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Lead ion-selective electrodes based on polyphenylenediamine as unique solid ionophores

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ABSTRACT

A novel membrane electrode for Pb(II) ion detection based on semi-conducting poly(*m*-phenylenediamine) microparticles as a unique solid ionophore was fabricated. The electrode exhibited significantly enhanced response towards Pb(II) over the concentration range from 3.16×10^{-6} to 0.0316 M at pH 3.0–5.0 with a low detection limit of 6.31×10^{-7} M, a high sensitivity displaying a near-Nernstian slope of 29.8 mV decade^{-1} for Pb(II). The electrode showed a long lifetime of 5 months and a short response time of 14 s. A systematical investigation on the effect of anion excluder and various foreign ions on the selectivity of the electrode by a fixed interference method suggests that all other metal ions hardly ever interfere with the determination of Pb(II) except high concentration Hg(II). The electrode was successfully used as an indicator electrode in the potentiometric titration of Pb(II) with EDTA. Furthermore, the electrode has been used to satisfactorily analyze four types of real-world samples like spiked human urine, spiked tap water, and river water containing interfering ions like Na(I), Ca(II), Mg(II), Zn(II), Pd(II), Fe(III), K(I), Cu(II) and Hg(II) up to 8.04×10^{-4} M, demonstrating fast response, high selectivity, good recovery (96.6–121.4%), good repeatability (RSD 0.31–6.45%), and small relative error (5.0%).

1. Introduction

Lead is hazardous but ubiquitous in the environment, which tends to accumulate in the bone structure when ingested in levels exceeding the natural elimination rate of about 300 μg Pb per day. The determination of the lead concentration in water seems to be urgent for living and production [1–3]. Because of various advantages including simple instrumentation, low cost, rapid response, and high selectivity, the ion-selective electrode (ISE) based on polymeric membranes containing ionophores is well known as a useful tool for clinical, chemical and environmental analyses [4–7]. During last decade, the potentiometric and voltammetric sensors based on the ionophores with high selectivity for specific metal ions have been developed to detect respective metal ions [7–9]. Unlike alkali metal and alkaline earth ions, the heavy metal ions with a consanguineous attraction connection with the soft coordination centers such as N, S, Se, P have been reported, so the function groups containing N, S, Se, P atoms in thioether, thiaayloxy, arylthiaalkoxy, pyridyl and benzothiazoyl groups would significantly improve the selectivity of the ionophore to the heavy metal ions [8,9]. Crown-ether [10–12], calixarenes [13–15], chalcogenide glasses [16], Schiff base [17–19], anthraquinone [20], derivatized tetrapyrazole [21,22], benzyl sulfide [23], piroxicam [24], dibenzyl phosphate [25], capric acid [26], aquatic humic substances [27], bisthioureas [28], and their derivatives as ionophores have been used for lead-ISEs.

Recently, oxidative conducting polymers from aromatic amines such as polyaniline were reported as ion carriers in ISEs for determining anions such as dodecyl sulfate [29] and dodecylbenzene sulfate anions [30]. Although the research of the aromatic amine polymers as the ion carriers in ISEs for determining cations is in its infancy, some progress has already been made. An 'organic–inorganic' composite material prepared via sol–gel mixing of organic polyaniline into the matrices of the inorganic, was used as the ionophore in the ISEs for the determination of Hg(II) [31] and Cd(II) [32], which exhibited excellent sensitivity and selectivity towards specific metal ions. However, no investigation on the conducting polymers as ionophore in the ISEs for the determination of Pb(II) was found so far.

Fine black poly(*m*-phenylenediamine)(P*m*PD) microparticles with numerous –NH–, –N=, and $-NH_2$ groups in their molecular chains have been reported to reversibly form a complex with Pb(II), possessing the high Pb(II) adsorbance [33]. This implies that the P*m*PD could be a potential good ionophore towards the Pb(II) ion. In the present study, the fabrication and characterization of new ISE based on the P*m*PD as ionophore have been described. The coordinating effect for the selective response of Pb(II) ion was investigated

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by using PVC membrane matrix. The response and selectivity of the P*m*PD-based ISE towards Pb(II) ion, together with the practicability of the ISE analyzing environmental water samples and biosample, have been revealed. Compared to the Pb(II)-ISE based on polyaminoanthraquinone as carrier studied by our group before, the Pb(II)-ISE based on the P*m*PD has a similar electrode performance but some additional advantages of low cost, simple synthesis and extremely high chemoresistance of the P*m*PD. For example, the oxidative polymerization of the *m*-phenylenediamine can easily be performed in neutral water, while the oxidative polymerization of the aminoanthraquinone must be carried out in acidic organic phase which would cause environmental pollution.

2. Experimental

2.1. Reagents

m-Phenylenediamine (*m*PD), ammonium persulfate ($(NH_4)_2S_2O_8$), high molecular-mass poly(vinyl chloride) (PVC, dielectric constant 1.4), cellulose diacetate (CDA, dielectric constant ca. 3.2), dioctyl phthalate (DOP, dielectric constant 5.1), dibutyl phthalate (DBP, dielectric constant 6.4), dimethyl sebacate (DMS, dielectric constant ca. 6.5), dioctyl adipate (DOA, dielectric constant 4.0), tetrahydrofuran (THF), acetone, sodium tetraphenylborate (NaTPB), nitrate salts, $BaCl_2$, glacial acetic acid, HNO_3, H_2O_2, and $HClO_4$ were commercially obtained as analytic reagents and used without further purification. Distilled deionized water was used throughout.

2.2. Preparation of standard solution

$Pb(NO_3)_2$ (3.310 g, 0.01 mol) was dissolved in 100 mL distilled deionized water to prepare 0.10 M $Pb(NO_3)_2$ standard solution, while $Hg(NO_3)_2$ (3.246 g, 0.01 mol) was used to prepare 0.10 M $Hg(NO_3)_2$ standard solution in 100 mL distilled deionized water. Other $Pb(NO_3)_2$ and $Hg(NO_3)_2$ standard solutions at the concentration from 10^{-9} to 10^{-1} M were prepared by dilution step-by-step.

2.3. Synthesis of poly(m-phenylenediamine) microparticles as an ionophore

The poly(*m*-phenylenediamine) (P*m*PD) microparticles were synthesized by a chemically oxidative polymerization of *m*-phenylenediamine in distilled water. The preparation procedure is shown in Scheme 1: 80 mmol *m*-phenylenediamine and 40 mmol ammonium persulfate as an oxidant were dissolved in 100 mL distilled water separately to prepare monomer and oxidant solutions, respectively. Both of them were put into a water bath at 30 °C for over 30 min. Ultrasonication was applied to promote the dissolution of the monomer for 3–5 min. The oxidant solution was dropwise added into the monomer solution at a rate of one drop (ca. 60 μL) every 3 s. After the dropwise addition of the oxidant, the mixture was magnetically stirred for 24 h before filtration to obtain the polymer microparticles which were then rinsed with distilled water to remove the residual water-soluble oligomers, oxidant and its reducing products until no SO_4^{2-} was detected using $BaCl_2$ solution. The resulting solid black powder, that is, an as-prepared P*m*PD salt, was left to dry in air at 50 °C for 3 days with the polymerization yield of 90.2%. The P*m*PD microparticles as the neutral carrier of the membrane electrode have the average particle size of 3.16 μm and the size polydispersity index of 1.17 by a Beckman Coulter LS230 laser particle-size analyzer, and the bulk electrical conductivity of 3.5×10^{-6} S cm^{-1} by a two-disk method with a multimeter at 15 °C. The P*m*PD particles are insoluble in almost all traditional solvents including water, HCl, NaOH, and organic solvents. A large number of amino and imino groups, amorphous supramolecular structure, reversible Pb(II) complexibility, and high reversible Pb(II) adsorbance of 142.7 mg Pb(II)/g sorbent of the P*m*PD particles have been confirmed by IR, wide-angle X-ray diffraction and batch adsorption measurements [33].

