Lead-selective PVC Membrane Electrodes Based on Bis(crown ether)s

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Lead-selective PVC membrane electrodes based on newly synthesized bis(crown ether)s containing 18-crown-6 moiety was prepared using standard PVC membrane composition. In order to monitor lead in environmental samples by lead sensor, especially good selectivity over alkali and alkaline earth metals has to be obtained. Thus, responses of the PVC membrane prepared with new bis(crown ether)s and Fluka ionophore V (crown ether) base to various cations include lead, alkali and alkaline earth metal ions were investigated for their use as a lead sensor. The polymeric liquid membrane based on *trans*-18-crown-6 ether exhibits the best overall potentiometric performances as a lead-selective electrode in terms of a wide linear dynamic range (between 10^{-6} and 10^{-2} M, Pb^{2+}), excellent detection limit (less than 10^{-6} M) and good durability within limited error. The preferences of lead over other cations, such as Ag^+, Hg^{2+}, Na^+, Ca^{2-} and even K^+ in the aforementioned electrode are much better than the Fluka ionophore V system.

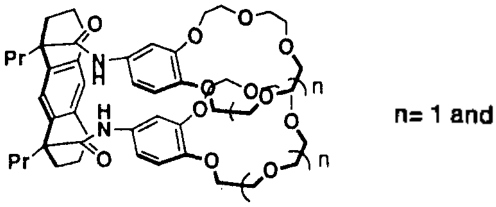
Introduction

The need for the determination of lead and other heavy metals in the environment has prompted the development of a number of neutral ionophores.[1-4] To date, much interest has been paid to the ionophore ligands as sensing materials for neutral carrier type ion-selective electrodes (ISEs) due to the unique properties of the compounds. The ionophores with oxygen donor atoms have been usually studied for alkali and alkaline earth metal ISEs, and many selective ligands have been found for these metal ions.[5,6] The lead ISEs were examined by using ionophores such as oxa- and dioxadicarbamides for PbX^- ion determination and dibenzo-18-crown-6 and its derivatives for Pb^{2+} ion determination.[7-11] Crown ethers are among the first synthetic complexing agents introduced to bind strongly and selectively to alkali metal ions.[12] Thus, reported lead ISEs based on crown ethers did not exhibit sufficient selectivity to alkali cations and similar sized cations such as Ag^+ and Hg^{2+}.[11]

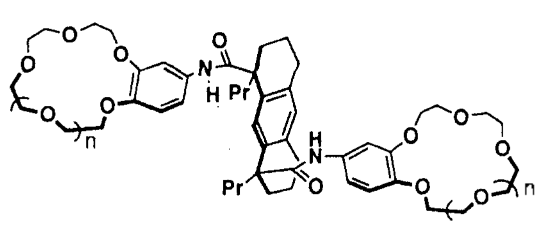
Bis (crown ether)s, which have two equivalent crown ethers, are successfully applied to potassium ionophores and considered as a cheap alternative to valinomycin. The structure-selectivity relationship obtained with crown compounds of different ring sizes reveals that selectivity of bis crown ether-based sensor may depend on their binding affinities toward certain cations by fitting ions in cavity sizes formed between two crown ethers. It was also expected that the two crown ether moieties in one molecule will increase the lipophilicity of the ligands and improve the kinetics of the complaxation, *i.e.* the life and the response times of such ionophores based sensors, respectively. Furthermore, for the development of efficient ISEs and synthetic ion transporters, highly lipophilic molecules should be incorporated into crown ethers. Recently, Chung, *et al.*[13] or Moriaty *et al.*[14] reported that the rigid and compact hydrocarbons such as xanthene or cubane are more relevant for this. Recently, we reported the newly synthesized geometrical isomer of *cis* and *trans* bis (benzocrown ether)s (Figure 1) which are derived from a structurally well-defined molecule, 1,2,3,4,5,6,7,8-octahydro-1,8-dipropyl-1,8-dicarboxylic acid, and evaluated their bis (15-crown-5 ether)s cation-binding properties.[15,16] Here, we investigated the potentiometric performances of two geometrical isomers of aforementioned bis (18-crown-6 ether)s as a lead sensor. We also evaluated the enhancement of lead selectivity toward other cations according to complex forming geometry.

Experimental Section

Reagents. Poly(vinyl chloride) (PVC), *o*-nitrophenyl octyl ether (NPOE), 18-crown-6 ether and lead ionophore V were purchased from Fluka (Ronkonkoma, NY). The new *cis* and *trans* bis (18-crown-6 ether)s are synthesized from 1,2,3,4,5,6,7,8-octahydro-1,8-dipropyl-1,8-dicarboxylic acid



***cis*-bis(benzocrown ether)s**



***trans*-bis(benzocrown ether)s**

Figure 1. The structure of bis (18-crown-6 ether)-based lead ionophores.

