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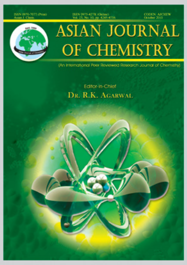

Lead(II) Ion Selective Electrode with PVC Membrane Based on 5,5'-Dithio*bis*-(2-Nitrobenzoic Acid) as Membrane Carrier

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The characteristics of PVC membrane for lead(II) ion-selective electrode based on 5,5'-dithio*bis*-(2-nitrobenzoic acid) as carrier was studied. The electrode displays an excellent Nernstian response for Pb^{2+} over a wide concentration range (1.0×10^{-5}~1.0×10^{-2} M). It has a rapid response time and can be used for at least 3 months without any divergence in potentials. The proposed electrode revealed good selectivities for Pb^{2+} over a wide variety of other metal ions in a pH range of 2.2-7.0. It was used as an indicator electrode in potentiometric titration of sulfate ions with a lead ion solution.

Key Words: Lead ion selective electrode, PVC membranes, Potentiometry, 5,5'-Dithio*bis*-(2-nitrobenzoic acid).

INTRODUCTION

During the last two decades, the introduction of new ion-selective membrane electrodes has developed the potentiometric measurements significantly. Extensive research work has been directed towards preparation of molecular carriers possessing electrical neutrality, lipophilic character and capability to selectively and reversibly bind given metal ions to induce a selective permeation of one type of metal ion through the membranes of electrodes[1]. Since the first introduction of the valinomycin based potassium ion-selective electrode[2], there has been an increasing interest on the development of poly(vinyl chloride) (PVC) membrane electrodes based on such suitable neutral ionophores[1,3]. In recent years, the electrochemical properties and preparation of several new lead ion selective membrane electrodes have been reported by using a variety of ion carriers[4-9]. Besides the solid-state membranes[10-15] and liquid ion-exchange membranes[16,17], there has been recently increasing interest to the use of ionophore ligands as sensing materials for neutral carrier type lead ion selective electrodes, mainly due to the unique selectivities of these compounds[18-22]. In this paper we report PVC membrane electrodes based on 5,5'-dithio*bis*-(2-nitrobenzoic acid) (DTBNBA) as a suitable ion carrier which exhibit significantly high selectivity to Pb^{2+} ions.

EXPERIMENTAL

Reagent grade dibutyl phthalate (DBP), oleic acid, 5,5'-dithio*bis*-(2-nitrobenzoic acid) (DTBNBA) and tetrahydrofuran (THF) were purchased from Merck and used as received. The nitrate salts of the cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Triply distilled deionized water was used throughout.

Electrode preparation: PVC membrane used was fabricated using the method as followed, using the following compositions:35 mg of powdered PVC, 50 mg of plasticizer *o*-nitrophenyl octyl ether, 20 mg of additive oleic acid and 10 mL of THF, 10 mg of ionophore 5,5'-dithio*bis*-(2-nitrobenzoic acid) and the solution was added to the above mixture and mixed well, the resulting mixture was transferred into a glass dish of 2 cm diameter. The THF was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s and then a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out of the solution and kept at room temperature for 1 h. The tube was filled with internal filling solution (1.0×10^{-3} M $Pb(NO_3)_2$ + 1.0×10^{-3} M NH_4Cl). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M solution of lead nitrate. A silver/silver chloride coated wire was used as an internal reference electrode.

EMF measurements: All EMF measurements were carried out with the following assembly: Ag-AgCl/internal solution (1.0×10^{-3} M $Pb(NO_3)_2$ and 1.0×10^{-3} M KCl)/PVC membrane/test solution/Ag-AgCl, KCl (saturated). A corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 ºC. The EMF observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. Activities were calculated according to the Debye-Huckel procedure[23].

RESULTS AND DISCUSSION

Because of its negligible solubility in water and the existence of two donating sulphur atoms in its structure, 5,5'-dithio*bis*-(2-nitrobenzoic acid) seemed to be a potential ion carrier for soft heavy metal ions in the PVC membrane electrodes. Thus, in preliminary experiments, it was used to prepare PVC membrane ion-selective electrodes for a wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. The potential responses of these electrodes are illustrated in Fig. 1. As seen, among these cations, those of hard acid character (*i.e.* alkali, alkaline earth and UO_2^{2+} ions[22]) show negligible responses, due to their weak interactions with the sulphur atoms of the carrier as soft bases.