2.4. Preparation of membrane electrode

PVC based Pb(II) membranes were prepared using 200 mg PVC and different weights of P*m*PD, plasticizer, and NaTPB in 5 mL THF as solvent, while CDA based Pb(II) membranes were made using 200 mg CDA and a certain amount of P*m*PD in 5 mL THF or acetone without any plasticizer. The mixture was stirred at 25 °C to a viscous solution while ultrasonic treatment was also performed to promote the dissolution or dispersion of the ionophore for 2 h and then poured onto a 10×10 cm^2 glass plate. After the solvent was allowed to evaporate at room temperature for 24 h, the resulting membranes were peeled off from the glass and the membrane discs of 14-mm diameter were cut out and finally glued onto a 10-mm inner diameter plastic tube. 0.10 M $Pb(NO_3)_2$ solution was used as an inner reference substance and Ag/AgCl electrode was employed as an inner reference electrode. The electrodes were conditioned in 10^{-3} M $Pb(NO_3)_2$ solution for 24 h for the first time and 2 h every time before used. Although the adsorption of Pb(II) ions onto the P*m*PD microparticles is very rapid and would reach an equilibrium in less than 20 min [33], the conditioning time of 24 h was taken in order to make sure a sufficient complexation between Pb(II) and P*m*PD, considering that the P*m*PD carriers were embedded in the PVC membrane.

2.5. EMF measurements

All response potentials were examined at 25 ± 0.5 °C by using the following assembly setup:

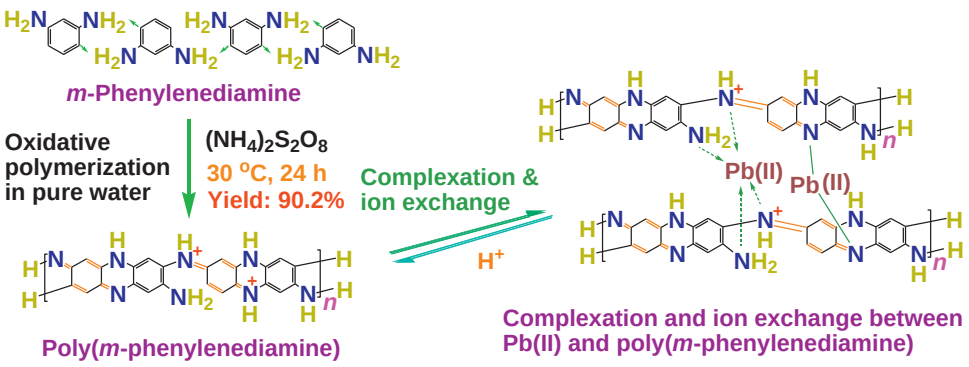
Inner reference electrode (Ag/AgCl) | Pb(II) inner solution | Membrane | test solution | external reference electrode (SCE)

Saturated calomel electrode (SCE) was applied as a reference electrode and the cell potential was measured by varying the concentration of test solutions in a range between 1.00×10^{-8} and 1.00×10^{-1} M, which is obtained by sequential dilution from stock solution of 1.00×10^{-1} M $Pb(NO_3)_2$. Potentials were measured with PHS-3C potentiometer (Shanghai Kangyi Instruments Factory, China) with a sensitivity of 0.6 mV and an input resistance of greater than 1×10^{12} Ω. The potential readings were recorded after the response potential kept a stable value (drift <1 mV/5 min). The potential response curves were plotted as a logarithmic function of Pb(II) activity. The activities of the primary ions were based on the activity coefficient, which is calculated according to Debye–Huckel equation (1):

$$\log r_i = -0.509 Z_i^2 \frac{I^{0.5}}{1 + B\,a\,I^{0.5}} \quad (1)$$

where I is the total ionic strength of the tested solution, Z_i is the valency of Pb(II), B is constant of 0.328 Å^{-1} at 25 °C, and a is volume coefficient of Pb(II), which is approximately equal to effective radius of Pb(II) (5 Å).

All pH adjustments were made with HNO_3 or NaOH solution, and the response time of the electrode was determined by measuring the time which elapses between the instant when the ISE and a reference electrode are brought into contact with a sample solution and the first instant at which the emf/time slope ($\Delta E/\Delta t$) becomes equal to 0.6 mV/min [34]. The lower detection limit was taken as the activity of Pb(II) at the point of intersection of the extrapolated linear midrange and final low concentration level segments of the calibration plot [34]. The selectivity coefficients of the electrode towards different cationic species were determined by the fixed



Scheme 1. Synthesis of poly(*m*-phenylenediamine) microparticles as an ionophore and their interaction with lead ions.

interference method (FIM). All experiments were repeated at least three times, giving mean values that are utilized throughout the manuscript.

2.6. Lifetime measurement

The lifetime of the ISE was measured by the following process: upon the ISE was fabricated, the detection performance of the ISE to Pb(II) was recorded about once a day. During daily use, the electrode was stored in a 1.00×10^{-3} M $Pb(NO_3)_2$ solution, while the electrode was allowed to dry out and reconditioned for 12 h in 1.00×10^{-3} M $Pb(NO_3)_2$ solution if there were several days between required uses. After the ISE has been used for a month, its performance including Nernstian slope, response time, and linear range should be measured again. If its performance data were above 95% of the first time, we considered that the ISE was in its lifetime, otherwise out of lifetime.

2.7. Real sample analysis

2.7.1. Real samples selected and their pretreatment

The real-world samples used to test the validity of the electrode included (1) tap water from our laboratory in Tongji University, China, (2) river waters from HuangPu river in Shanghai, China and (3) wastewater from Printing House of Fudan University, Shanghai, China. The pretreatment of the real sample was as follows: filtration with qualitative filter paper and adjusting the solution pH to 4.0 with concentrated HNO_3. The solution pretreated thus was directly and repetitively analyzed with the proposed Pb(II)-ISE by a calibration curve 10 times. The Pb(II) concentrations in the solution were also analyzed by inductively coupled plasma (ICP) mass spectrometry (Plasma Quad 3 model ICP-MS instrument, VG, UK) the RF power 1350 W at argon flowing rate 13.5 L min^{-1} and mass resolution 0.8 amu for scanning time 2 s per element and used as real values for calculation of relative error.

A biological sample, such as human urine, obtained from a volunteer student of Tongji University in Shanghai, China, was also selected. The urine sample must undergo assimilation by a following procedure: 10 mL urine was treated with a mixture of 5.0 mL 3.0 M HNO_3 and 3 mL 30% H_2O_2 at 50 °C for 6 h, to which 2–3 mL glacial acetic acid/3.0 M HCl/1.0 M $HClO_4$(1/1/1 vol.) was further added. After a complete assimilation of 1 day, the mixture assimilated was heated in an oil bath at 120 °C for ca. 2 h to remove the acids until the pH is higher than 4.0. The resulting digested solution was brought to 500 mL, in which Pb(II) concentrations were repetitively measured with the proposed Pb(II)-ISE 4 times. To avoid the interference from background ions in the real sample, Gran's plot was used to conduct the measurement.

2.7.2. Gran's plot

Gran's plot was also employed for determination of Pb(II) in real samples. While a 50 mL of real sample was being stirred, a steady potential was first recorded as an initial potential at $V_{si} = 0$ with the Pb(II)-ISE. Then, to the 50 mL of real sample, 5 given volumes of 0.5 mL standard solutions of 1.0×10^{-4} M $Pb(NO_3)_2$ were successively added, and one-by-one recorded the new steady response potentials of the mixture solution after each addition. In this case, a Nernstian equation (2) can be written as follows:

$$E_i = k + S\,lg\left[\frac{C_x V_x + C_s V_{si}}{V_x + V_{si}}\right] \quad (2)$$

where E_i is response potential of the electrode after the *i*th standard Pb(II) solution was added, C_s Pb(II) concentration of standard Pb(II) solution, C_x Pb(II) concentration of real water sample tested, V_{si} total volume of standard Pb(II) solution added in the tested solution after the *i*th time.

