Lead(II)-Selective Coated Graphite Electrode Based on Benzo-18-crown-6

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A lead(II)-selective coated graphite electrode based on benzo-18-crown-6 (B18C6) was prepared. This electrode with the membrane composition of 20 % dioctylphthalate, 55 % poly(vinyl chloride), 20 % carbon powder and 4 % benzo-18-crown-6, exhibited a near Nernstian response toward Pb(II) cation over a concentration range 1.0×10^{-5} to 1.0×10^{-1} M with a slope of 28.8 mV per decade and detection limit of 5.0×10^{-6} M. Furthermore, it showed a response time of 30 s and can be used for 3 months without any divergence in potentials. The useful pH range of this electrode is 1.5-5.0. To assess its analytical applicability, the constructed electrode was successfully applied as an indicator electrode in the potentiometric titration of Pb(II) ion solution with EDTA.

Key Words: Benzo-18-crown-6, Pb(II), Coated graphite electrode, Potentiometry.

INTRODUCTION

The need for the determination of lead and other heavy metals increased during the last few years because of growing environmental problems[1]. Lead, a toxic chemical pose a vast range of dangers to human's health. In addition to renal disease, cardiovascular effects and reproductive toxicity, lead may cause irreversible neuralgic damage. The increased industrial use of lead and its serious effect on human health have resulted in the extensive study of the electrochemical properties and preparation of lead sensors[2].

Common analytical methods for lead determination are furnace AAS and polarography. In spite of good sensitivities of these methods, they are very expensive and time consuming in practice. Furthermore, we need chemical sensors for monitoring purposes. Besides the necessity of very low detection limits, the other main problem is to reach good selectivity properties.

Ion selective electrodes (ISEs) for different cations have been widely used with polymeric membranes containing appropriate carriers (*i.e.*, ionophores). These ionophores have been examined so that they could be incorporated to form complexes with metal ions within the membrane. The quest for the new ligands capable of specific and effective molecular recognition of metal ions in carrier assisted membranes or polymeric membranes based on ion selective electrodes (ISEs) is a topic of current interest[3-5]. Macrocycles are a favoured class of compounds in this area as their complexes have high stability constants, lipophilicity to remain in the membrane phase and sufficient conformational flexibility for rapid ion exchange[6].

The chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometry. Currently a great deal of attention is being focussed on macrocyclic ligands because they play an important role in many aspects of chemistry, medicine and the chemical industry. Reviews on macrocyclic ethers[7-9] provide a good comprehensive survey of the literature. It shows that benzo-18-crown-6 (B18C6) has not been used as an ionophore in making Pb^{2+} selective electrode. Thus it was used as a potential ionophore for preparing lead selective electrode.

Ion-selective electrodes are established tools that are capable of directly determining the activities of many analytes[10,11]. A variety of ion-selective electrodes have been reported for determination of lead. In these electrodes different compounds in a PVC-based membrane are used for detection of Pb^{2+}[12-15]. Most of these electrodes have classical arrangement, *i.e.*, internal solution ion-selective electrodes (IS-ISEs). There are only a few solid-contact lead-selective electrodes have fabricated[16-19].

Due to extremely simple, inexpensive and easy preparation as well as possibility of elimination of the internal filling solution and the stability of potentials in coated graphite electrode (CGE), we report on the fabrication of new coated graphite liquid membrane electrode based on B18C6 for determination of Pb^{2+} ions. To the best of our knowledge, there is no previous report on a B18C6-based ion-selective membrane coated on graphite electrode for lead ion.

EXPERIMENTAL

Reagent grade benzo-18-crown-6 (B18C6), dibutylphthalate (DBP), dioctylphthalate (DOP), tetrahydrofuran (THF) and high molecular weight poly(vinyl chloride) were purchased from E. Merck (Germany) and used as received. The nitrate salts of all the cations used (all from Merck) were of analytical grade and used without any further purification. The solutions of metal salts were prepared in doubly distilled water and standardized whenever necessary.

Electrode preparation: To prepare the coated graphite electrodes, spectroscopic grade graphite rods 10 mm long and 3 mm in diameter were used. A shielded copper wire was glued to one end of the graphite rod and the electrode was sealed into the end of a poly(vinyl chloride) tube of about the same diameter with epoxy resin. The working surface of the electrode was polished with fine alumina slurries on a polishing cloth, sonicated in distilled water and dried in air.