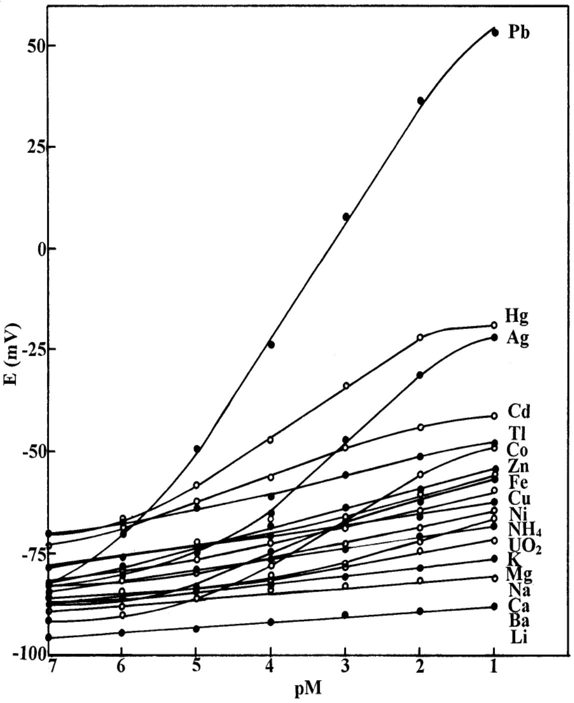

Fig. 1. Potential response of various ion-selective electrodes based on 5,5'-dithio*bis*-(2-nitrobenzoic acid). Membrane composition: 33 % PVC; 42 % dibutyl phthalate; 9 % 5,5'-dithio*bis*-(2-nitrobenzoic acid); 16 % oleic acid

On the other hand, the metal ions of soft acid character (*i.e.* Tl^+, Ag^+, Cd^{2+}, Hg^{2+} and especially Pb^{2+} [22]) show the most sensitive potential response in the series, among which Pb^{2+} provides the most suitable ion-selective electrode. It is thus obvious that the Pb^{2+} ions are more easily attracted to the PVC-5,5'-dithio*bis*-(2-nitrobenzoic acid) membrane which results in a Nernstian potential- concentration response over a wide range.

Since the sensitivities and selectivities obtained for a given ionophore depend significantly on the membrane ingredients and the nature of solvent mediators and additives used[18,23-25], we investigated the influence of membrane composition on the potential response of the Pb^{2+} sensor. The results are summarized in Table-1. It is seen that the increased amount of ionophore, up to a value of 9 %, results in the best sensitivity and linear range, although the slope of emf *versus* log concentration plot in this case is about one-third of the expected Nernstian value. However, addition of 16 % oleic acid will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a Nernstian behaviour. It is well known that the presence of lipophilic anions in cation-selective membrane electrodes not only diminishes the ohmic resistance[26] and enhances the response behaviour and selectivity[27], but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes[3]. In general, the thickness and hardness of the membrane depend upon the amount of PVC used. At higher PVC content, the membrane becomes too dense, which makes the transport of cations into the membrane more difficult and results in the increased resistance. A decrease in PVC causes an increased linear range of the electrode. However, at lower PVC content, the membrane becomes mechanically weak and swells up easily in aqueous solution. Therefore, the optimum composition of membrane No. 10 was used for further studies.

The concentration of the internal solution $Pb(NO_3)_2$ in the electrode was changed from 1.0×10^{-3} M to 1.0×10^{-5} M and the potential response of the Pb^{2+} selective electrode was obtained. It was found that the variation of the concentration of the internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of the reference $Pb(NO_3)_2$ solution is quite appropriate for smooth functioning of the electrode system. The

TABLE-1
OPTIMIZATION OF MEMBRANE INGREDIENTS

Membrane number	Composition (%)				Slope (mV per decade)	Linear range (M)
	PVC	Dibutyl phthalate	5,5'-dithio*bis*-(2-nitrobenzoic acid)	Oleic acid		
1	70	30	-	-	0	-
2	68	29	3	-	6	5.0×10^{-3}–1.0×10^{-2}
3	67	28	5	-	9	5.0×10^{-3}–1.0×10^{-2}
4	65	28	7	-	10	5.0×10^{-3}–1.0×10^{-2}
5	64	27	9	-	11	5.0×10^{-3}–1.0×10^{-2}
6	61	26	13	-	11	5.0×10^{-3}–1.0×10^{-2}
7	58	25	9	8	24	5.0×10^{-3}–1.0×10^{-2}
8	50	25	9	16	28	7.0×10^{-5}–1.0×10^{-2}
9	42	33	9	16	29	5.0×10^{-5}–1.0×10^{-2}
10	33	42	9	16	29	6.0×10^{-6}–1.0×10^{-2}
11	25	50	9	16	29	4.0×10^{-6}–1.0×10^{-2}
12	58	25	-	17	0	8.0×10^{-6}-1.0×10^{-2}