The Nernstian equation (2) can be transformed into Eq. (3)

$$(V_x + V_{si})10^{E_i/S} = 10^{k/S}(C_x V_x + C_s V_{si}) \quad (3)$$

The intercept V_0 (a negative value), which corresponded to zero value of $(V_x + V_{si})10^{E/S}$, was obtained by extrapolating a straight plot line of $(V_x + V_s)10^{E/S}$ versus V_s to cross section abscissa. As a result, the Pb(II) concentration of real water sample tested could be calculated by Eq. (4)

$$C_x = -\frac{V_0 C_s}{V_x} \quad (4)$$

2.7.3. Precision and accuracy of the measurements

Average Pb(II) concentration ($\bar{C}$), relative error (RE) and relative standard deviation (RSD) were calculated according to the following equations:

$$\bar{C} = \frac{C_1 + C_2 + C_3 + \cdots + C_n}{n} \quad (5)$$

$$\mathrm{RSD} = \frac{\{[(C_1 - \bar{C})^2 + (C_2 - \bar{C})^2 + \cdots + (C_n - \bar{C})^2]/(n-1)\}^{1/2}}{\bar{C}} \quad (6)$$

$$\text{Relative error} = \frac{\bar{C} - C_{\mathrm{True}}}{C_{\mathrm{True}}} \quad (7)$$

3. Results and discussion

3.1. Response to Pb(II) and Hg(II)

Good adsorption of Pb(II) and Hg(II) onto the P*m*PD microparticles signified that the P*m*PD-based ISE possibly has Nernst response to the both heavy-metal ions [33]. Fig. 1 has shown the performance of two ISEs using P*m*PD as carrier to Pb(II) and Hg(II) solutions separately. Obviously, the membrane electrodes both have good Nernst

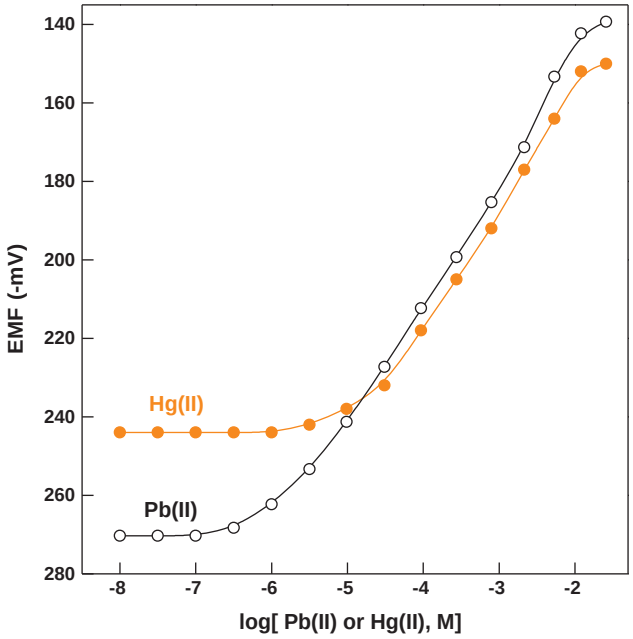


Fig. 1. The performance of two ISEs to Pb(II) and Hg(II) separately using P*m*PD as carrier in the membrane electrode containing P*m*PD:PVC:DOP:NaTPB weight ratio of 1.0:33.0:65.0:1.0.

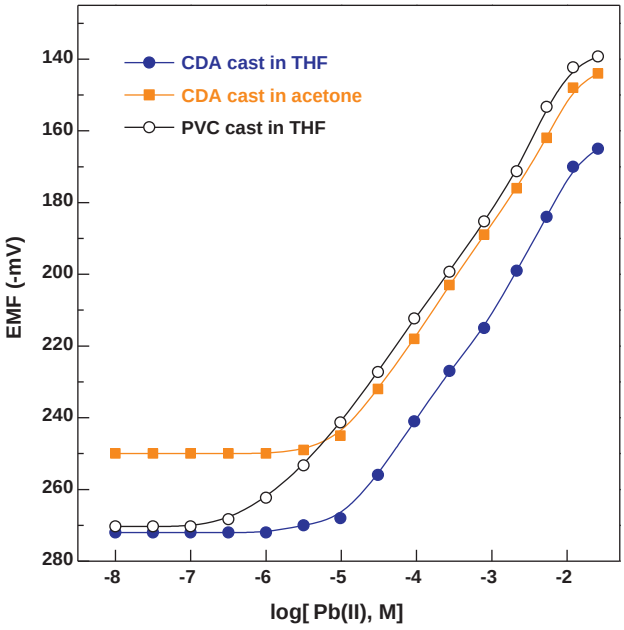


Fig. 2. Nernstian response of ISEs (Nos. 4, 10 and 11 in Table 1) to Pb(II) based on PVC and CDA.

response, while the linear response to Pb(II) is even better than to Hg(II). One of the possible reasons is that the interaction between P*m*PD and Hg(II) includes complexation and redox reaction simultaneously, whereas the interaction between P*m*PD and Pb(II) only includes complexation without redox reaction [35]. The electrode used for determining the concentration of Pb(II) displayed superior property with a nearly Nernstian slope of 29.8 mV decade^{-1} while that is 30.8 mV decade^{-1} for Hg(II). A wider linear response range towards Pb(II) appeared in the ISE based on P*m*PD and the detection limit is reduced 1–2 orders of magnitude, regardless of their similar response time. As a result, the membrane electrode using the P*m*PD as carrier would satisfactorily be used for more sensitively sensing Pb(II). This also implied that high concentration Hg(II) would cause a foresighted interference to the determination of Pb(II) if using this electrode based on the P*m*PD. Actually, the interference of Hg(II) has been found in most of Pb(II)-ISEs reported [17,18,20,22,27,36–42].

3.2. Selection of membrane matrix

As a membrane matrix, chemical resistance and inertness are firstly required, i.e., no chemical interaction between the matrix and additives/Pb(II) solution. PVC as a widely used membrane matrix possesses wonderful chemical stability, mechanical and electrical properties, but a plasticizer is needed. CDA as an ISE membrane matrix has an advantage, that is, no plasticizer is demanded. It is known that the plasticizer in membrane would bring about the leakage of membrane, consequently shortening the lifetime of the electrode. Note that the plasticizer is vital for the PVC-based membrane with good flexibility. By the way, fine P*m*PD microparticles can uniformly be dispersed in the PVC and CDA membranes without any plasticizers. Fig. 2 shows the Nernstian response of ISEs to Pb(II) based on PVC and CDA and corresponding performance of the electrodes is summarized in Table 1. Apparently, the Pb(II)-ISE based on PVC displayed faster response with wider linear range and lower detection limit than that based on CDA because the PVC membrane has lower dielectric constant but higher flexibility than the CDA membrane, resulting in more effective interaction to the Pb(II) in the PVC-based membrane. It could be speculated that the plasticizers would also enhance the performance of CDA-based membrane. However, the poor miscibility between the plasticizers and CDA results in a serious leakage of the DOP and DBP from CDA membrane.

3.3. Optimization of membrane composition

As the response of the ion-selective electrodes remarkably depends on the nature of ionophore, plasticizer and anion excluder, while the selectivity of the electrodes depends on the nature of ionophore only [18], the ISE membrane compositions should carefully be optimized to produce the best response and selectivity towards Pb(II). Several Pb(II)-ISE membrane electrodes from No. 1 to No. 9 with different amount of plasticizer, anion excluder, and P*m*PD ionophore in Table 1, were investigated to reveal the optimal membrane composition.

3.3.1. Plasticizer

As mentioned above, the plasticizer is requisite for the preparation of membrane only based on PVC. It should be noted that the plasticizer influences the dielectric constant of the membranes in which the dielectric constant controls the mobility of metal ions [18]. Four kinds of plasticizers having representative dielectric constants given in Section 2 were inspected in this study. Among them, the membrane plasticized by DMS having the largest dielectric constant exhibited the slowest response, the lowest response slope, the narrowest linear range, and the most inferior detection limit, as depicted in Fig. 3 and Table 1. Similarly, the membrane plasticized with DBP having the second largest dielectric constant demonstrated the highest response slope, the second narrowest linear range, and the second worst detection limit. Contrarily, the membrane plasticized by DOA having the smallest dielectric constant produced the second slowest response, the second highest response slope, the second narrowest linear range, and the third worst detection limit. Fortunately, the membranes plasticized with DOP possessing moderate dielectric constant demonstrated the fastest response, the nearest Nernstian response slope, the widest linear range, and the best detection limit. All of these imply that both high and low dielectric plasticizers do not seem to be favorable

Table 1
Characteristics of different Pb(II) ion-selective electrodes. The measurement has been carried out at least 3 times and the standard deviations range from 0.30 to 0.55%.

