

1-1-2000

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İŞILDAK, İBRAHİM (2000) "All Solid-State Contact Lead(II) Ion-selective PVC Membrane Electrode Using Dimethylene Bis(4-methylpiperidinedithiocarbamate) Neutral Ionophore," *Turkish Journal of Chemistry*. Vol. 24: No. 4, Article 10. Available at: <https://journals.tubitak.gov.tr/chem/vol24/iss4/10>

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All Solid-State Contact Lead(II) Ion-selective PVC Membrane Electrode Using Dimethylene Bis(4-methylpiperidinedithiocarbamate) Neutral Ionophore

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Received 14.04.2000

All solid-state contact PVC membrane electrodes for lead(II) ion were developed by using dimethylene bis(4-methylpiperidinedithiocarbamate) as neutral carrier and nitrophenyloctyl ether or dioctylsebacate as plasticizers. Response properties of the all solid-state contact PVC membrane electrode prepared with nitrophenyloctyl ether were better than those of the membrane electrode prepared with dioctylsebacate. The nitrophenyloctyl ether plasticized the all solid-state contact PVC membrane electrode and exhibited a good linear response of 30 mV/decade for lead(II) ion within the concentration ranges $0.1 - 5 \times 10^{-6}$ mol dm⁻³ lead(II) nitrate, good selectivity over alkali, alkali-earth and transition metal ions including copper(II) ion by a factor of at least 10^3 , 10^4 and 10^2 respectively, and a short response time. The useful pH range was between 2.0 and 6.0.

Key Words: All solid-state contact lead(II) ion-selective membrane electrode; Dimethylene bis(4-methylpiperidinedithiocarbamate) Ionophore

Introduction

The construction of ion-selective electrodes, mainly those based on neutral carriers in a solvent polymeric membrane, has increased in recent years¹. Myrocyclic ethers can form stable complexes with metal ions depending on many factors, e.g., relationship of ether cavity size and metal ion diameter, the member and the positioning of the ether oxygens, the type of the donor atom in the polyether ring, and the medium. Taking advantage of their ion discrimination ability, myrocyclic ethers have been shown to be useful neutral carriers for metal ion-selective electrodes, especially for alkali and alkali-earth metal ions²⁻⁴.

The lead ion-selective membrane electrodes were also examined by using myrocyclic ethers, in which each ligand has oxygen donor atoms^{5,6}. On the other hand, it is well known that the sulfur donor atom coordinates with transition metal ions to form metal complexes. With the use of thiacycrown ethers in which the oxygen donor atoms are partly replaced with sulfur, the preference over alkali and alkali-earth metal

ions can be expected to be reduced. However, several organo sulfur compounds such as thiocarbamates as neutral carriers have been shown to be useful for copper(II) or lead(II) ion-selective membrane electrodes⁷.

We have recently demonstrated the synthesis of the dithiocarbamate incorporating 4-methylpiperidine unit, which possesses strong complexes with transition and heavy metal ions, and the use of its mercury complex as an electroactive compound for the sulfite/hydrogen sulfite selective electrode⁸.

This paper reports an all solid-state contact PVC membrane electrode system with high selectivity for lead(II) ion. The membrane incorporates the lipophilic neutral ionophore of the dimethylene bis(4-methylpiperidinedithiocarbamate)₂ with either nitrophenyloctyl ether or dioctylsebacate as the plasticizers.

Experimental

Chemicals and Apparatus

Potassium salt of 4-methylpiperidinedithiocarbamic acid (4MPDC) was synthesized as previously described.⁸ High molecular mass poly(vinylchloride) (PVC), o-nitrophenyloctyl ether (NPOE), dioctylsebacate (DOS) and potassium tetrakis(p-chlorophenyl)borate (KTPClPB) were obtained from Fluka (Buchs, Switzerland). All other reagents and solvents used in this study were of Analar grade and were supplied by E. Merck (Darmstadt, Germany).

All the standard solutions of cations were prepared from their analytical reagent grade chemicals in deionized water, and then diluted to the desired concentrations.

