Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1319–1326

Lead(II)-Selective Electrode Based on Dibenzodiaza-15-crown-4

HAMID REZA POURETEDAL* and MOHAMMAD HOSSEIN KESHAVARZ
Chemistry Department, Malek-ashtar University of Technology (MUT
Shahin-shahr, Iran, P.O. Box 83145/115
E-mail: hrpouretedal@yahoo.com

A PVC-based membrane of dibenzodiaza-15-crown-4 reveals a Nernstian potentiometric response for Pb^{2+} over a wide linear range (5.0×10^{-6}–1.0×10^{-2} mol/L) with detection limit of 3.5×10^{-6} mole/L. It has a response time of about 15 s and can be used for at least 3 months without any divergence. The proposed membrane sensor revealed good selectivity for Pb^{2+} over a wide variety of alkali, alkaline earth and transition metal ions. The electrode was used as an indicator electrode in potentiometric titration of lead.

Key Words: PVC-membrane electrode, Dibenzodiaza-15-crown-4, Lead(II).

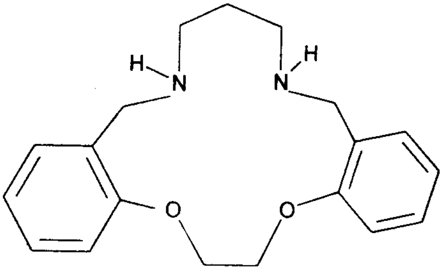
INTRODUCTION

Crown ethers[1] have been widely used as suitable neutral carriers for the selective and efficient transport of alkali and alkaline earth cations through liquid membranes[2, 3] and for constructing membrane-selective electrodes for these cations[4–7], mainly due to the specific selectivity and extraction efficiency for metal ions.

Meanwhile, the substitution of some oxygen atoms of crown ethers by nitrogen atom results in complexation properties that are intermediate between those of the ordinary crown ethers and those of all nitrogen macrocyclic ligands[8, 9]. Such mixed and controllable, complexation properties make the aza-substituted crown ethers ideal candidates for use as ion carrier in the construction of transition and heavy metal ion-selective electrodes[10–18] where facile complexation and decomplexation of the ionophore are of vital importance.

Due to the increased industrial use of lead, on one hand, and its serious hazardous effects to human health, on the other[19], the electrochemical properties and preparation of lead ion-selective electrodes have been extensively investigated by using different active materials, so that several Pb^{2+} -selective electrodes have been commercially available during the past three decades[20]. However, the use of aza-crown ethers may result in suitable carrier for selective detection of lead with ion-selective electrodes.

In this paper we report a PVC membrane electrode based on 5,6,14,15-dibenzo-1,4-dioxa-8-12-diazacyclopentadeca-5,14-diene (dibenzodiaza-15-crown-4,DBDA DBDA15C4) (Fig. 1) which exhibits significantly high selectivity to Pb^{2+} ions over alkali, alkaline earth and several transition metal ions.



I

Fig. 1

EXPERIMENTAL

Reagents grade benzyl acetate (BA), acetophenone (AP), *o*-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), sodium tetraphenyl borate (STB), high relative molecular weight PVC and tetrahydrofuran (THF) (all from Merck) were of the highest purity available and used without any further purification except vacuum drying over P_2O_5. The ionophore DBDA15C4 (from Merck) was used after recrystallization from pure acetonitrile and vacuum drying. Triply distilled deionized water was also used throughout.

Electrode preparation: The general procedure for casting the ion-sensing membranes is the following: PVC (30.9 mg), DBP as a plasticizer (62.9 mg), DBDA15C4 (4.6 mg) and STB as additive (1.6 mg) were dissolved in 5 mL of THF. The resulting solution was transferred into a glass dish of 2 cm diameter. The solvent was evaporated until an oily concentrated mixture was obtained. A Pyrex tube (5 mm internal diameter) was dipped into the mixture for about 5 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 kept at room temperature for about 3 h. After drying the THF, an internal filling solution (1.0×10^{-2} mol/L lead nitrate) was set up into the electrode. Conditioning of the resulting electrodes was done by soaking in the 1.0×10^{-1} mol/L solution of lead nitrate overnight. A silver/silver chloride coated wire was used as an internal reference electrode.