ISE no.	Matrix/plasticizer/ solvent	P*m*PD:matrix: plasticizer:NaTPB	Response time (s)	Slope (mV decade^{-1})	Linear range (M)	Detection limit (M)	Life time (month)
1	PVC/DOA/THF	1.0:33.0:65.0:1.0	15	30.4	$10^{-5.0}$–$10^{-1.5}$	2.91×10^{-6}	5
2	PVC/DMS/THF	1.0:33.0:65.0:1.0	18	24.5	$10^{-4.5}$–$10^{-2.5}$	1.45×10^{-5}	
3	PVC/DBP/THF	1.0:33.0:65.0:1.0	14	30.7	$10^{-5.0}$–$10^{-1.5}$	4.03×10^{-6}	
4	PVC/DOP/THF	1.0:33.0:65.0:1.0	14	29.8	$10^{-6.0}$–$10^{-1.5}$	6.31×10^{-7}	
5	PVC/DOP/THF	1.0:33.3:65.7:0	20	31.0	$10^{-5.0}$–$10^{-2.0}$	2.43×10^{-6}	
6	PVC/DOP/THF	1.6:32.3:64.5:1.6	14	31.2	$10^{-4.5}$–$10^{-2.0}$	2.77×10^{-6}	
7	PVC/DOP/THF	1.0:33.2:65.3:0.5	18	31.0	$10^{-5.0}$–$10^{-1.5}$	2.69×10^{-6}	
8	PVC/DOP/THF	0.8:32.8:65.6:0.8	14	32.5	$10^{-4.5}$–$10^{-1.5}$	5.34×10^{-6}	
9	PVC/DOP/THF	1.0:32.7:64.3:2.0	14	31.1	$10^{-5.0}$–$10^{-1.5}$	2.24×10^{-6}	
10	CDA/–/THF	2.9:94.2:0:2.9	25	31.6	$10^{-5.0}$–$10^{-1.5}$	8.03×10^{-6}	2.5
11	CDA/–/acetone	2.9:94.2:0:2.9	25	31.2	$10^{-5.0}$–$10^{-1.5}$	6.67×10^{-6}	2.5

environments for the complexation between Pb(II) and P*m*PD. Only DOP with proper dielectric constant is the most effective mediator for the fabrication of the Pb(II)-ISEs [43]. Therefore, DOP was selected as the plasticizer for further investigations.

3.3.2. Anion excluder

NaTPB was incorporated into the membrane to examine whether the ionic additive changed the electrode response. For comparison, the calibration graphs of the electrodes Nos. 4, 5, 7, and 9 with four NaTPB contents are shown in Fig. 4 and Table 1. Both the response slope and linear range of the electrode potentials display a maximum whereas the response time displays a minimum when the P*m*PD:NaTPB weight ratio is 1:1. This implies that the addition of NaTPB produced a mixed response to Pb(II) and PbA(I) whose theoretical slope is 59.2 mV decade^{-1}, where A stands for anion (NO_3^- or OH^-) present in the sample solution, just like other Pb(II) electrodes [25]. Since bulky anion TPB^- may be embedded in the membrane, a charge layer would form on the membrane surface that could inhibit the anion transfer through the membrane. However, it does not seem that a further increase in the NaTPB amount obviously enhances the electrode performance. It should be noticed that the presence of anion excluder in cation-selective membrane electrodes could decrease ohmic resistance and then improve the response and selectivity. The P*m*PD:NaTPB (1:1) membrane has the higher conductivity (2.87×10^{-7} S cm^{-1}), while the NaTPB-free membrane has lower conductivity (3.52×10^{-8} S cm^{-1}). That is to say, the addition of NaTPB indeed decreases the ohmic resistance, leading to more sensible membrane electrode.

3.3.3. PmPD content

The crucial part in the ISE is the sensitive membrane, which not only separates the inner solution from sample solution, but also causes a selective response to some active species forming a membrane potential. It is the membrane carrier such as P*m*PD microparticles that can cause the selective response to Pb(II). The carrier P*m*PD microparticles embedded in PVC membrane reversibly complex Pb(II) through the active sites including –N═, –NH–, and $–NH_2$ groups or exchange with protons in the molecular chains of PmPD (Scheme 1). Thereby, a certain Pb(II) concentration is formed in the membrane and on its surface. During the detection of Pb(II), the difference of Pb(II) concentration in the membrane, inner reference solution and sample solution produces an ion exchange. Accordingly, because of the different exchange rates a potential difference forms on two sides of the membrane, thus the membrane potential appears. It is obvious that the complexation degree increases as the carrier content rises. However, excessive carrier will cause defects even leakage in the phase interface. So it is necessary to optimize carrier content in the electrode.

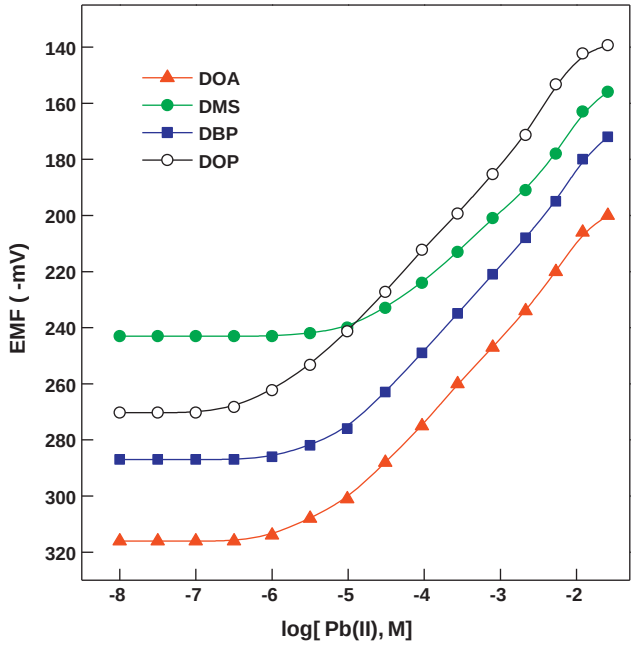


Fig. 3. Effect of plasticizer on the response potential of the membrane electrode with P*m*PD:PVC:plasticizer:NaTPB weight ratio of 1.0:33.0:65.0:1.0.

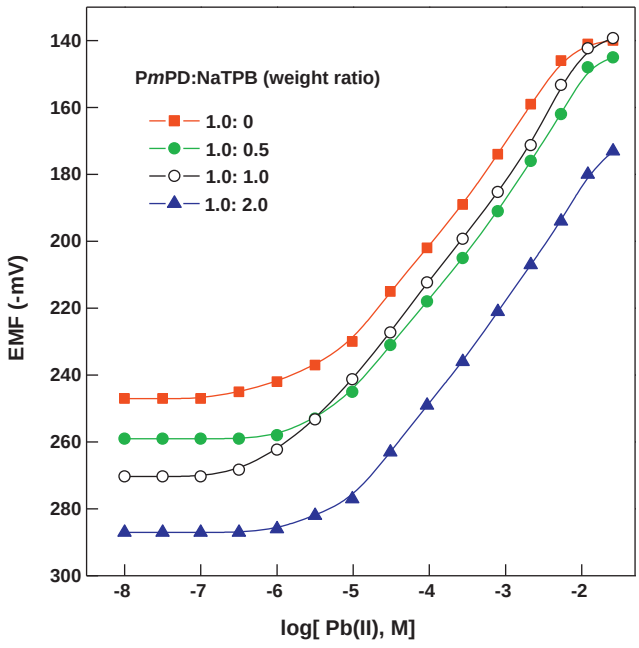


Fig. 4. Effect of NaTPB on the response potential of the membrane electrode with P*m*PD:PVC:DOP weight ratio of 1:33:65.