The potentiometric measurements were performed with an Olivetti-286 home computer equipped with a custom built (Molspin instruments, Newcastle Upon Tyne, UK) analog/digital input/output board and electrode interface module controlled by laboratory written software.

All potential measurements were made with reference to a porous-plug double-junction saturated calomel electrode (Russell, Auchtermuchty, Fife, UK) in solutions without stirring.

Preparation of Dimethylene Bis(4-methylpiperidinedithiocarbamate)

The preparation of dimethylene bis(4-methylpiperidinedithiocarbamate), (DMB4MPDC), as the neutral ionophore, was carried out as described by Kamata et al.⁵ Potassium salt of 4MPDC acid (0.04 mol) was dissolved in ethanol (250 cm³), and ethylene dibromide (0.02 mol) was added slowly to the solution with refluxing and stirring for 8 h. The final compound, DMB4MPDC, which is shown in Figure 1, was obtained in white crystal form and recrystallized from ethanol, yield 4.2 g, 56%; IR (KBr), cm⁻¹; 676(ν_{c-s-c}), NMR (CDCl₃), δ (ppm); 0.93 (d 6H), δ (ppm); 2.1 (m 8H), δ (ppm); 1.85 (m 2H), δ (ppm); 3.80 (t 8H), δ (ppm); 4.10 (t 4H).

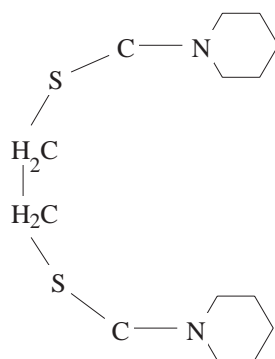


Figure 1. Neutral ionophore for lead(II) ion.

Preparation of All Solid-state Contact PVC Membrane Electrodes

The epoxy resin mixture used to bind the graphite in preparing the all solid-state contact of electrodes was made from epoxy and hardener in THF solvent in the proportion 1 : 0.5. The powdered graphite was mixed with epoxy resin mixture in the proportion 1 : 0.5. After mixing, the solution was left to stand about 20-30 min in air. When appropriate viscosity was attained, a shielded copper wire (approx. 0.5-1 mm in diameter and 5-10 cm long) end was polished and dipped in the solution several times to obtain a uniform coating, and then allowed to stand overnight in an oven at 40°C. The all solid-state contacts were dipped in membrane solution five times and then coated membranes were allowed to dry in air for at least 3 h. The ion-selective membrane solution comprised the electroactive material (4% w/w), NPOE or DOS plasticizers (67% w/w), KTpClPB (as the reducer of the membrane resistivity) (1% w/w) and PVC (28% w/w) dissolved in 5 cm³ THF. The prepared membrane electrodes were then soaked in a 1 × 10⁻² mol dm⁻³ solution of lead(II) nitrate for 20 h before use. Performance characteristics of the prepared electrodes were subsequently examined by measuring the emfs of lead(II) nitrate solutions within a concentration range of 0.1 to 1 × 10⁻⁷ mol dm⁻³. The electrochemical cell was as Cu/all solid-state contact PVC membrane/measured solution/reference electrode.

Results and Discussion

Potentiometric selectivity can be defined as the ability of an electrode to respond primarily to only one species in the presence of other species. Lead(II) ion-selective membrane electrodes based on PVC using macrocyclic ether derivatives, in which each ligand has oxygen donor atoms, reported so far do not exhibit sufficient electrode response and selectivity⁹ Ion-selective electrodes based on methylene bis(diisobutyldithiocarbamate) neutral carrier, and its derivatives, for lead(II) ion showed improved selectivity⁷. Sulfur donor atoms in the electrode membranes may bring about efficient electrode selectivity and sensitivity. Therefore in this study DMB4MPDC, which possesses sulfur donor atoms, was used as the neutral carrier for the lead(II) ion-selective PVC membrane electrode.

