Potentiometric Lead (II) Ions Recognition by Liquid Membrane Electrodes Incorporating Methoxy Substituted Arylenevinylene Derivatives

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Abstract

The potentiometric responses towards lead ions of liquid membrane electrodes containing arylenevinylene derivatives are reported. The membranes respond to lead ions in the activity range 10^{-6} - 10^{-3} M and show good selectivity against common interfering mono- and doubly-charged cations. The new ligands demonstrate low affinity for protonation. 1 mol % (vs the ionphore) of potassium tetrakis(p-chlorophenyl)borate was used as a lipophilic anionic salt to improve the selectivity. The ligands selected for the present study allow estimating the influence of olefinic double bounds, the number of aromatic rings and the number and position of methoxy groups on recognition process of the lead ions.

Keywords: liquid membrane electrodes, potential response, lead ions, arylenevinylene derivatives

Introduction

The importance of controlling the levels of environmental pollutants in natural waterways and potable water has generated increasing interest in the development of novel sensors for the detection of heavy metals [1].

The use of ion –selective electrodes (ISEs) for the detection of lead (II) ions has gained much interests. Compared with other methods of trace analysis, potentiometry is extremely inexpensive technique. Because of that it can compete with the very sophisticated methods used for the lead determination such as electrothermal Atomic Absorption Spectroscopy (AAS) [2,3], anodic stripping voltammetry [4,5], X-ray absorption spectroscopy [6], differential pulse polarography [7]. These methods demand the very specific sample preparation, including preconcentration, or application of complexing agents. In the comparison, potentiometric sensors are known to only minimally perturb the sample, that way they should be especially well suited for speciation analysis.

Many ligands have been studied as lead sensing agents in electrodes based on ionophore-incorporated poly(vinyl chloride) membranes [8-10]. Among them are thiacrown ethers [11, 12], diazacrown ethers [13], calixarene phosphine oxide [14], acyclic amides [15, 16], oxamides, acyclic dithiocarbamates [17, 18]. One of the major problem

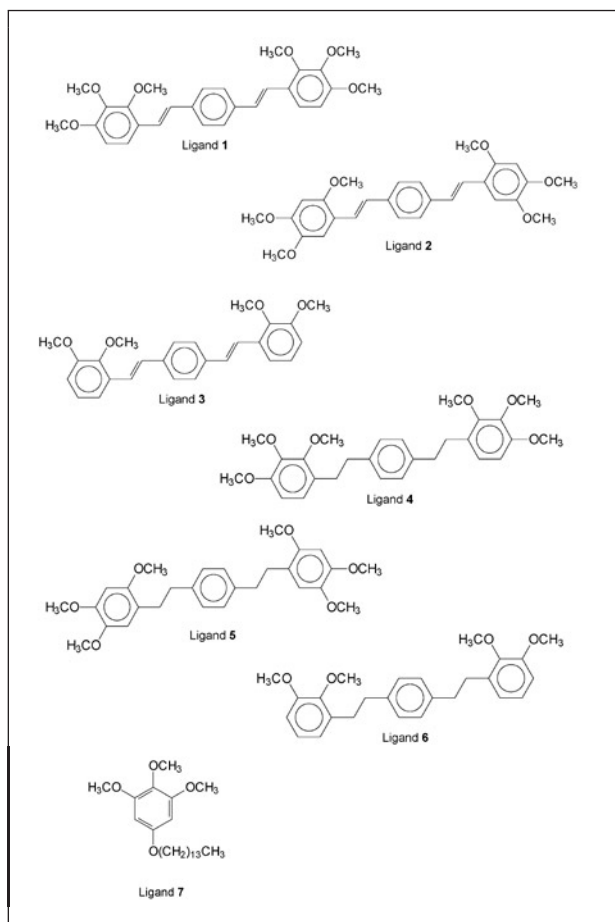Fig. 1. The chemical structures of ligands.

still remaining to be solved is the strong interferences caused by Cd^{2+} and Cu^{2+} which tend to be found in association with Pb^{2+} in water samples.