PVC-based membrane of 5,5'-dithio*bis*-(2-nitrobenzoic acid) generates stable potentials when placed in contact with Pb^{2+} solutions. The critical response characteristics of the Pb^{2+} selective electrode were assessed according to IUPAC recommendations[28]. The emf response of the membrane at varying activity of Pb^{2+} (Fig. 1) indicates a rectilinear range from 1.0×10^{-2} to 4.0×10^{-6} M. The slopes of the calibration curves were 29.0 ± 0.3 mV per decade of lead concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 1.5×10^{-6} M.

The average time required for the Pb^{2+} selective electrode to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of lead ion solutions, each having a 10-fold difference in concentration, was measured. The static response time thus obtained was 70s for concentration $\leq 1.0 \times 10^{-3}$ M and potentials stayed constant for more than 5 min, after which only a very slow divergence was recorded. The standard deviation of ten replicate measurements was ± 0.3 mV. The sensing behaviour of the membrane remained unchanged when the potentials recorded either from low to high concentrations or *vice versa*. The ion-selective membranes prepared could be used for at least 3 months without any measurable divergence.

The pH dependence of the membrane electrode was tested over the pH range 2-11 at Pb^{2+} concentration of 1.0×10^{-3} M and the results are shown in Fig. 2. As seen, the potential was constant from pH 2 to 7, beyond which a gradual drift was observed. The observed drift at higher pH values would be due to the ionization of the ionophore and or the formation of some hydroxy complexes of Pb^{2+} in solution.

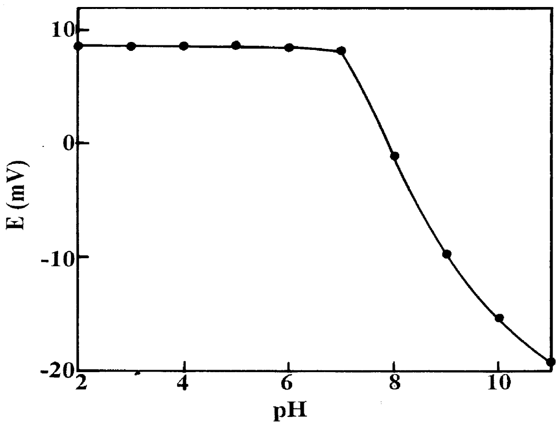

Fig. 2. Effect of pH of test solution on the potential response of the Pb^{2+} selective electrode

In order to investigate the selectivity of the proposed Pb^{2+} selective electrode, perhaps as the most important characteristic of a membrane sensor, its response was examined in the presence of various foreign ions. The potentiometric selectivity coefficients (K^{pot}_{Pb}) were evaluated graphically by the mixed solution method[29,30] from potential measurements on solutions containing a fixed amount of Pb^{2+} (1.0×10^{-3} M) and varying amounts of the interfering ions (M^{n+}) according to the equation:

$$K^{pot}_{Pb}\, a^{1/n}_{M} = a_{Pb}\{\exp[(E2-E1)F/RT]\}-a_{Pb} \qquad (1)$$

where, E1 and E2 are the electrode potentials for the solution of Pb^{2+} alone and for the solution containing interfering ions (M^{n+}) and Pb^{2+} ions. According to eqn. (1), the K^{pot}_{Pb} values for diverse ions can be evaluated from the slope of the graph of $a_{Pb}\{\exp[(E2-E1)F/RT]\}-a_{Pb}$ *versus* $a^{1/n}_{M}$.