Membrane solution was prepared by thoroughly dissolving ionophore, powdered poly(vinyl chloride), plasticizer and carbon powder in 5 mL of tetrahydrofuran (composition given in Table-1). The resulting clear solution was evaporated slowly at room temperature until an oily concentrated mixture was obtained. The polished graphite electrode was then coated with the prepared membrane solution and the solvent was allowed to evaporate at room temperature. A membrane was formed on the graphite surface and the electrode was allowed to stabilize overnight.

Conditioning of membranes and potential measurements: The ratio of membrane ingredients, time of contact and concentration of equilibrating solution was optimized so that the potentials recorded were reproducible and stable. The electrode was equilibrated for 2 days in a 1.0×10^{-1} M Pb(NO$_3$)$_2$ solution.

The potentials were measured by varying the concentration of Pb(NO$_3$)$_2$ in test solution in the range 1.0×10^{-6} to 1.0×10^{-1} M. Standard Pb(NO$_3$)$_2$ solution was obtained by gradual dilution of 0.1 M Pb(NO$_3$)$_2$ solution. The emf measurements with the coated graphite electrode were carried out on a Metrohm potentiometer at 25 ± 0.1 ºC using saturated Ag/AgCl electrode as reference electrode with the following cell assembly:

CGE‖Test solution‖Ag/ AgCl‖KCl(satd.)

Activity coefficients were calculated according to the Debye-Huckel procedure[20].

RESULTS AND DISCUSSION

Optimization of membrane composition: Various studies have shown that the composition of membrane affect the performance characteristics significantly. Thus, we investigated the influence of membrane composition on the potential response for lead(II) sensor. The results are summarized in Table-1. Thus the results of varying the amount of membrane ingredients have shown that the best performance was obtained by the coated graphite electrode No. 2 having composition of its ingredients in the ratio B18C6: PVC: DOP:C as 4:55:20:20 (%, w/w).

The electrodes containing dioctylphthalate generally showed better potentiometric responses, *i.e.* better sensitivity and linearity of the calibration plots. It seems that dioctylphthalate, as a low polarity compound among other plasticizers provides more appropriate conditions for incorporation of the highly liphophilic Pb^{2+} ion into the membrane. Therefore, dioctylphthalate was used as a suitable plasticizer for further studies.

It was also observed that the potentiometric response of the electrode toward Pb^{2+} depends on the concentration of the ionophore incorporated within the membrane. Increasing the amount of the ionophore up to 4 % worsened the electrode response, most probably due to saturation of the membrane or due to some non-uniformity of the membrane.

Potentiometric response characteristics: The critical response characteristics of the sensor were assessed in accordance with the IUPAC recommendations[21]. The calibration graph of this sensor is given in Fig. 1 which shows that this electrode gives a linear response to the activity of Pb^{2+} cation over the working concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with a Nernstian slope of 28.8 ± 0.1 mV decade^{-1} of this heavy metal cation. The limit of detection, as determined from the intersection of the two segments of the calibration graph, was 5.0×10^{-6} M. The S.D. of four replicate potential measurements was ± 0.1 mV.

Effect of pH: The dependence of the potentiometric response of the proposed ISE on the pH value of the Pb^{2+} solution was tested at Pb^{2+} concentrations (1.0×10^{-3} M) over the pH range between 0.5 and 9. It is seen from Fig. 2 that the potential response remains almost constant over the pH range from 1.5 to 5.

As a result, this range can be taken as the working pH range of the proposed electrode The declined potential at higher pH values may be ascribed to the formation of some hydroxy complexes of Pb^{2+} such as Pb(OH)$^+$ and Pb(OH)$_2$, leading to a decreased Pb^{2+} concentration, while at lower pH could be reasonably related to the response of the sensor to the hydrogen ions.

Response time: The response time of an ion-selective electrode is an important factor in analytical application. In this study, the practical response time was determined by measuring the time required to achieve a steady potential in Pb^{2+} solution with three concentrations of 1.0×10^{-2}, 1.0×10^{-3} and 1.0×10^{-4} M. It is found that the response time is 30 s.