In this paper, we report the potentiometric response to lead ions of poly(vinylchloride) (PVC) matrix liquid membranes based on ligands pictured in Figure 1. Some arylenevinylene derivatives have been already applied as sensory elements of lead sensitive liquid membrane electrodes [19]. In the present study, ligands selected allow estimating the influence of olefinic double bounds, number of aromatic rings and number and position of methoxy groups on the recognition process of the lead ions.

The possible application of arylene-vinylene incorporating liquid membrane electrodes has been evaluated by exploring the influence of natural river matrix on lead ions determination.

Experimental
Reagents

Compounds **1** through **7** were used as sensory elements of liquid membrane electrodes. 1,4-Bis[2-(2,3,4-trimethoxyphenyl)ethenyl]benzene (ligand **1**), 1,4-bis[2-(2,4,5-trimethoxyphenyl)ethenyl]benzene (ligand **2**) and 1,4-bis[2-(2,3-dimethoxyphenyl) ethenyl]benzene (ligand

3) were synthesized as described previously [20]. 1,4-Bis[2-(2,3,4-trimethoxyphenyl)ethyl]benzene (ligand **4**), 1,4-bis[2-(2,4,5-trimethoxyphenyl)ethyl]benzene (ligand **5**) and 1,4-bis[2-(2,3-dimethoxyphenyl)ethyl]benzene (ligand **6**) were synthesized from compounds **1**, **2** and **3**, respectively, by hydrogenation over 10 % Pd/C in ethanol. Then, the reaction mixture was filtered free of catalyst and the solvent was evaporated. The yield was almost 100 %.

The ligand **7** (1,2,3-trimethoxy-5-tetradecyloxybenzene) was synthesized according to unpublished procedure [21].

Other membrane components: bis(2-ethylhexyl) phtalate (DOP), poly(vinyl chloride) (PVC), were purchased from Wako Pure Chemical, Japan and potassium tetrakis(p-chlorophenyl)borate (K-TClPB) - from Dojindo Laboratories, Kumamoto, Japan. Tetrahydrofuran (THF) was obtained from POCh, Gliwice, Poland, and was distilled from solid NaOH just before use. All cations, as nitrate salts of analytical grade, were used without additional purification. Solutions were prepared with Mili-Q water (resistance 18.2 MΩcm).

The validation of lead ions determination by arylenevinylene incorporating liquid membrane electrodes has been done with using natural water matrix from Hańcza lake and Łyna river, which contains ca. 3.0 mM $CaCl_2$, 3.0 mM $NaHCO_3$, 3.0 mM $MgSO_4$ [22].

Electrode Preparation and Potential Measurements

PVC matrix liquid membranes based on ionophores **1** through **7** were prepared according to the standard procedure [19,23]. The membranes contained: 1 wt % ligand, 66 wt % DOP, 33 wt % PVC and 1 mol % of K-TClPB *vs.* the ionophore. The mixtures thus prepared were dissolved in 2 ml freshly distilled THF and then placed onto a glass ring of 30 mm diameter and left for 24 h to allow
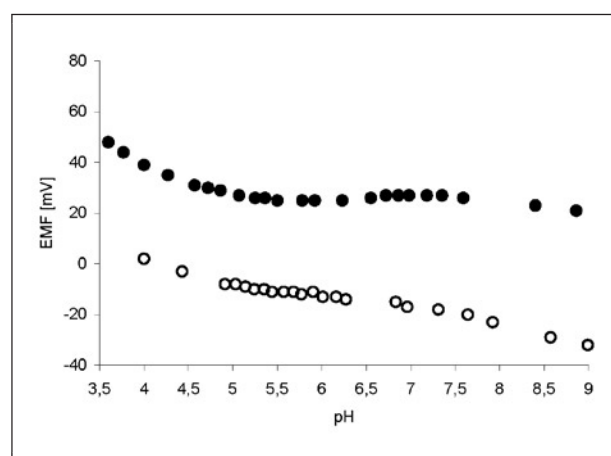

Fig. 2. Potential – pH profile for solvent membrane (●) and membrane incorporated with ligand 1 (○).

Measuring conditions: sample solution (10^{-2}M H_2SO_4) was adjusted by adding appropriate amounts of NaOH solution containing 1.0 x 10^{-2} M Na_2SO_4.