Emf measurements: The electrochemical cell for the emf measurements was

$$\text{Ag-AgCl} \mid 1.0 \times 10^{-2}\ \text{mol/L}\ Pb(NO_3)_2,\ 2.0 \times 10^{-3}\ \text{mol/L}\ NH_4Cl \mid$$
$$\text{PVC membrane} \mid \text{sample solution} \mid Hg\text{-}Hg_2Cl_2,\ \text{KCl (satd)}.$$

The emf observations were carried out relative to double junction saturated electrode (SCE, Philips) by the chamber filled with an ammonium nitrate solution. The activities of the metal ions were calculated according to the Debye-Huckel equation[21]. A Model 624 Metrohm digital research pH-meter was used for the potential measurements at 25 ± 0.5°C.

RESULTS AND DISCUSSION

It is well known that crown ethers are able to form complexes with alkali, alkaline earth, transition and heavy metal ions in some nonaqueous solvents. The existence of two NH— groups in DBDA15C4 was expected to increase both the stability and selectivity of transition and heavy metal complexes over alkali and alkaline earth cations[8, 9]. The presence of two benzo rings on the 15-crown-4 cavity provides a rigid cavity. Thus, in preliminary experiments, it was used to prepare PVC-based membrane electrodes based on DBDA15C4 as ion carrier for a variety of cations. As it is obvious from Fig. 2, among different cations tested, Pb^{2+} with the most sensitive response seems to be suitably determined with the electrode. This is probably due to the suitable cavity size of lead ion diameter in comparison to the other ions.

Some important features of the PVC membranes such as the nature and properties of the plasticizer, ionophore, additives and the plasticizer/PVC ratio are reported to significantly influence the sensitivity and selectivity of the ion-selective electrodes[12–18, 22–24]. Therefore, various aspects of the membrane preparation based on DBDAl 5C4 for Pb^{2+} were optimized. The results are given in Table-1.

TABLE-1
OPTIMIZATION OF MEMBRANE INGREDIENT

No.	Composition (%)				Slope (mV/decade)
	PVC	Plasticizer	DBDA15C4	STB	
1	33.0	DBP-64.0	3.0	–	22.0
2	32.6	BA-63.4	3.0	–	20.3
3	33.4	AP-63.7	2.9	–	19.9
4	32.8	NPOE-64.1	3.1	–	20.6
5	33.6	DBP-63.0	3.4	–	22.4
6	32.9	DBP-63.0	3.3	0.8	25.1
7	33.0	DBP-62.0	3.8	1.0	26.3
8	31.5	DBP-63.0	4.4	1.1	27.1
9	30.9	DBP-62.9	4.6	1.6	28.2
10	30.0	DBP-63.0	5.0	2.0	26.8

The nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of the ligands[25, 16]. Thus, the effect of different plasticizers is investigated on the ion-selective characteristics. As seen from Table-1, among AP, BA, NPOE and DBP, the dibutyl phthalate can act as superior plasticizer in the construction of the lead-selective electrode.

The optimization of the permselectivity of membrane sensors is known to be highly dependent on the incorporation of additional membrane component[25]. In fact, it has been demonstrated that the presence of lipophilic additives with negative charge can improve the potentiometric behaviour of certain cation-selective electrodes by reducing the ohmic resistance, improving the response behaviour, selectivity and catalyzing the exchange kinetics at the sample-membrane interface[27–30]. The data given in Table-1 showed that, in the presence of sodium tetraphenyl borate as a lipophilic additive (no. 6) sensitivity of the PVC membrane electrode increases in comparison with no. 1 in the absence of STB. The sensitivity of Pb^{2+}- selective electrode based on DBDA15C4 increases with the amount of STB in the composition of PVC membrane (no. 6 to no. 9).

