioning time for the membrane sensor in a 1.0×10^{-3} mol L $^{-1}$ lead nitrate solution is 24 h. It then generates stable potentials when placed in contact with Pb^{2+} solutions. The average time required for the Pb^{2+} ion-selective electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of lead ion solutions, each having a 10-fold difference in concentrations, was measured. The static response time thus obtained was < 16 s for concentrations $\leq 1.0 \times 10^{-3}$ mol L $^{-1}$, and potential stayed constant for about 5 min, after which only a very slow divergence within the solution of the pH meter was recorded. The sensing behavior of the membrane electrode remained unchanged when the potentials recorded either from low to high concentrations or vice versa. The membrane electrodes prepared could be used for at least 8 weeks without any measurable divergence.

3.6. Selectivity

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining whether a reliable measurement in the target sample is possible. To investigate the selectivity of the membrane electrode proposed, its potential response was investigated in the presence of various interfering foreign cations using the mixed solution method (MSM) [28,30,42,14,16,31]. The potential measured in solutions containing a fixed amount of Pb^{2+} ion (1.0×10^{-4} mol L $^{-1}$) and varying amounts of the interfering ions (M^{n+}), and the potentiometric selectivity coefficients ($K_{\text{Pb,M}}^{\text{pot}}$) were evaluated according to

$$K_{\text{Pb,M}}^{\text{pot}} a_{\text{M}}^{2/n} = a_{\text{Pb}} \left\{ \frac{\exp(E_2 - E_1)F}{RT} \right\} - a_{\text{Pb}}$$

where E_1 and E_2 are the electrode potentials for the solution of Pb^{2+} alone and for the solution containing interfering ions and lead ions, respectively. According to this equation, the $K_{\text{Pb,M}}^{\text{pot}}$ values for diverse ion can be evaluated from the slope of the linear graph of $a_{\text{Pb}} \{ \exp(E_2 - E_1)F/RT \} - a_{\text{Pb}}$ vs $a_{\text{M}}^{2/n}$, and the resulting $K_{\text{Pb,M}}^{\text{pot}}$ values are summarized in Table 2.

In Table 3 are compared the response characteristics of the proposed membrane electrode based on macrocyclic diamide L2 with

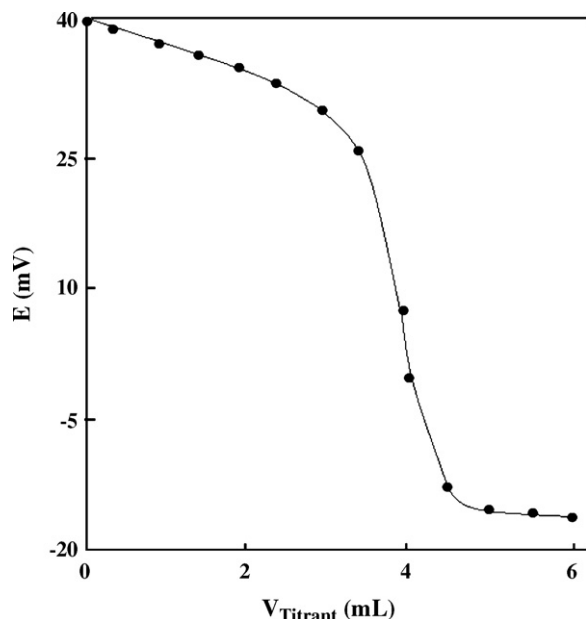


Fig. 5. Potentiometric titration curve of 40 mL of 1.0×10^{-3} mol L⁻¹ of Pb²⁺ solution with 1.0×10^{-2} mol L⁻¹ Na₂CrO₄, using the proposed sensor as an indicator electrode.

the corresponding values previously reported for three randomly taken lead ion-selective membrane electrodes based on different ionophores [7–9]. As can be seen, with the exception of Ba²⁺, for all diverse ions used, selectivity coefficients of cations tested are in the order of 8.6×10^{-3} or smaller, which seems to indicate that these metal ions exert negligible disturbances on the functioning of the Pb²⁺ membrane sensor. It can be noted not only linear range but also detection limit of this membrane is better than others.

4. Analytical application

The proposed lead-selective membrane electrode introduced not only be used for direct determination of Pb²⁺ ions, but also it can be useful as an indicator electrode in titration of Pb²⁺ with Cr₂O₄²⁻. The results of the titration 40 mL of 1.0×10^{-3} mol L⁻¹ solution of Pb²⁺ ion with a 1.0×10^{-2} mol L⁻¹ sodium chromate solution are shown in Fig. 5. The potential of the electrode was decreased upon addition of the chromate precipitation agent. It is clear that the concentration of lead ion in solution can be accurately determined from the resulting neat titration curve providing a sharp end point.

5. Conclusions

In this study, for improving the discrimination ability of a macrocyclic diamides toward lead ion, five kinds of ligands were synthesized, and the fundamental properties of a PVC membrane electrode based on these ligands were evaluated by potentiometry. The proposed electrode exhibited a fast response (<16 s), a wide linear range (1.3×10^{-2} to 3.6×10^{-6} mol L⁻¹) with a limit of detection of 0.4 ppm. The practical utility of membrane sensor demonstrated by its used as an indicator electrode in the potentiometric titration of Pb²⁺ with Cr₂O₄²⁻.

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