THF to evaporate. A circle of 6 mm diameter was cut and mounted on a liquid membrane type Philips ISE body (Glasbläserei Möller, Zűrich, Switzerland).

The potentiometric measurements were carried out with the following cell assembly:

Ag/AgCl | 3 M KCl | 1 M CH₃COOLi | sample solution | | PVC membrane | 0.01 M KCl | Ag/AgCl

EMF response was measured at room temperature (*ca.* 20ºC) by means of multichannel station pH-meter made by DonauLab (Warsaw, Poland).

The potentiometric selectivity coefficients ($K_{A,B}^{MPM}$) were determined by the matched potential method in mixed solutions [24-27]. The activity coefficients were calculated according to Debye - Hűckel equation [9, 28].

Results and Discussion

EMF Responses of Membranes Containing Arylenevinylene Derivatives Towards Pb²⁺ Ions

Proton uptake by ligands incorporated in liquid membrane electrodes can be a serious drawback from an application point of view. Thus, the affinity of the ligands studied towards protons has been checked. Figure 2 illustrates the potential-pH profiles for the membrane based on ligand **1** and for so-called "solvent" membrane (without ligand). These results are also representative for the other ligands. The membrane potential does not change significantly with the increase of H⁺ concentration, within the pH range from 4.0 to 9.0. So, it could be concluded, that protons do not interfere in Pb²⁺ determination. Therefore, the sample solutions could be prepared for the measurements with ISEs containing the new arylenevinylene derivatives without using a buffer.

It is well known that the addition of lipophilic ionic sites to an ion-selective liquid membrane electrodes based on neutral ionophore is necessary to reduce the interference of lipophilic counterions, to shorten response times, to decrease the electrical resistance of the membrane, and to improve the selectivity [29-33]. Thus, for the present study, 1 mol % of the lipophilic anionic salt potassium tetrakis(p-chlorophenyl)borate (K-TClPB) relative to the selected ionophores was added. This optimal concentration was found experimentally.

Figure 3 represents the curves illustrating the relationship between the potentials measured with electrodes modified with the ionophores studied in the relation to
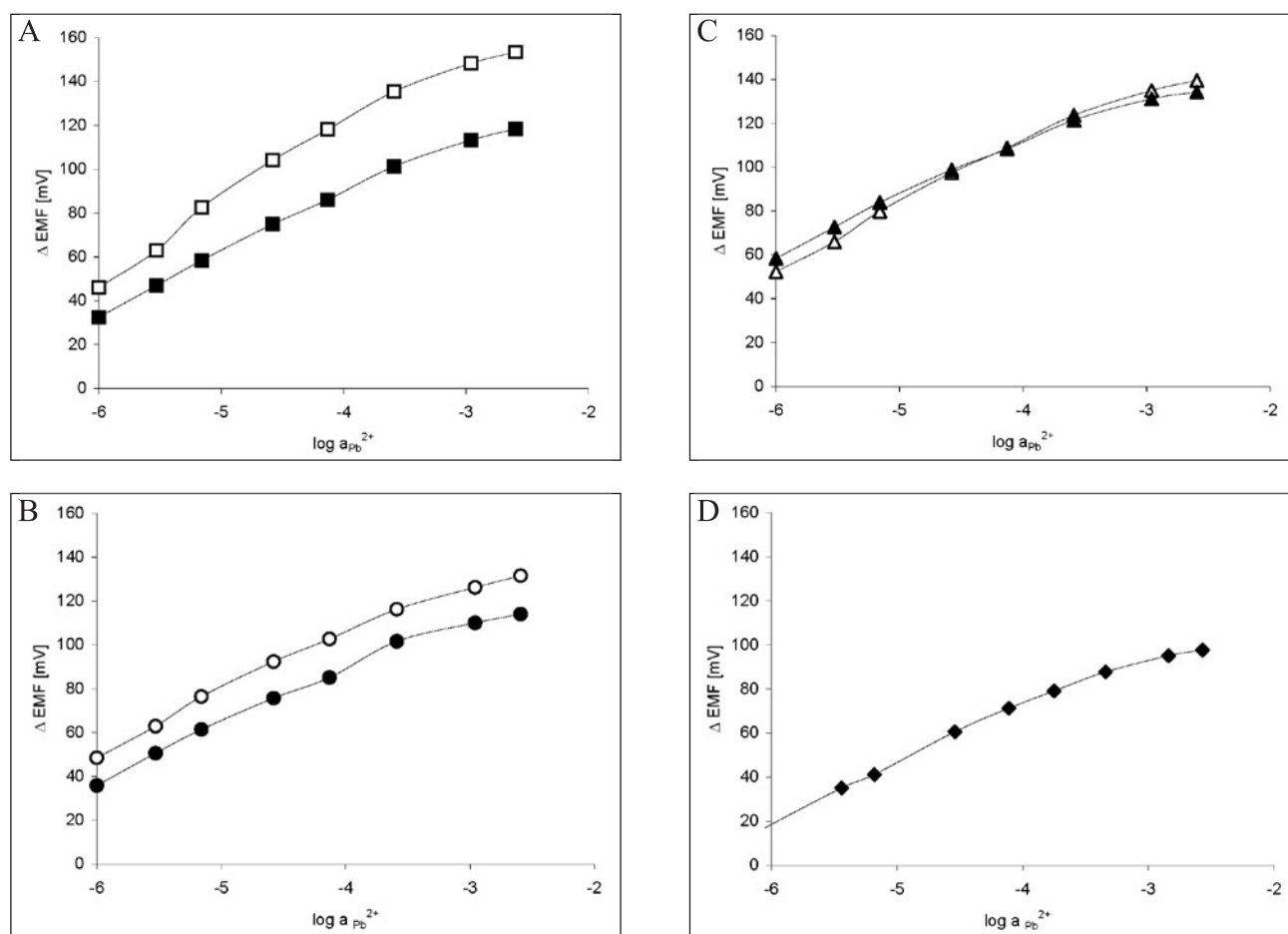