The amount of DBDA15C4 as ionophore also influences the linear range, detection limit and the slope of calibration curve. However, membrane 9 with a PVC : DBP : DBDA15C4 : STB per cent ratio of 30.9 : 62.9 : 4.6 : 1.6 resulted in Nernstian behaviour of the membrane electrode over a wide concentration range.

The concentration of the internal solution $Pb(NO_3)_2$ in the electrode was changed from 1.0×10^{-4} mol/L to 1.0×10^{-1} mol/L and the potential response of the Pb^{2+} ion-selective electrode was obtained. The results do not show any significant difference in the corresponding potential response except in the intercept of the obtained Nernstian plots. A 1.0×10^{-2} mol/L lead nitrate solution was found quite appropriate for the smooth functioning of the electrode.

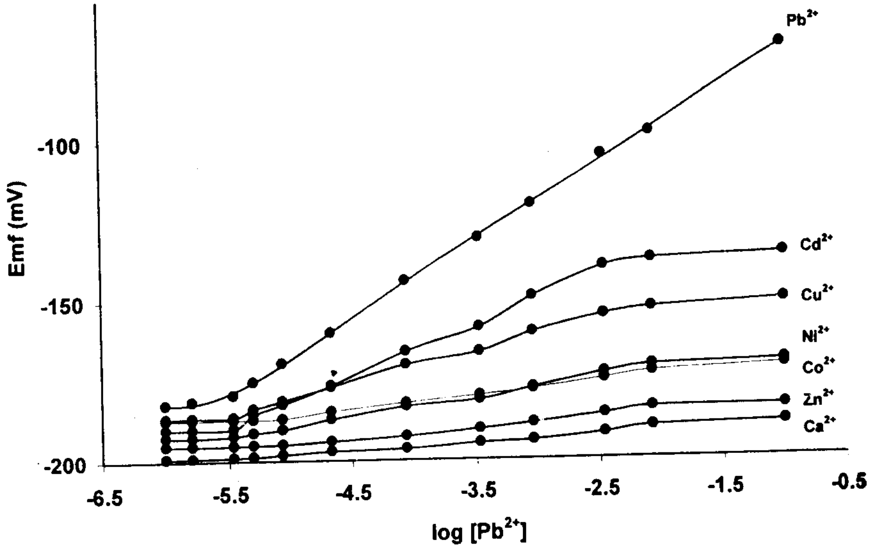


Fig. 2. Potential response of different ion-selective membrane based on DBDA15C4. Conditions: membrane ingredients, 33% PVC, 64% DBP, 3% DBDA15C4, internal solution, 0.01 mol/L M^{2+}.

The time of contact and concentration of equilibrating solution were optimized so that the sensor generated stable and reproducible potentials at relatively short response time. The optimum equilibration time in a 1.0×10^{-1} mol/L $Pb(NO_3)_2$ solution was *ca.* 12 h. The average time required to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of Pb^{2+} ion solution, each having a 10-fold difference in concentration was measured for the proposed ion-selective electrode. Thus, the obtained static response time of the membrane electrode was about 15 s over the entire concentration range. Potentials stayed constant for 5 min so that only a very slow divergence was recorded either from high to low concentration or *vice versa*. The lifetime of the membrane sensor was at least three months without any measurable divergence.

The critical response characteristics of the electrode were assessed according to IUPAC recommendation[28]. The emf response of the membrane at varying concentration of Pb^{2+} indicates a rectilinear range from 1.0×10^{-2} mol/L to 5.0×10^{-6} mole/L. The slope of the calibration curve was 28.2 ± 0.3 mV per decade of lead concentration at 25°C. The limit of detection was 3.5×10^{-6} mol/L, as evaluated from the intersection of two extrapolated segments of the calibration graphs.

The influence of pH on the response of the Pb^{2+} ion-selective electrode to 5.0×10^{-3} mol/L lead concentration over a pH range from 2.0 to 12.0 was studied. The results are shown in Fig. 3. As indicated, the membrane electrode can be suitably used in the range of pH 4.0–9.0. At low pH, the potentials decreased, showing that the membrane sensor responds to hydrogen ions. The observed drift at higher pH values could be due to the formation of some hydroxy complexes of Pb^{2+} in solution.