TABLE-1
OPTIMIZATION OF MEMBRANE INGREDIENTS

No.	Composition (wt%)					Response time (s)	Slope (mV/decade)	Linear range (M)
	PVC	B18C6	DBP	DOP	Carbon powder			
1	55	4	20	–	20	60	27.2 ± 0.2	1.0×10^{-5} to 10^{-1}
2	55	4	–	20	20	30	28.8 ± 0.1	1.0×10^{-5} to 10^{-1}
3	53	6	–	20	20	50	19.4 ± 0.3	1.0×10^{-5} to 10^{-1}
4	53	6	20	–	20	70	13.4 ± 0.1	1.0×10^{-4} to 10^{-1}
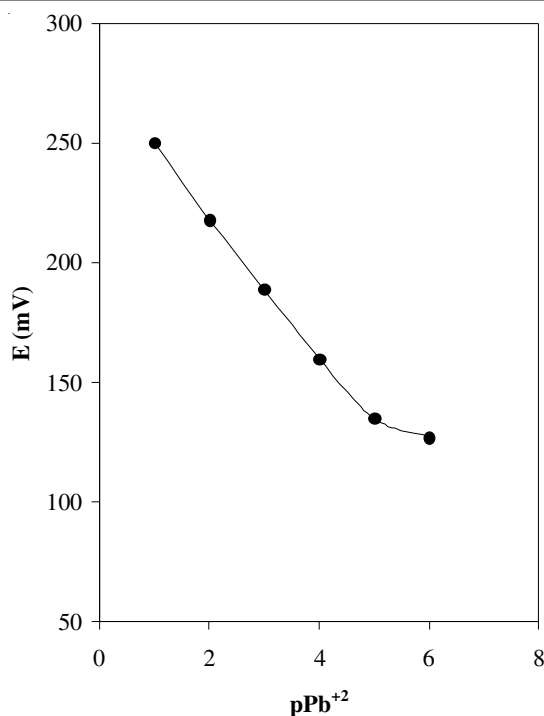
Fig. 1. Calibration graph for the Pb^{2+} ion-selective electrode
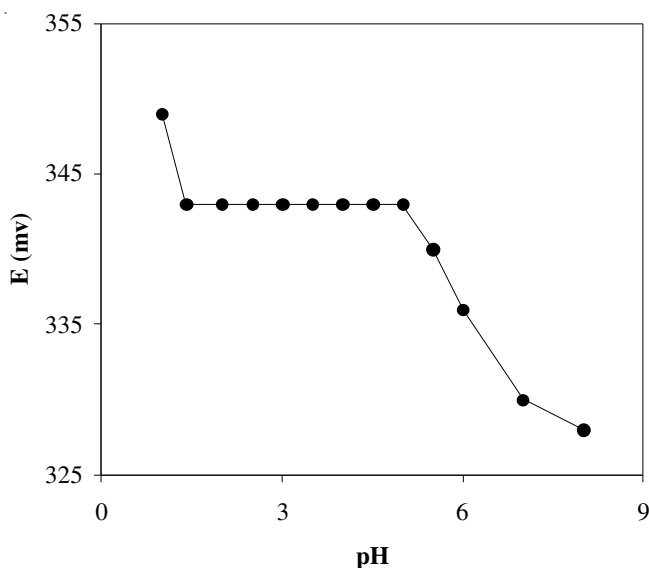
Fig. 2. Effect of pH of test solution on the potential response of the Pb^{2+} ion-selective electrode

Lifetime of the electrode: The major factor limiting the lifetime of the ion selective membrane in potentiometric measurements is the loss of components into the contacting aqueous solutions. For continuous monitoring with membranes electrodes, especially ionophore must be sufficiently lipophilic to ensure a long and stable response of the ion-selective electrode[22]. The lifetime of the electrode was studied by performing periodic calibration with standard solutions. During this period, the electrode was daily used for extended period (2 h day^{-1}) and from the calibration plots working concentration range, slopes and detection limit were measured. It was found that the electrode worked well over the period of 3 months without showing any significant divergence in performance characteristics.

Selectivity: The selectivity behaviour 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[23-26]. The potential measured in solutions containing a fixed amount of Pb^{2+} ion (1.0×10^{-3} mol L^{-1}) and varying amounts of the interfering ions (M^{n+}) and the potentiometric selectivity coefficients ($K_{Pb,M}^{pot}$) were evaluated according to

$$K_{Pb,M}^{pot} a_M^{2/n} = a_{Pb}\left(\frac{\exp(E_2 - E_1)F}{RT}\right) - a_{Pb} \qquad (1)$$

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 $K_{Pb,M}^{pot}$ values for diverse ion can be evaluated from the slope of the linear graph of $a_{Pb}\{\exp(E_2 - E_1)F/RT\} - a_{Pb}$ vs. $a^{2/n}$ and the resulting K_{Pb}^{pot} values are summarized in Table-2.