Fig. 3. Potential response toward Pb²⁺ ions of the electrodes containing ligands (for the composition see Experimental part)
A - (□) 1 and (■) 4; B - (○) 2 and (●) 5; C - (Δ) 3 and (▲) 6; D - (♦) 7; (n = 3; 1.3 < SD < 5.9).

Table 1. Potentiometric selectivity coefficients (log $K^{MPM}_{Pb2+,j}$) for the arylene-vinylene liquid membrane electrodes against various interfering cations.

	Ca	Cd	Cu	K	Mg	Na	Ni	Zn
Ligand 1	-1.39	-1.28	-0.17	-1.66	-1.30	-1.33	-1.11	-1.30
Ligand 2	-1.35	-1.20	-0.25	-1.64	-1.35	-1.45	-0.85	-1.10
Ligand 3	-1.46	-0.98	-0.10	-1.68	-1.49	-1.69	-0.96	-1.13
Ligand 4	-1.18	-1.03	-0.58	-1.41	-1.27	-1.37	-1.22	-1.24
Ligand 5	-1.10	-1.13	-0.38	-1.48	-1.36	-1.27	-1.17	-1.42
Ligand 6	-1.25	-1.12	-0.11	-1.49	-1.52	-1.60	-1.03	-1.14
Ligand 7	*	-1.07	*	-1.11	*	*	-0.83	*

Log $K^{MPM}_{Pb2+,j}$ was determined by the matched potential method (MPM) [17-20] in mixed solution with 1.0×10^{-4} M Pb^{2+} as the background and calculated for the potential change of 1 mV. Mean values of three repetitions are given; standard deviations: $0.03 < SD < 0.24$.

* - anionic potentiometric response

changes of the Pb^{+2} activity in the sample solution. The slope of curves obtained for the membranes incorporating the new saturated and unsaturated ionophores are slightly sub-Nernstian (about 26 mV/decade) in a lead activity range from 10^{-6} to 10^{-3} M. The membrane incorporated with ligand **1** is the only one exception. In this case the response is slightly over Nernstian (35 mV/decade). The response time of the membranes studied was found to be less than 20 s over the range of lead ions activity measured.