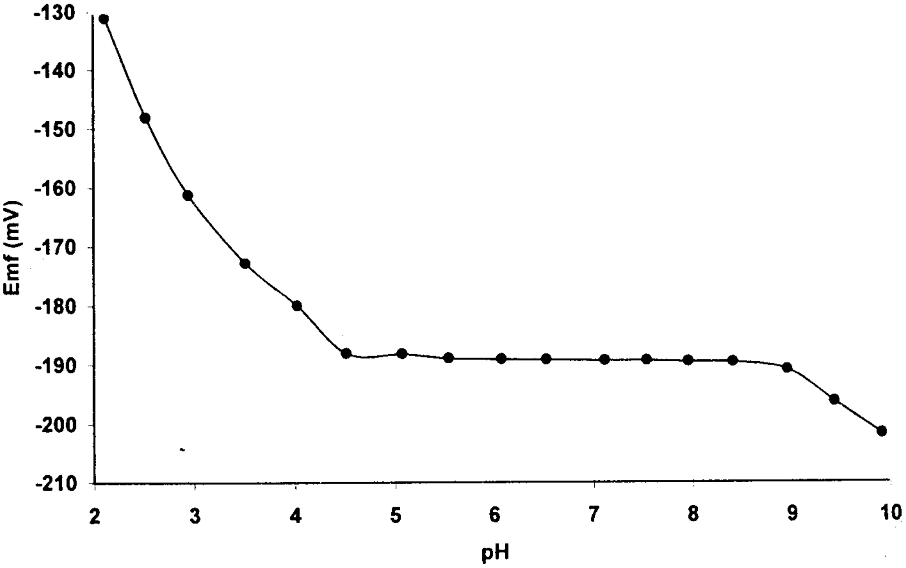


Fig. 3. Effect of pH of sample solution on the potential response of the Pb^{2+} ion-selective electrode.

The selectivity coefficient, $K^{Pot}_{A,B}$, is usually used for describing the influence of interfering ions on the response behaviour of ion-selective membrane electrodes. The recommended matched potential method (MPM) is used for measuring selectivity coefficients[29, 30]. A specified activity (concentration) of primary ion (A) is added to reference solution, according to the matched potential method (MPM)[31], the potential is measured. In another experiment, interfering ions (B) are successively added to an identical reference solution up to the time that the measured potential matches the one obtained before by adding primary ions. Therefore, the MPM selectivity coefficients, $K^{MPM}_{A,B}$, can be given by the ratio of resulting primary ion to interfering ion activity (concentration) $K_{A,B}^{MPM} = a_A/a_B$. The applied experimental conditions as well as the obtained values are given in Table-2. As seen, the selectivity coefficients of alkali and alkaline earth (except Ca^{2+} ion) and Ce^{3+} ions used are in the order of 10^{-4}, and therefore, they do not seem to interfere unless present at very high concentrations. For other cations, the selectivity coefficients are in the order of 10^{-3}, indicating that they would not significantly disturb the functioning of the Pb^{2+} ion-selective electrode.

TABLE-2
SELCTIVITY COEFFICIENTS OF VARIOUS INTERFERING IONS

Interfering ion	$K_{A,B}^{Pot}$	Interfering ion	$K_{A,B}^{Pot}$
Li^{2+}	2.8×10^{-4}	Co^{2+}	3.1×10^{-3}
Na^{+}	3.1×10^{-4}	Ni^{2+}	3.5×10^{-3}
K^{+}	2.9×10^{-4}	Cu^{2+}	3.8×10^{-3}
Mg^{2+}	4.1×10^{-4}	Zn^{2+}	2.7×10^{-3}
Ca^{2+}	1.1×10^{-3}	Cd^{2+}	8.7×10^{-3}
Sr^{2+}	4.8×10^{-4}	Ce^{3+}	1.1×10^{-4}
Ba^{2+}	6.2×10^{-4}	Mn^{2+}	1.5×10^{-4}