TABLE-2 SELECTIVITY COEFFICIENTS OF VARIOUS INTERFERING IONS	
Interfering ion	Selectivity coefficient
Cd^{2+}	7.4×10^{-4}
Fe^{2+}	3.9×10^{-4}
Cu^{2+}	9.6×10^{-4}
Zn^{2+}	1.0×10^{-2}
Co^{2+}	3.0×10^{-2}
Ni^{2+}	2.7×10^{-2}
Ca^{2+}	3.1×10^{-2}
Mg^{2+}	5.6×10^{-2}
Na^+	4.2×10^{-1}
K^+	1.1×10^{-1}
Ag^+	1.1×10^{-1}

The data given in this table present that the selectivity coefficients of the proposed Pb^{2+} membrane sensor for all the tested divalent ions are 5.6×10^{-2} or smaller, which seems to indicate negligible interferences in the performance of the electrode assembly. The selectivity coefficients for all the univalent ions are in the order of 4.2×10^{-1} or smaller. However, it should be noted that such deceptively larger coefficients arise from the term $a^{2/n}$ in eqn. 1, the smaller the charge of interfering ion, n, the larger the selectivity coefficient, K_{Pb}^{pot}.

It should be noted that an even more severe interference effect from these cations on the functioning of other Pb^{2+} ion selective electrodes has been reported in the literature[27-29].

Comparison of the electrode performance with other electrodes: Table-3 summarized the comparison of the response characteristics of the proposed membrane electrode with the corresponding values previously reported for 8 randomly taken lead ion-selective membrane electrodes based on different ionophores[30-37]. As can be seen from the Table-3, many of the reported lead-selective electrodes respond to lead with less than linear range and lifetime also near Nernstian slope respect to proposed lead-selective electrodes.

TABLE-3
COMPARISON OF PERFORMANCE CHARACTERISTICS OF THE PROPOSED
ELECTRODE WITH PREVIOUS LEAD(II)-SELECTIVE ELECTRODE

Working concentration range (M)	Slope (mV/decade)	Detection limit (M)	Response time (s)	Life time (month)	Ref.
$5.0 \times 10^{-5} - 5.0 \times 10^{-1}$	28.9	1.0×10^{-6}	30	3	[30]
$1.0 \times 1 0^{-5} - 1.0 \times 10^{-1}$	30.0	4.0×10^{-6}	45	3	[31]
$5.0 \times 10^{-5} - 1.0 \times 10^{-2}$	29.3	2.8×10^{-5}	10	10	[32]
$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	28.0	1.4×10^{-6}	17	56	[33]
$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	28.5	8.0×10^{-6}	20	2	[34]
$2.0 \times 10^{-5} - 5.0 \times 10^{-2}$	29.2	1.0×10^{-5}	240	–	[35]
$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	26.8	1.0×10^{-5}	10	–	[36]
$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	29.4	5.0×10^{-6}	10-20	–	[37]
$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	28.8	5.0×10^{-6}	30	3	This work

Analytical application: The electrode can be useful as an indicator electrode in titration of Pb^{2+} with EDTA. The results of the titration 20 mL of 5.0×10^{-3} mol L^{-1} solution of Pb^{2+} ion with a 1.0×10^{-2} mol L^{-1} EDTA solution at pH 5.0 are shown in Fig. 3. The potential of the electrode was decreased upon addition of EDTA. It is clear that the concentration of lead(II) ion in solution can be accurately determined from the resulting neat titration curve providing a sharp end point.
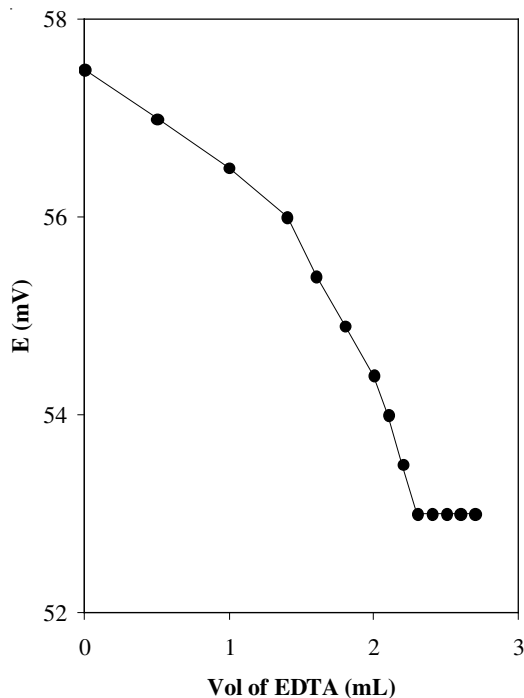

Fig. 3. Potentiometric titration curve of 20 mL of 5.0×10^{-3} mol L^{-1} of Pb^{2+} solution with 1.0×10^{-2} mol L^{-1} EDTA at pH 5.0 using the proposed electrode as an indicator electrode

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