Comparing the results for the saturated and unsaturated ligands showed that the presence of double bounds in the molecular structure have no strong influence on the sensitivity towards lead ions. The results obtained indicate that the presence of metoxy groups and their position are more crucial for the signal generation. This corroborates the conclusion of our previous paper [19]. The membranes containing ligands having three methoxy groups in 1, 2, 3 positions (ligand **1**) are the most sensitive towards lead ions.

Membrane incorporating the ligand **7**, having only three methoxy groups and one C16 alkyl chain, without arylene-vinylene part, also responded towards lead ions
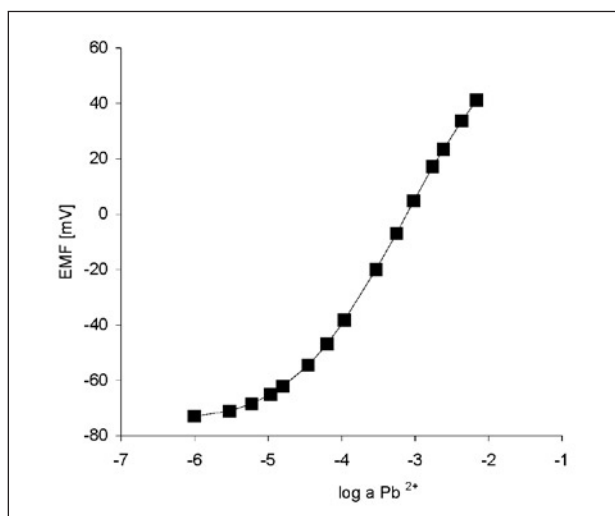

Fig. 4. The Pb^{2+} calibration curve obtained for electrode incorporated with ligand 1 (n = 3; 2.1 < SD < 4.5) at the presence of acetate buffer (10.0^{-2} M, pH =4.0) (n = 3; 2.1 < SD < 4.5).

(Figure 3). These results give the evidence that methoxy groups substituted in benzene ring are responsible for the lead ions recognitions.

Nevertheless, the presence of arylene-vinylene part in the host molecule improve the sensitivity and selectivity of lead potentiometric determination (Table 1).

Potentiometric Selectivity of Arylenevinylene Liquid Membrane Electrodes

To estimate the interference of common monovalent and divalent cations on the Pb^{2+} determination by ISEs incorporating the new ligands, selectivity coefficients were determined by the matched potential method [24-27]. Table 1 presents the results. This method is suitable for the selectivity coefficient determination when target and interfering ions have different charge. Also, this method does not depend on Nicolsky-Eisenmann equation at all [26], because the potentiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions.

A solution containing 1.0×10^{-4} M Pb^{2+} was used as the background. For the calculation Δ EMF = 1.0 mV has been used. Measurements were performed using the nitrate salts of commonly interfering cations. Results showed that the cations studied caused low interference on the Pb^{2+} potential response determined by membranes incorporating the new ligands. Only for the membrane incorporating ligand **7**, without arylene-vinylene part, anionic potentiometric response occurred. The similar phenomenon was observed during determination of selectivity coefficients for membranes free of ionophore [4]. From these results it might be conclude that, apart methoxy groups, arylene – vinylene part of host molecules may also contributes to the cation selectivity by providing a rigid structure and π binding sites.