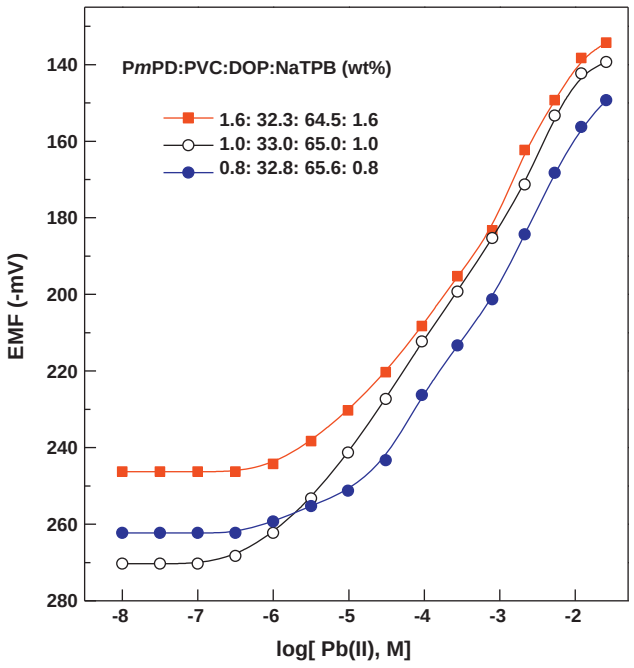


Fig. 5. Effect of the P*m*PD carrier content on the response potential.

It is seen from Fig. 5 and Table 1 that the response time has not been affected mostly by the P*m*PD content, but the Nernstian slope and linear range were indeed influenced. The electrode with P*m*PD:PVC:DOP:NaTPB weight ratio of 1.6:32.3:64.5:1.6 showed the poorest response because at higher Pb(II) concentration, the positively charged P*m*PD–Pb(II) complex formed in the membrane phase resulted in electrostatic repulsion to the analyte. The membrane containing the least carriers with P*m*PD:PVC:DOP:NaTPB ratio of 0.8:32.8:65.6:0.8 also exhibited inferior performance due in part to insufficient P*m*PD carrier in the membrane. Unfortunately, the P*m*PD:PVC:DOP:NaTPB (0:33.0:66.0:1.0) membrane with the thickness of 160 μm has much lower potential stability and lower conductivity than the P*m*PD:PVC:DOP:NaTPB (1.0:33.0:65.0:1.0) membrane [41]. Consequently, no reliable potential response towards Pb(II) ion or a near-Nernstian slope would be obtained if using the P*m*PD:PVC:DOP:NaTPB (0:33.0:66.0:1.0) membrane without the P*m*PD ionophore. Apparently, the P*m*PD-free electrode is unsuitable to detect the potential response. Only the electrode with medium carrier content, i.e., P*m*PD:PVC:DOP:NaTPB weight ratio of 1.0:33.0:65.0:1.0, had the optimal potential response with a Nernstian slope of 29.8 mV decade^{-1}, a detection limit of 6.31×10^{-7} M, and linear range between $10^{-6.0}$ and $10^{-1.5}$ M. This great improvement of electrode performance should mainly result from the addition of an optimal amount of P*m*PD ionophore. Therefore, this membrane composition has been utilized in the following investigation.

3.4. Effect of ionic strength of solution

Calibration curves were also plotted by measuring known amounts of $Pb(NO_3)_2$ containing respective 0.100 M and 0.0100 M KNO_3 to inspect the effect of ionic strength of electrolyte on the Pb(II) response behavior. A high concentration of KNO_3 was chosen for ionic strength adjustment of the solution since the interference from potassium ions was relatively weak. The calculated values of total ionic strengths of the Pb(II) solution containing additional electrolyte are listed in Table 2. The potential responses of the Pb(II)-ISE based on the membrane consisting of P*m*PD:PVC:DOP:NaTPB (1.0:33.0:65.0:1.0) are shown in Fig. 6. It

Table 2
Calculated ionic strengths of Pb(II) solution with additional electrolyte KNO_3 at respective 0.010 M and 0.10 M KNO_3.

Concentration of the additive electrolyte KNO_3 (M)	Concentration of $Pb(NO_3)_2$ (M)	Calculated total ionic strength (M)	Activity of Pb(II) (M)
0.0100	$10^{-6.00}$	0.010	$10^{-6.17}$
	$10^{-5.50}$	0.010	$10^{-5.67}$
	$10^{-5.00}$	0.010	$10^{-5.17}$
	$10^{-4.50}$	0.010	$10^{-4.67}$
	$10^{-4.00}$	0.0103	$10^{-4.18}$
	$10^{-3.00}$	0.013	$10^{-3.20}$
	$10^{-2.00}$	0.04	$10^{-2.31}$
0.100	$10^{-6.00}$	0.10	$10^{-6.42}$
	$10^{-5.50}$	0.10	$10^{-5.92}$
	$10^{-5.00}$	0.10	$10^{-5.42}$
	$10^{-4.50}$	0.10	$10^{-4.92}$
	$10^{-4.00}$	0.10	$10^{-4.42}$
	$10^{-3.00}$	0.10	$10^{-3.43}$
	$10^{-2.00}$	0.13	$10^{-2.46}$

seems that high ionic strength in the presence of high concentration of KNO_3 has a significant influence on the linear response behavior of the Pb(II)-ISE with ca. 1.5 orders of magnitude deterioration relative to the Pb(II) solution without KNO_3. Therefore, high ionic strength of solution is not favorable to detection of Pb(II) at concentration lower than $10^{-4.5}$ M.

3.5. Effect of pH

The response of the electrodes at three Pb(II) concentrations of 1.00×10^{-2}, 1.00×10^{-3} and 1.00×10^{-4} M of different pH values is illustrated in Fig. 7 where the pH was adjusted by properly adding dilute NaOH or HNO_3 solutions. The potential plateau appears in a pH range from 3.0 to 5.0, slightly depending on Pb(II) concentration, which is a comparable range with previously reported ISEs for lead ions [27,36,38,39,41]. It can also be seen that the upper limit of pH range was influenced by Pb(II) concentration because of the low

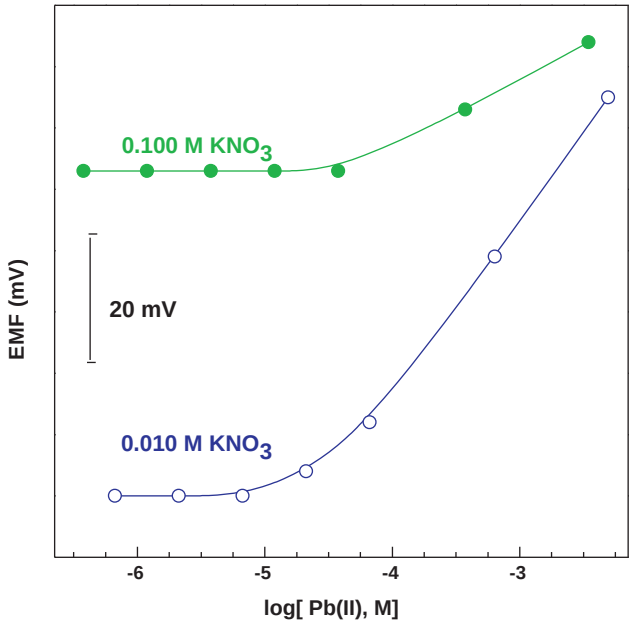


Fig. 6. Potential response of the Pb(II)-ISE based on membrane with a composition of P*m*PD:PVC:DOP:NaTPB = 1.0:33.0:65.0:1.0 in the presence of KNO_3 at respective concentration of 0.0100 M and 0.100 M.

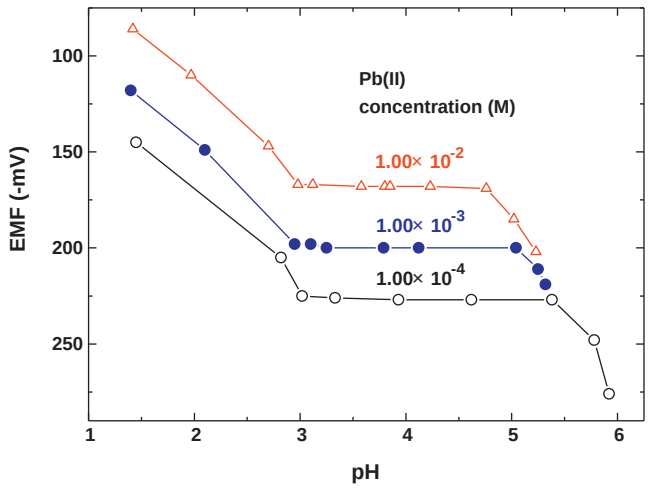


Fig. 7. Effect of pH on the response potential at three Pb(II) concentrations of the electrode with P*m*PD:PVC:DOP:NaTPB weight ratio of 1.0:33.0:65.0:1.0.

solubility product constant of $Pb(OH)_2$ of about 1.42×10^{-20}. At a pH of higher than 5.0, the response changed considerably with the formation of $Pb(OH)_2$. At a pH of lower than 3.0, as a result of the high concentration of H^+ that can exchange with Pb(II) adsorbed on the P*m*PD molecules, the potential cannot keep constant either. It is concluded that pH range of 3.0–4.8 is a suitable working range for proposed membrane electrode.