Table 1. The compositions of lead ion-selective membranes

Membrane	1	2	3
Ionophore (1 wt %)	*trans* *bis*-18-crown-6	*cis* *bis*-18-crown-6	18-crown-6
Matrix (33 wt %)	PVC[a]	PVC	PVC
Plasticizer (66 wt %)	NPOE[b]	NPOE	NPOE

[a]Poly(vinyl chloride) high molecular weight. [b]2-Nitrophenyl octyl ether

according to the published method.[15] All other chemicals including metal nitrate salts were analytical reagent grade and used without further purification. Standard solutions and buffers were prepared with deionized water.

Preparation and evaluation of polymer membranes and electrodes. PVC matrix membranes were prepared according to the method reported previously.[17] The composition of PVC-based cation selective membrane was 1 wt % ionophore, 33 wt % PVC and 66 wt % plasticizer with total weight of 200 mg. The detail compositions of membranes used in this experiment are listed in Table 1. The membranes were prepared by dissolving the mixture in 5 mL, THF. In each case, after curing, small disks (5.5 mm) were punched from the cast films and mounted in Philips electrode bodies (IS-561; Glasblaserei Muller, Zurich, Switzerland).

The potentiometric behavior of the membrane electrodes was evaluated with conventional ISE configuration. For all electrodes, mixture of 0.1 M $AgNO_3$ and 0.1 M $Pb(NO_3)_2$ was employed as the internal filling solution. The external reference electrode was an Orion sleeve-type double junction Ag/AgCl electrode (Model 90-02). Electrodes were connected through a high impedance amplifier to an IBM AT-type computer equipped with an analog-to-digital converter. The cell potentials were measured at ambient temperature (22 °C) by immersing ISEs and the reference electrode in a beaker containing 200 mL of the working buffer (0.05 M magnesium acetate, pH 4.5), and the calibration data were obtained from additions of standard solutions. The solutions were magnetically stirred throughout and equilibrium potentials were recorded. Selectivity coefficients were estimated according to the separate solution method at an interfering cation concentration of 10^{-3} M.[18] The detection limits of the membrane electrodes were obtained from the calibration plots following the recommended procedure.[19] The response of an electrode toward pH was obtained by titrating a universal buffer of pH 2.8 (11.4 mM boric acid; 6.7 mM citric acid; 10.0 mM sodium dihydrogen phosphate) with small aliquots of LiOH, while simultaneously monitoring the pH of the sample solution with a combination glass pH electrode.

Results and Discussion

The dynamic potential responses of lead-selective PVC membrane electrodes with 18-crown-6 ether and newly synthesized bis (18-crown-6 ether)s are shown in Figure 2. The membrane electrode with *trans* bis(crown ether) (Membrane 1: Figure 2, trace A) showed a slope of 33.9 mV with the linear range between 10^{-2} and 3.6×10^{-6} M $Pb(NO_3)_2$. Obviously the dominant species complexed is Pb^{2+}, but this may not be the only species which are complexed or extracted. On the other hand, the membrane electrode with *cis* bis(crown ether) (Membrane 2: Figure 2, trace B) exhibited a below-Nemstian slope of 21.3 mV with similar linear range as that of the membrane electrode 1. The membrane with Fluka ionophore V (15-crown 5 ether) showed similar potentiometric response to lead (slope: 30 mV between 10^{-1} to 2.5×10^{-5} M Pb^{2+}).[11] However, membrane electrode with mono 18-crown-6 ether (Membrane 3: Figure 2, trace C) almost did not respond to lead and other transition metal cations. That phenomenon could be caused by that cavity of purchared crown ether might be preoccupied by cations. The *trans*-compound and Fluka ionophore V exhibited slightly over-Nernstian slope, which is possible if Pb^{2+} and $Pb(OH)^+$ simultaneously respond. $PbOH^+$ may not be fitted in the cavity of bis *cis*-compound, resulting in poor potentiometric response.

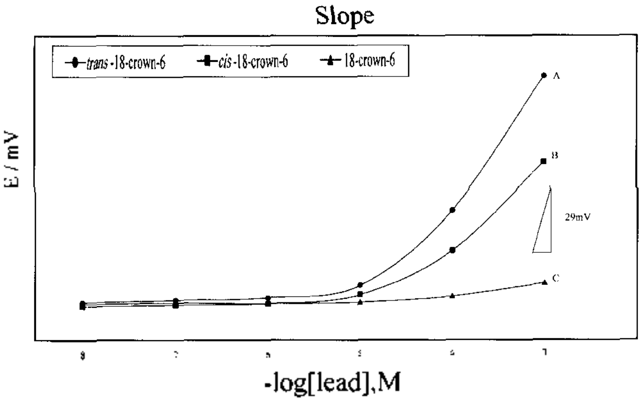

Slope

Figure 2. Potential responses of lead-selective electrode based on (A) *trans* bis(18-crown-6 ether) (B) *cis* bis(18-crown-6 ether) (C) 18-crown-6 ether in pH 5.5.