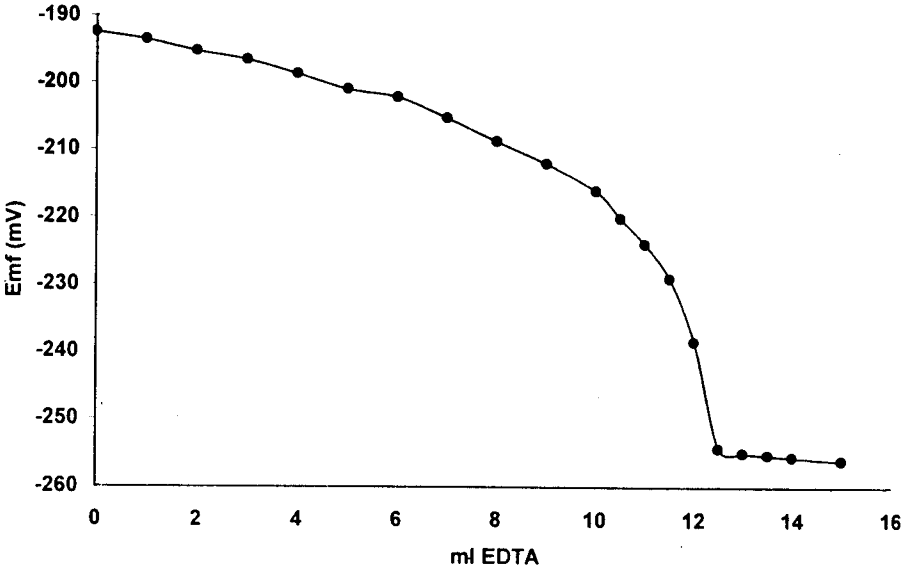


Fig. 4. Potential tiratian curve of 25.0 mL of 5.0×10^{-3} mol/L $Pb(NO_3)_2$ with 1.0×10^{-2} mol/L EDTA using proposed electrode as an indicator electrode.

In order to investigate the performance of proposed sensor as a working electrode in an electrochemical cell, it is used in the titration of Pb^{2+} solution (5.0×10^{-3} mol/L) with EDTA (1.0×10^{-2} mol/L) titrant solution. The resulting curve is shown in Fig. 4. As seen, the amount of Pb^{2+} in solution can be accurately determined with the electrode.

In Table-3 have been compared the analytical properties of the proposed electrode with some previously reported values for lead-selective electrodes. As seen, the Pb^{2+} ion-selective electrode based on DBDA15C4 shows a wide dynamic range and a suitable detection limit that is comparable with the other proposed sensor for lead ions. However, a short time response is an advantage of the new electrode.

TABLE-3

ANALYTICAL PROPERTIES OF SOME Pb^{2+} ION-SELECTIVE ELECTRODES

Ref.	Slope (mV/decade)	Linear range (mol/L)	Detection limit (mol/L)	Response time
18	–	2.0×10^{-6}–2.0×10^{-3}	–	30 s
32	29.2	2.0×10^{-5}–5.0×10^{-2}	1.0×10^{-5}	–
33	28.5	1.0×10^{-5}–1.0×10^{-2}	8.0×10^{-6}	–
34	29.8	2.5×10^{-6}–1.0×10^{-2}	1.5×10^{-5}	–
35	29.3	2.0×10^{-6}–1.0×10^{-2}	1.2×10^{-6}	45 s
36	29.0	1.0×10^{-5}–1.0×10^{-2}	6.0×10^{-6}	–
This work	28.2	5.0×10^{-6}–1.0×10^{-2}	3.5×10^{-6}	15 s