3.6. Response time and lifetime

It is evidenced from Fig. 8 that the time taken for the electrode to achieve 95% of the stable potential is usually less than 14 s for Pb(II) concentration from 1.00×10^{-3} to 1.00×10^{-5} M and correspondent response potential remains constant for up to 5 min. This response time is shorter than that of most of the previously reported Pb(II) ISEs [22–24,27,37–40].

The membrane electrode has been used repeatedly for 5 months without any substantial deterioration, which is longer than most of other electrodes reported so far [18,27,37,40,41]. The potential detected here was from high Pb(II) concentration to low concentration, and a similar result could be observed from low Pb(II) concentration to high concentration after previous detection has been finished. During daily use, the electrode was either stored in 1.00×10^{-3} M $Pb(NO_3)_2$ solution or allowed to dry out and then reconditioned for 12 h in 1.00×10^{-3} M $Pb(NO_3)_2$ solution to reuse. The optimum loading was sufficient to maintain a steady performance during these 5 months because the solid ionophore utilized in this study will never lose during long-term use regardless of a possible loss of the liquid plasticizer. Such a long lifetime is mainly contributed to the solid ionophore, which is one of the evidences that the proposed ISE has improved analytical features compared to existing ISEs.

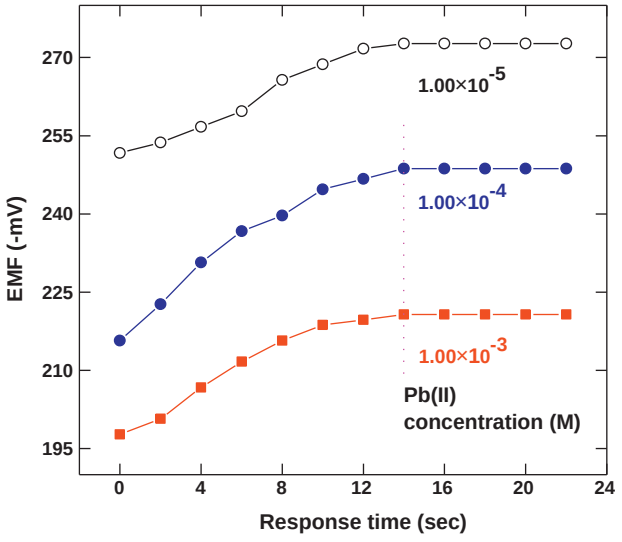


Fig. 8. Response time profile of the Pb(II) ion-selective electrode with P*m*PD:PVC:DOP:NaTPB weight ratio of 1.0:33.0:65.0:1.0.

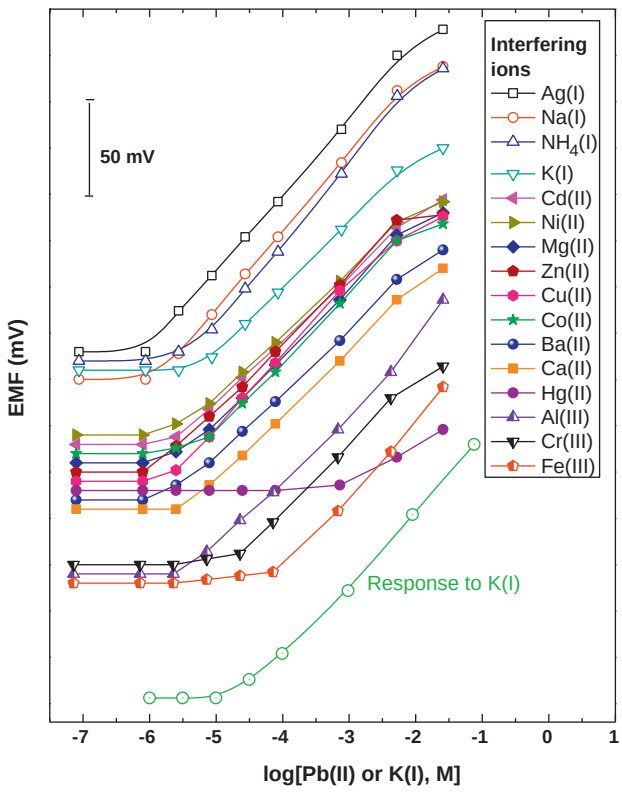


Fig. 9. Response curves of the Pb(II)-ISE by fixed interference method at an interfering ion concentration of 1.00×10^{-3} M.

3.7. Response selectivity

The selectivity of the membrane electrodes is the most important characteristics, determining their practical applicability in real-sample measurement. The selectivity coefficients represent their response to the species to be measured over other ions coexisted in the solution. The following expression:

$$K^{\text{pot}}_{\text{Pb,B}} = \frac{a_{\text{Pb}}}{a_{\text{B}}^{2/Z_{\text{B}}}} \quad (8)$$

was used to calculate selectivity coefficients, where a_{Pb} is the activity of Pb(II) ion, a_{B} the activity of the interfering ion, and Z_{B} the valence number of the interfering ion [39,42,44]. Considering the electrode shows linear response to individual potential interfering ions at a concentration range from 1.00×10^{-3} M to 1.00×10^{-1} M like a linear response curve for K^+ (Fig. 9, green line i.e. the bottom curve), a fixed concentration of 1.00×10^{-3} M for interfering ions has been chosen to assess the selectivity coefficients because the electrode exhibits a linear response to both principal and interfering ions [34,45–47]. The true selectivity coefficients towards Pb(II) against 16 kinds of interfering ions from the nitrates or chlorides are summarized in Table 3, and their corresponding response

Table 3
Logarithmic selectivity coefficients for the Pb(II)-ISE by a fixed interference method at an interfering ion concentration of 1.00×10^{-3} M.

Compound	Interfering ion	Detection limit a'_{Pb} (M)	Selectivity coefficient $K^{pot}_{Pb,B}$	Logarithmic selectivity coefficient log $K^{pot}_{Pb,B}$
$AgNO_3$	Ag(I)	$10^{-6.08}$	$10^{-6.08}/(10^{-3})^2 = 10^{-0.08}$	−0.08
$NaNO_3$	Na(I)	$10^{-5.89}$	$10^{-5.89}/(10^{-3})^2 = 10^{0.11}$	0.11
NH_4NO_3	NH_4(I)	$10^{-5.48}$	$10^{-5.48}/(10^{-3})^2 = 10^{0.52}$	0.52
KNO_3	K(I)	$10^{-5.25}$	$10^{-5.25}/(10^{-3})^2 = 10^{0.75}$	0.75
$Ca(NO_3)_2$	Ca(II)	$10^{-5.43}$	$10^{-5.43}/10^{-3} = 10^{-2.11}$	−2.43
$Mg(NO_3)_2$	Mg(II)	$10^{-5.56}$	$10^{-5.56}/10^{-3} = 10^{-2.56}$	−2.56
$Ba(NO_3)_2$	Ba(II)	$10^{-5.7}$	$10^{-5.7}/10^{-3} = 10^{-2.27}$	−2.70
$Cu(NO_3)_2$	Cu(II)	$10^{-5.73}$	$10^{-5.73}/10^{-3} = 10^{-2.73}$	−2.73
$Zn(NO_3)_2$	Zn(II)	$10^{-6.00}$	$10^{-6.00}/10^{-3} = 10^{-3.00}$	−3.00
$Co(NO_3)_2$	Co(II)	$10^{-5.32}$	$10^{-5.32}/10^{-3} = 10^{-2.32}$	−2.32
$Ni(NO_3)_2$	Ni(II)	$10^{-5.63}$	$10^{-5.63}/10^{-3} = 10^{-2.63}$	−2.63
$CdCl_2$	Cd(II)	$10^{-5.69}$	$10^{-5.69}/10^{-3} = 10^{-2.69}$	−2.69
$Hg(NO_3)_2$	Hg(II)	$10^{-3.27}$	$10^{-3.27}/10^{-3} = 10^{-0.27}$	−0.27
$AlCl_3$	Al(III)	$10^{-5.62}$	$10^{-5.62}/(10^{-3})^{2/3} = 10^{-3.62}$	−3.62
$Cr(NO_3)_3$	Cr(III)	$10^{-4.78}$	$10^{-4.78}/(10^{-3})^{2/3} = 10^{-2.78}$	−2.78
$FeCl_3$	Fe(III)	$10^{-4.05}$	$10^{-4.33}/(10^{-3})^{2/3} = 10^{-2.33}$	−2.33