The static response time of the bis (crown ether) based-membrane sensor was 20 sec or less at 10^{-3} M Pb^{2+}, and it increased with decreasing lead concentrations. The properties of examined crown ether-based electrodes are summarized in Table 2. One membrane can be used for more than 6 month in laboratory condition, if properly stored (dipped in water) and cross contamination is avoided.

Table 2. Potentiometric performances of lead-selective membranes

	Pb(II)-Selectivity Membrane Electrodes			
Ionophore	*trans* 18-crown-6	*cis* 18-crown-6	18-crown-6	Ionophore V[a]
Detection limit (x10^{-6} M)	2.2	2.3	6.3	25
Slope (mV/decade)	34	21	2	30
Response time (sec)	19	20		30
pH range	3-8	3-8		3-6

[a] Reference to Fluka Selectophore book

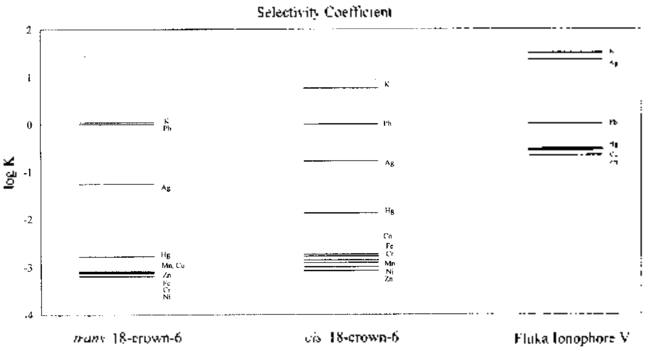


Figure 3. Selectivity coefficients of various interfering ions for lead ion-selective electode based on crown ether.

The pH response profiles for electrodes were examined by use of 10^{-3} M $Pb(NO_3)_2$ solution, adjusted with nitric acid and LiOH as acidic and alkaline media. Generally, at above pH 5.5, the potential decreases due to the formation of lead hydroxide in solution, while, at a low pH, potential increased, indicating that the electrode responded to hydrogen ion. Thus the working buffer (0.05 M, magnesium acetate, pH 4.5) was employed throughout the experiment, even though emf of the prepared membranes remain constant in the pH range of 3-8.

The selectivity coefficient values for the electrodes are summarized in Figure 3. The electrode based on Fluka ionophore V suffer from large interferences to most monovalent cations including potassium ($LogK^{pot}_{Pb,K}=1.5$), sodium (1.5), ammonium (1.2) and silver ion (1.36).[11] The both electrodes based on *trans* and *cis* bis(crown ether)s also exhibit large interfering response to potassium ion (0 for membrane 1; 0.7 for membrane 2), but these electrodes did show less interference by other monovalent cations such as sodium (-2.79 for membrane 1; -2.35 for membrane 2), ammonium ion (-3.9 for membrane 1 and 2) and silver ion (-1.26 for membrane 1; 0.78 for membrane 2) than other crown ether based ionophores.

Newly synthesized *cis* and *trans* bis(18-crown-6 ether) have the identical molecular components but their geometries are different from each other. They are expected to show structural advantage due to the improvement in preorganization property in comparison with the 15-crown-5 ether based commercial ionophore such as Fluka ionophore V, because the bridge between two crown ethers is solidified and gives higher lipophilicity. From the comparison of the potentiometric performance of two structurally isomeric bis (crown ether) reveals that lead ion prefer the formation of sandwich type complex with ionophore to mono crown like complex. The stability and selectivity upon complexation generally depend on the complementary sizes of metal cations and crown ether cavities. However, this bis crown effect is not, however, well fitted to the results, because *trans* compound exhibited superior overall performance as lead sensor. The size correlation might be the one contributing factor for selectivities. But it may not be the sole reason that *trans* shows better potentiometric behavior as lead sensor, because it is inferred from potentiometric results of the membrane. In order to pursuit the distinctive evidences of the structure correlation between ionophores and selectivity to certain cations, it needs further experiments.

In conclusion, *trans* isomer of newly synthesized bis (18-crown-6 ether) is considered as an alternative lead ionophore under designated conditions.

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