A possible application emerged for the membrane incorporating ligand **1**. This membrane displayed the highest sensitivity and good selectivity among the membranes studied. The lead calibration curves obtained with using this type of electrode at the presence of acetate buffer (Figure 4) and natural water matrix are illustrated in Figure 5 A, B. The presence of both matrix decreases the
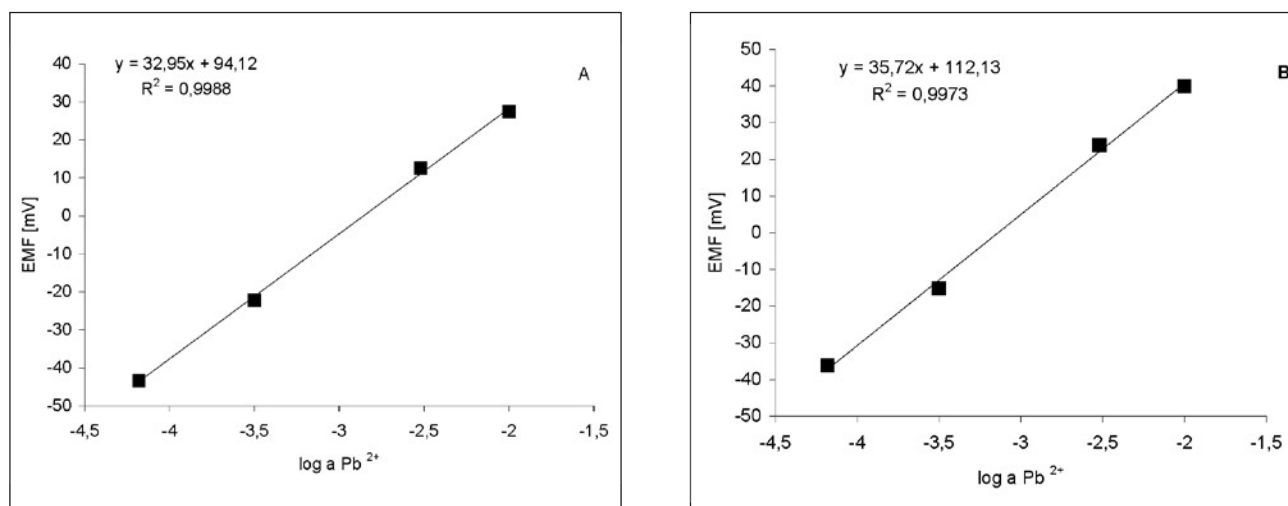
Fig. 5. The regression calibration curve obtained for electrode incorporated with ligand **1**:(A) at the presence of river water and acetate buffer (10.0^{-2} M, pH =4.0); (B) at the presence of lake water adjusted to pH 4.0 by HNO_3.

sensitivity and dynamic range, as it has been observed in the case of thiacrown ethers incorporating liquid membranes [4]. Nevertheless, the arylene –vinylene electrode still responds towards Pb^{2+} ions and a slope 33 - 36 mV/ decade was kept within the concentration range: $4.2 \times 10^{-4} – 2.0 \times 10^{-2}$ M.

The recovery test was successfully performed by determination of the amount of lead ions added to the natural water matrix. The linear regressions of calibration curve for Pb^{2+} in the presence of natural water were presented in Figure 5 A,B. The recovery of 107.5 ± 5.0 % and 105.4 ± 1.8 % was obtained for the lead determination in the presence of 10^{-2} M of acetate buffer pH 4.0 and when pH of water was adjusted by HNO_3 , respectively (Table 2).

Slightly better results were obtained without acetate buffer. The adjusting of pH of natural water by HNO_3 is sufficient and might be recommendable for the determination of lead ions. The natural components of water ($CaCl_2$, $NaHCO_3$, $MgSO_4$) also posses buffer properties. Thus, the additional buffer is not necessary.

The life time of membrane electrode doped with ligand **1** was at least one month, during which any measurable divergence was not observed.

Conclusions

The liquid membrane electrodes incorporated with the new class of ligands displayed significant potentiometric responses towards lead ions. They showed good lead ions selectivity at the presence of other common cations, including protons.

The methoxy groups and their position in the ligand structure are more crucial for the potentiometric signals generation in the presence of lead ions. The arylene – vinylene part of the ligands studied improved the selectivity of the lead ion recognition process, by providing the rigid host structure and π binding sites. The arylene – vinylene

Table 2. The recovery test of lead ions added to the matrix of natural water performed with using the membrane incorporated with ligand **1** (n=3; ± s).

Pb^{2+} added [µM]	Pb^{2+} determined [µM]*	Recovery [%]
pH 4.0 (10^{-2} M acetate buffer)		
65.9	70.8 ± 3.3	107.5 ± 5.0
pH 4.0 (adjusted by HNO_3)		
65.9	69.5 ± 1.2	105.4 ± 1.8

*Average of tree determinations; calculation based on the calibration curves in Fig. 5 A, B.

membranes, particularly the one with ligand **1** exhibited good parameters such as: sensitivity, selectivity and durability. Thus, the membrane with ligand **1** might be recommended for the direct potentiometric determination of lead ions in water samples.

Acknowledgements

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