curves are also shown in Fig. 9. It appears that the P*m*PD as an ionophore is selective towards Pb(II) ion against all divalent or trivalent interfering ions examined since all of the logarithmic selectivity coefficients are smaller than −2 except for Hg(II). As for monovalent interfering ions, the selectivity coefficients are just smaller than 1, which is much higher than the divalent or trivalent interfering ions in view of numerical values. However, it must be noted that a direct comparison of the numerical values of two selectivity coefficients for two interfering ions with different charges is not meaningful [46]. In fact, the interferences are comparable for the divalent ISE in the presence of 1.00×10^{-3} M monovalent or divalent interfering ions with logarithmic selectivity coefficients of 1 or −2, respectively. It is easily understood directly from response curves of the Pb(II)-ISE (Fig. 9) that their lower detection limits are comparable for the Pb(II)-ISE in the existence of 1.00×10^{-3} M monovalent or divalent interfering ions. It should be pointed out that the electrode shows an excellent selectivity of Pb(II) over Ag(I) than most other PVC membrane based one, such as ETH5234-polyurethane ionophore based Pb(II)-ISE [48] (−0.08 versus >6.5 for logarithmic selectivity coefficient).

The tolerated concentration of interfering ions depends on the selectivity coefficient, i.e., the lower the selectivity coefficient, the higher the tolerated concentration of interfering ion is. Apparently, the tolerance level of the electrode towards Hg(II) should be low because of its high selectivity coefficient. Contrarily, the tolerance level of the electrode towards Na(I), K(I), Ba(II), Ca(II), and NH_4(I) should be high. The potential response curves of the electrode in the presence of three fixed concentrations of Hg(II) ions, i.e., 1.00×10^{-3}, 1.00×10^{-4}, and 1.00×10^{-5} M, are displayed in Fig. 10. The 1.00×10^{-4} and 1.00×10^{-5} M Hg(II) concentrations can be tolerated with detection limit of $10^{-6.14}$ and $10^{-5.86}$ M. On the other hand, in the existence of 1.00×10^{-5} M Hg(II), the response linear slope of 30.3 mV decade^{-1} remains almost the same as that for pure Pb(II) solution. Taking account to both the lower detection limit and response linear slope, the tolerable Hg(II) concentration would be high up to 1.00×10^{-5} M without losing Nernstian response. To further evaluate the practical anti-interference of the electrode, practical detection results of the Pb(II) in the solutions containing several representative heavy metal ions are listed in Table 4. It is observed that the interfering ions of lower than 1.00×10^{-4} M would not interfere with the detection of 1.00×10^{-2} M Pb(II), whereas the interfering ions of not higher than 1.00×10^{-5} and 1.00×10^{-6} M would not interfere with the detection of 1.00×10^{-3} and 1.00×10^{-4} M Pb(II).

It is distinct that the strategy for using a solid semiconducting polymer as ionophore is significant since the Pb(II)-ISE fabricated thus shows lower detection limit of down to submicromolar level, higher selectivity over other metal ions, and long lifetime of 5 months at the same time. Pretsch and Bakker have developed Pb(II)-ISE by a variety of techniques to eliminate undesired leaching of primary ions that restricts the lower detection limit to maintain micromolar level, and also eliminate super-Nernstian slope behavior resulting from depletion of the primary ion in the sample solution due to primary ion flux from sample into membrane. By these methods, the analytical range of Pb(II)-ISE was extended to subnanomolar concentration range. One of their pioneering work is that by using ionophores that were covalently binded to polymer backbones, the lower detection limit of 1.7×10^{-9} has been achieved in spite of a sophisticated synthesis route of the ionophores [48]. They also developed a technique using an ion buffer in inner filling solution of electrode, by which the detection limit was lowered down to 5.0×10^{-12} M [49] or 8.0×10^{-11} M [50]. However, this approach tends to shorten the lifetime of electrodes to even less than one week [51]. In this work, we consider quite

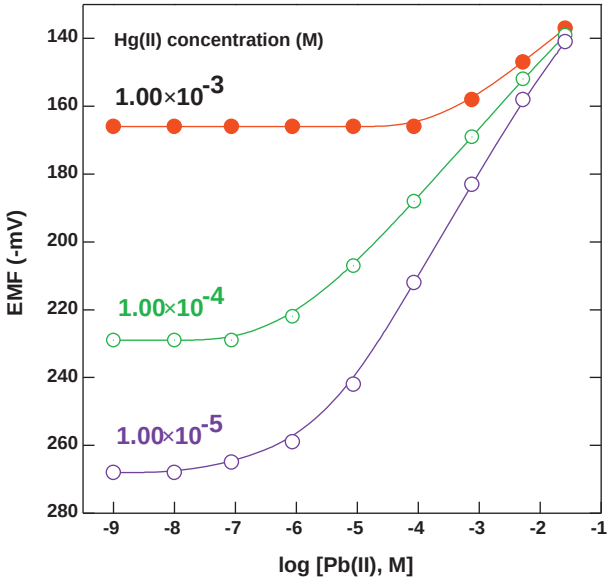


Fig. 10. Variation of response curve of the Pb(II)-ISE in the presence of Hg(II) of different concentrations.

Table 4
Recovery of the Pb(II) in the solutions containing several heavy metal interfering ions using the ISE based on P*m*PD as detection electrode. The number of assays is at least 3 times and the standard deviations range from 0.55% to 1.0%.

Pb(II) concentration (M)	Interference ion concentrations (M)	Recovery (%)
1.00×10^{-2}	$1.00 \times 10^{-4.5}$ Hg(II)	97.6
	$1.00 \times 10^{-4.5}$ Cu(II)	97.6
	$1.00 \times 10^{-4.5}$ Ag(I)	95.0
	$1.00 \times 10^{-4.5}$ Hg(II) + $1.00 \times 10^{-4.5}$ Cu(II)	95.0
	$1.00 \times 10^{-4.5}$ Hg(II) + $1.00 \times 10^{-4.5}$ Cu(II) + $1.00 \times 10^{-4.5}$ Ag(I)	92.5
1.00×10^{-3}	1.00×10^{-5} Hg(II)	98.8
	1.00×10^{-5} Cu(II)	98.8
	1.00×10^{-5} Ag(I)	98.8
	1.00×10^{-5} Hg(II) + 1.00×10^{-5} Cu(II)	96.3
	1.00×10^{-5} Hg(II) + 1.00×10^{-5} Cu(II) + 1.00×10^{-5} Ag(I)	96.3
1.00×10^{-4}	1.00×10^{-6} Hg(II)	99.2
	1.00×10^{-6} Cu(II)	99.2
	1.00×10^{-6} Ag(I)	99.2
	1.00×10^{-6} Hg(II) + 1.00×10^{-6} Cu(II)	99.2
	1.00×10^{-6} Hg(II) + 1.00×10^{-6} Cu(II) + 1.00×10^{-6} Ag(I)	99.2

otherwise to develop durable Pb(II)-ISE based on easily synthesized semiconducting P*m*PD polymer microparticles as ionophores, achieving lower detection limit down to submicromolar concentration with the conventional inner filling solution. Here we describe only an original fundamental scientific study and we believe that there is still room for optimization of the electrode with regard to improvement of the lower detection limit and lifetime.