The response properties of the all solid-state contact lead(II) ion-selective PVC membrane electrodes prepared with NPOE and DOS were evaluated with lead(II) nitrate solutions of different concentrations (Fig 2). The membrane electrode consisting of NPOE showed a slope of 30 mV/decade with a straight line between 0.1 and 5 × 10⁻⁶ mol dm⁻³ of lead nitrate. When the lead(III) ion-selective PVC membrane

electrode prepared with DOS was used, a slope of 27 mV/decade was observed in the same concentration region. The properties of both electrodes are summarized in the Table 1.

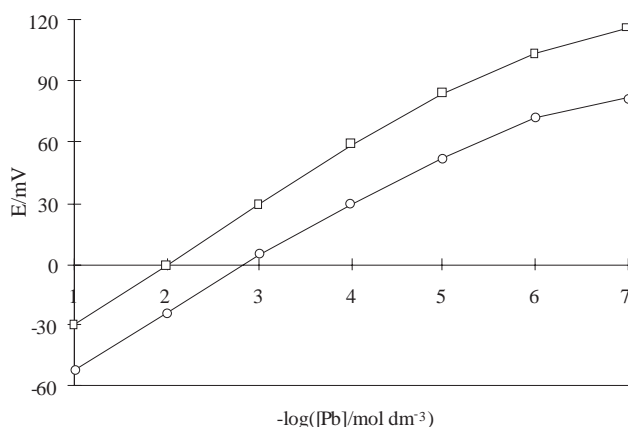


Figure 2. Emf response of the all solid-state contact NPOE (□) and DOS (○) plasticized PVC membrane electrodes to lead(II) ion in solution.

Table 1. Response properties of lead(II) ion-selective all solid-state contact PVC membrane electrodes prepared with NPOE and DOS as plasticizers.

Plasticizer	NPOE	DOS
Detection limit, mol dm ⁻³	3×10^{-7}	5×10^{-7}
Slope mV/decade	30	27
Linearity range, mol dm ⁻³	$0.1-5 \times 10^{-6}$	$0.1-1 \times 10^{-5}$
Response time, s	<15	<20
pH range*	2.0-6.0	2.5-6.0

*Measured in 1×10^{-3} mol dm⁻³ lead (II) nitrate solution

The response time of each electrode in $1 \times 10^{-5} - 1 \times 10^{-6}$ mol dm⁻³ solution was about 20 s, and in $0.1 - 1 \times 10^{-4}$ mol dm⁻³ solution it was less than 15 s. This indicates a fast rate of complex formation within the membrane phase at each concentration level. The electrode can be used for at least 2 months with practically unimpaired performance.

The pH dependence of the all solid-state contact lead(II) ion-selective PVC membrane electrode prepared with NPOE was also tested over the pH range 1-9 at a 1×10^{-3} mol dm⁻³ fixed lead(II) nitrate concentration (Fig. 3). The pH of the test solution was adjusted by adding small volumes of 0.1 mol dm⁻³ HNO₃ or 0.1 mol dm⁻³ NaOH, maintaining the ionic strength of the test solution approximately constant. In the pH range 2-6, the potential remained unchanged. At pH > 6, the potential increased, probably because of Pb(OH)₂ precipitation in solution, while, at pH < 2, the potential decreased indicating that the electrode responded to the hydrogen ion.

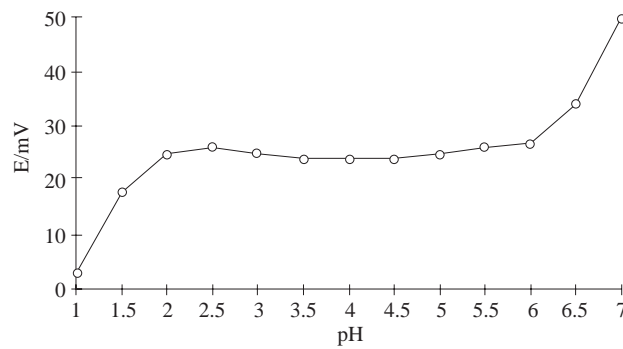


Figure 3. The effect of the pH on the response of the all solid-state contact NPOE-plasticized PVC membrane electrode for 1×10^{-3} mol dm^{-3} lead(II) ion.