REFERENCES

1. C.J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
2. R.M. Izatt, G.A. Clark, J.S. Bradshow, J.D. Lamb and J. Christensen, *Sep. Purif. Methods*, **15**, 121 (1986).
3. H.C. Visser, D.N. Reinhoudt and F. De Jong, *Chem. Soc. Rev.*, 75 (1994).
4. D. Ammann, W.E. Morf, P. Anker, P.C. Meier, E. Pretsch and W. Simon, *Ion-selective Electrode Rev.*, **5**, 3 (1983).
5. M.A. Arnold, M.E. Meyerhoff, *Crit. Rev. Anal. Chem.*, **20**, 149 (1988).
6. J. Janata, *Anal. Chem.*, **64**, 196R (1992).
7. J. Janata, M. Jasowic and D.M. Devaney, *Anal. Chem.*, **66**, 207R (1994).
8. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.*, **85**, 271 (1985).
9. R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening, *Chem. Rev.*, **91**, 1721 (1991).
10. M.T. Lai and J.S. Shih, *Analyst*, **111**, 891 (1986).
11. Z. Brzozk, *Analyst*, **113**, 1803 (1988).
12. M.H. Mashhadizadeh and M. Shamsipur, *Anal. Chim. Acta*, **381**, 111 (1999).
13. M.F. Mousavi, N. Alizadeh, M. Shamsipur and N. Zohari, *Sensors and Actuators B*, **66**, 98 (2000).
14. M. Shamsipur and M.H. Mashhadizadeh, *Talanta*, **53**, 1065 (2001).

15. A.R. Fakhari, M.R. Ganjali and M. Shamsipur, *Anal. Chem.*, **69**, 3693 (1997).
16. M. Javanbakhat, M.R. Ganjali, H. Eshghi, H. Sharghi and M. Shamsipur, *Electroanalysis*, **11**, 81 (1999).
17. X. Yang, N. Kumar, H. Chi, D.B. Hibbert and P.W. Alexander, *Electroanalysis*, **9**, 549 (1997).
18. N. Tavakkoli and M. Shamsipur, *Anal. Lett.*, **29**, 2269 (1996).
19. D.R. Lynarn, L.G. Plantanida and J.F. Cole, Envirnmental Lead, Academic Press, New York (1975).
20. Y. Umezawa, CRC Handbook of Ion-Selective Electrode, CRC Press, Boca Raton, FL (1990).
21. J.M. Lehn, *Pure Appl. Chem.*, **49**, 857 (1977).
22. M. Shamsipur, M. Yousefi and M R. Ganjali, *Anal. Chem.*, **72**, 2391 (2000).
23. S. Kamata, K. Yamasaki, M. Higo, A. Bhale and Y. Fukunaga, *Analyst*, **113**, 45 (1988).
24. M.T. Lain and J.S. Shih, *Analyst*, **111**, 891 (1986).
25. E. Bakker, P. Buhlmann and E. Pretsch, *Chem. Rev.*, **97**, 3083 (1997).
26. X. Yang, N. Kumar, H. Chi, D.D. Hibbert and P.N.W. Alexander, *Electroanalysis*, **9**, 549 (1997).
27. R. Eugster, T.M. Gehring, W.E. Morf, U. Spichiger and W. Simon, *Anal. Chem.*, **63**, 2285 (1991).
28. IUPAC Analytical Chemistry Division, Commission on Analytical Nomenclature, Recommendations for Nomenclature of Ion-Selective Electrodes, *Pure Appl. Chem.*, **48**, 127 (1976).
29. Y. Umezawa, K. Umezawa and H. Sato, *Pure Appl. Chem.*, **67**, 507 (1995).
30. E. Bakker, *Electroanalysis*, **9**, 7 (1997).
31. ———, *Anal. Chem.*, **69**, 1061 (1997).
32. A. Abbaspour and F. Tavakol, *Anal. Chim. Acta*, **378**, 145 (1999).
33. M. Shamsipur and S. Sadeghi, *Anal. Lett.*, **33**, 17 (2000).
34. A. Rahmani, M. Barzegar, M. Shamsipur and M.F. Mousavi, *Anal. Lett.*, **33**, 2611 (2000).
35. A. Abbaspour and B. Khajeh, *Anal. Sci.*, **18**, 987 (2002).
36. M.R. Fathi, F. Darvich and M.R. Ganjali, *Anal. Lett.*, **33**, 1025 (2000).

(*Received*: 2 September 2003; *Accepted*: 3 March 2004) AJC-3364