3.8. Practical application

The membrane electrode was successfully used as an indicator electrode in the potentiometric titration of Pb(II) with EDTA. 20.00 mL $Pb(NO_3)_2$ solutions at 1.00×10^{-3} and 1.00×10^{-4} M were titrated against 1.00×10^{-3} M EDTA solution at pH 4.5 adjusted by NaOH or HNO_3 solutions. Despite non-standard sigmoid shape of the plot in Fig. 11, the observed sharp break point respectively at 19.50 and 1.95 mL corresponds to the stoichiometry of Pb(II)–EDTA complex, implying that the $Pb(NO_3)_2$ solutions are 9.75×10^{-4} and 9.75×10^{-5} M, respectively, having the same small relative error of 2.5% [14]. The deviation in shape may be due to some interference caused by Na(I) from the titrant EDTA. The similar curves have been observed for other ionophore-containing Pb(II)-ISE earlier [9,14]. Anyway, the titration curve can provide an obvious breakpoint for us to judge the end point.

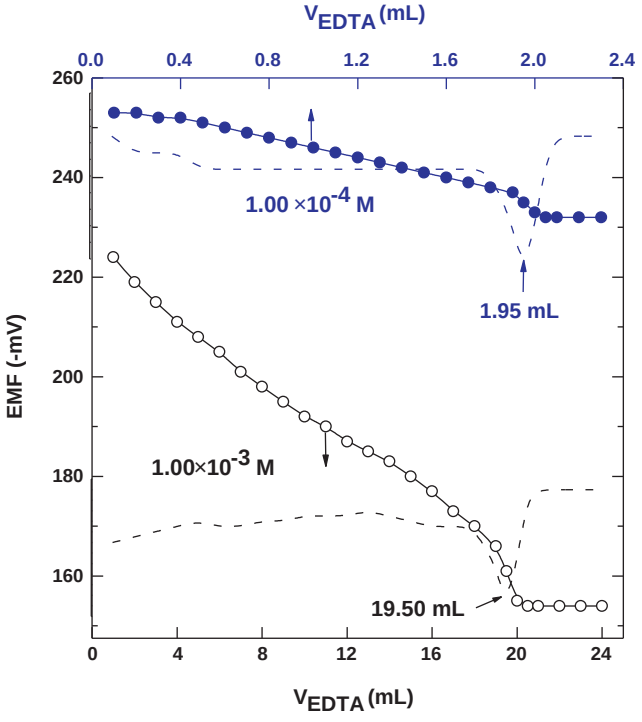


Fig. 11. Potentiometric titration plot of 1.00×10^{-3} and 1.00×10^{-4} M Pb(II) solution (20.00 mL) with 1.00×10^{-3} M EDTA.

Tap water sample was analyzed by the electrode to detect lead(II) concentration by spiked sample. Before the analysis, the tap water samples have been boiled for 5 min to remove chlorine and adjusted to the pH value of 4.0 by HNO_3 solution. The recoveries of 96.6–103.0% and RSD of 0.6–6.45% shown in Table 5 clearly indicate that the Pb(II)-ISE is feasible to detect Pb(II) in the polluted tap water.

River water from HuangPu River, Shanghai, China, was analyzed by the P*m*PD:PVC:DOP:NaTPB (1.0:33.0:65.0:1.0) ISE fabricated in this study. According to ICP-MS result, the river water contains nine interferents such as Na(I) (8.04×10^{-4} M), Ca(II) (3.54×10^{-4} M), Mg(II) (1.71×10^{-4} M), Zn(II) (2.35×10^{-5} M), Pd(II) (7.09×10^{-6} M), Fe(III) (9.71×10^{-7} M), K(I) (7.42×10^{-7} M), Cu(II) (2.33×10^{-7} M), and Hg(II) (2.49×10^{-8} M). Ten-time ISE examination revealed that the response potentials of the real solution are 221, 221, 220, 220, 221, 219, 220, 221, 220, and 220 mV with an average potential of 220.1 mV and RSD of 0.31%. The concentration of Pb(II) could be calculated according to the linear calibration equation (3) obtained by the ISE based on the P*m*PD:PVC:DOP:NaTPB (1.0:33.0:65.0:1.0) membrane in Fig. 5:

$$E = 89.7 + 29.8 \ \log[\mathrm{Pb(II)}] \quad (9)$$

Thus, Pb(II) concentration of 4.20×10^{-5} M is determined, which is close to the result (4.00×10^{-5} M) by ICP-MS with a relative error of 5.0%. Therefore, the ISE would substantially be reliable regardless of these nine interferents in a concentration range from 2.49×10^{-8} to 8.04×10^{-4} M.

Furthermore, the wastewater discharged from Printing House of Fudan University, Shanghai, China, was also tested by the electrode. Unfortunately, no stable potential value could be observed

Table 5
Recovery of the detection of lead(II) in tap water and human urine by the P*m*PD-based Pb(II)-ISE. The number of assays is at least 4 times and the standard deviations range from 0.6% to 6.45%.

Real sample	Pb(II) added (M)	Pb(II) detected (M)	Recovery (%)
Tap water 1	1.00×10^{-5}	1.03×10^{-5}	103.0
Tap water 2	5.00×10^{-5}	4.83×10^{-5}	96.6
Tap water 3	1.00×10^{-4}	0.97×10^{-4}	97.0
Tap water 4	5.00×10^{-4}	5.08×10^{-4}	101.2
Human urine	1.96×10^{-6}	2.38×10^{-6}	121.4

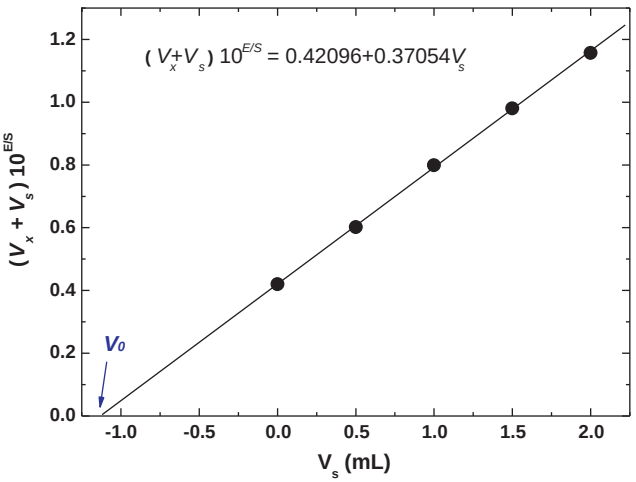


Fig. 12. Determination of Pb(II) concentration of 50.00 mL digested urine by Gran's plot. Pb(II) standard solution added was 1.00×10^{-4} M $Pb(NO_3)_2$.

and consequently it is impossible to obtain satisfactory results. Perhaps the sensing membrane had suffered from smearing by the residual printing ink in the wastewater.

A biological sample, i.e., assimilated human urine, was also selected to evaluate the applicability of the electrode. No Pb(II) could be detected possibly since the Pb(II) concentration is lower than the detection limit of the electrode. So a spiked urine was further used to examine the possibility of the application of the ISE for Pb(II) content measurement in urine. When the urine was spiked to 1.96×10^{-6} M by adding 1.00 mL standard Pb(II) solution at 1.00×10^{-4} M to 50.00 mL digested urine, four-time ISE examination by Gran's plot was conducted, just like a representative straight line shown in Fig. 12. From the intersection at X axis, a negative V_0 has been obtained, giving a Pb(II) concentration of the real sample according to Eq. (4). Four-time tests demonstrate Pb(II) concentration of 2.35×10^{-6} M, 2.21×10^{-6} M, 2.49×10^{-6} M, 2.49×10^{-6} M with an average concentration of 2.38×10^{-6} M and RSD of 6.45%, and recovery of 121.4%, as summarized in Table 5. Slightly higher recovery is related to the interference of a large amount of Na(I), K(I), and Ca(II), which cause the extra potential response of the electrode.

4. Conclusions

A new membrane electrode incorporating novel P*m*PD microparticles as ion carriers has been fabricated as a Pb(II)-ISE exhibiting fast potential response, wide working pH range, and good selectivity over other interfering metal ions. The membrane electrode with the mass ratio of P*m*PD:PVC:DOP:NaTPB of 1.0:33.0:65.0:1.0 displays the optimal Nernstian response to Pb(II). Most metal ions would not seriously affect the selectivity of the lead(II) electrode. The membrane electrode can be served as an indicator electrode in potentiometric titration of Pb(II) with EDTA, and can also be used to monitor Pb(II) in tap water, real river water, and even urine containing various interfering metal ions.

Acknowledgements

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