The resulting values are summarized in Table-2. As can be seen, with the exception of Ag^+, Cu^{2+}, Cd^{2+} and Hg^{2+}, for all diverse ions used, the selectivity coefficients are in the order of 10^{-3} or smaller, indicating that they would not significantly disturb the functioning of the Pb^{2+} selective membrane. However, Ag^+, Cu^{2+}, Cd^{2+} and Hg^{2+} with the selectivity coefficients in order of 10^{-2} reveal some reversible interfering effect in the Pb^{2+} selective electrode functioning. It should be noted that an even more severe interference effect from these cations on the functioning of other Pb^{2+} selective electrodes has been reported in the literature[16,17,31]. The proposed Pb^{2+} membrane electrode was found to work well under laboratory conditions. It was successfully applied to the titration of a Pb^{2+} solution with sodium chromate and the resulting titration curve is shown in Fig. 3. As seen, the amount of Pb^{2+} in solution can be accurately determined with the electrode. The electrode was also applied to the direct measurement of Pb^{2+} in local spring waters from the Calsimine lead and zinc mines (Dandi, Zanjan, Iran). The water samples were adjusted to pH of about 5.5 using 0.01 M ammonium nitrate buffer and their potentials were measured by direct potentiometry. The results obtained were compared with those from atomic absorption spectrometric (AAS) analysis (Table-3). The Zn^{2+} and Cd^{2+} contents of the water samples were also determined by atomic absorption spectrometric. As seen, the agreement is good and we conclude that the membrane electrode may have applications in the environmental monitoring of Pb^{2+}.

TABLE-2
SELECTIVITY COEFFICIENTS OF DIVERSE IONS

Diverse ion	K^{pot}_{Pb}	Diverse ion	K^{pot}_{Pb}
Li^+	1.5×10^{-4}	Co^{2+}	4.4×10^{-3}
Na^+	1.4×10^{-4}	Ni^{2+}	3.0×10^{-3}
K^+	1.3×10^{-4}	Cu^{2+}	9.1×10^{-3}
NH_4^+	1.4×10^{-4}	Zn^{2+}	7.8×10^{-3}
Ag^+	1.0×10^{-2}	Cd^{2+}	1.2×10^{-2}
Tl^+	2.9×10^{-3}	Hg^{2+}	4.3×10^{-2}
Mg^{2+}	2.7×10^{-4}	UO_2^{2+}	9.9×10^{-4}
Ca^{2+}	3.7×10^{-4}	Fe^{3+}	1.2×10^{-3}
Ba^{2+}	3.9×10^{-4}	–	–

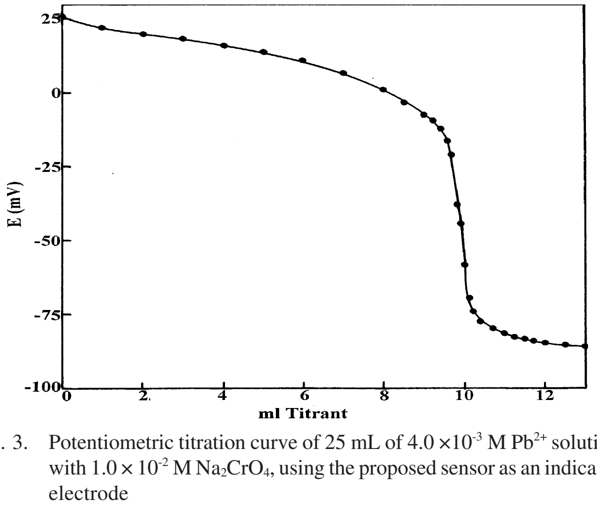

Fig. 3. Potentiometric titration curve of 25 mL of 4.0×10^{-3} M Pb^{2+} solution with 1.0×10^{-2} M Na_2CrO_4, using the proposed sensor as an indicator electrode

TABLE-3
ANALYTICAL DATA FOR THE WATER SAMPLES

Method	Ion	x^{-} (ppm)	S.D. (n = 4)	RSD (%)
AAS	Zn	21.7	0.4	1.8
	Cd	1.8	0.1	5.5
	Pb	14.1	0.3	2.1
ISE(direct)	Pb	14.9	0.7	4.7
ISE(titration)	Pb	14.1	0.6	4.2

Conclusion

The membrane electrode incorporating 5,5'-dithio*bis*-(2-nitrobenzoic acid) as an ion carrier can be used in the development of a PVC-based lead ion-selective electrode. The electrode responds to Pb^{2+} in a Nernstian fashion and displays a good selectivity and detection limit. The electrode is characterized by a relatively fast response, reasonable long-term stability and responsive potential stability. The proposed Pb^{2+} -membrane electrode was applied to the titration of Pb^{2+} solution with sodium chromate as well as the direct determination of lead in water samples.

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