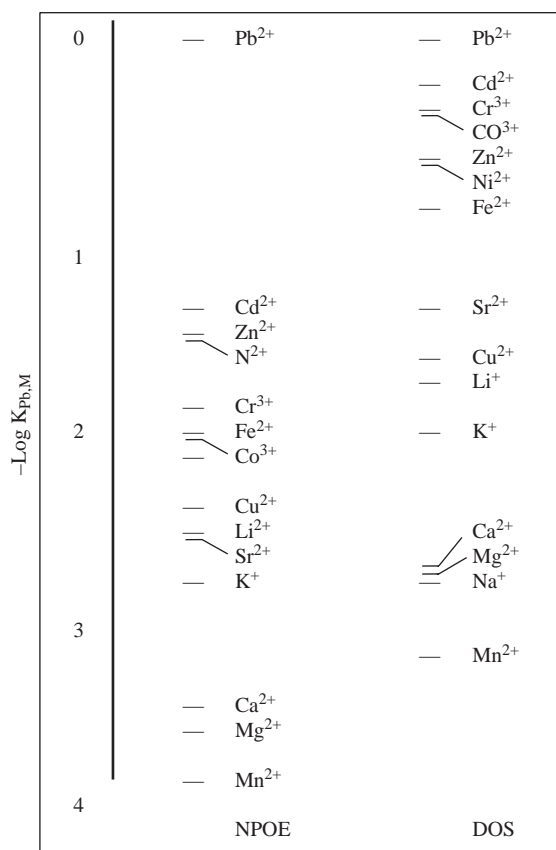


Figure 4. Selectivity coefficients of the all solid-state contact NPOE and DOS-plasticized lead(II) ion-selective PVC membrane electrode. The plasticizer is indicated at the bottom of the figure.

The selectivity coefficients obtained with these membranes are shown in Fig. 4. The potentiometric selectivity coefficients ($K_{Pb,M}$) of each electrode for various cations were determined using the mixed solution method, with a fixed concentration of interfering ion, M, for which the constant background concentrations were 0.1 mol dm^{-3} for alkali and alkali-earth metal ions and $1 \times 10^{-3} \text{ mol dm}^{-3}$ for heavy and transition metal ions in lead(II) nitrate solutions ranging from 0.1 to $1 \times 10^{-7} \text{ mol dm}^{-3}$. The target selectivity coefficients were calculated using the Nikolskij-Eisenman equation¹⁰ based on a contribution of less than 1%, by the

activity of the interferent ion, in comparison with the activity of the primary ion. The smaller its value, the higher the performance for the primary ion relative to the interfering ion, and the more selective the electrode.

From the selectivity coefficients in Figure 4, it can be proposed that the electrode membrane exhibited better selectivity for lead(II) ion than that of the other cations including the copper(II) ion. This suggests that the electrode membrane coordinates more strongly with the lead(II) ion. For the sake of convenience, I also tested the selectivity characteristics of the all solid-state contact membrane electrode conditioned in copper(II) nitrate solution. The electrode also exhibited better selectivity for lead(II) ion than that of copper(II) ion and others.

The all solid-state contact NPOE-plasticized lead(II) ion-selective membrane electrode showed better selectivity factors for different cations than that of the DOS-plasticized membrane electrode. This means that the coordination of lead(II) ion by the ionophore can also be related to the type of the plasticizer, which is usually added to such membranes. The reason may be greater interactions between π -electrons over nitrophenyl ring and π -electrons of sulfur donor atoms, which may result in the conformation of the electroactive compound being more coordinative within the membrane. The $-\log K_{Pb,M}$ values obtained for the all solid-state contact NPOE-plasticized membrane electrode compare reasonably well with the results of Kamata et al.⁷

It can be concluded that the complexing reagent containing nitrogen and sulfur atoms as coordination centers is a sufficiently selective ionophore in NPOE-plasticized PVC membranes for lead(II) ion.

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