

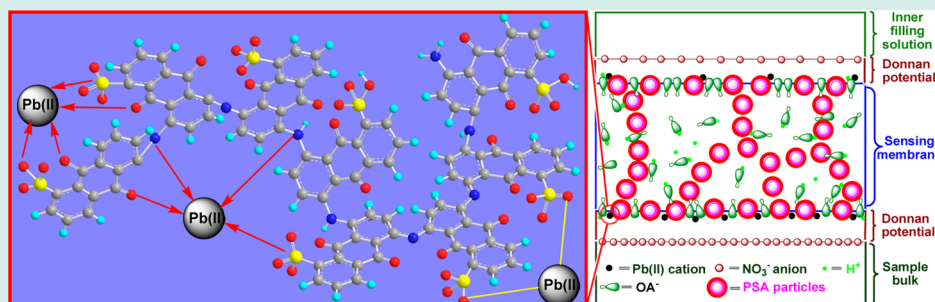
# Combinatorial Screening of Potentiometric Pb(II) Sensors from Polysulfoaminoanthraquinone Solid Ionophore

Mei-Rong Huang,<sup>\*,†</sup> Yong-Bo Ding,<sup>†</sup> and Xin-Gui Li<sup>\*,†,‡</sup>

<sup>†</sup>Institute of Materials Chemistry, Key Laboratory of Advanced Civil Engineering Materials of the Ministry of Education, College of Materials Science and Engineering, Tongji University, 1239 Si-Ping Road, Shanghai 200092, China

<sup>‡</sup>Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, U.K.

## S Supporting Information



**ABSTRACT:** A potentiometric Pb(II)-selective sensor was fabricated by a combinatorial screening of electrically conducting polysulfoaminoanthraquinone (PSA) nanoparticles as a solid ionophore, ion exchangers (oleic acid (OA) and NaTPB), plasticizers in a polyvinyl chloride (PVC) matrix, membrane thickness, inner filling ion species, and concentration. The membrane sensor with the composition of PSA/PVC/DOP (dioctyl phthalate)/OA (1.0:33:61:5.0) exhibited the best performance, including a slope of 29.3 mV decade<sup>-1</sup> in the concentration range 10<sup>-6.3</sup>–10<sup>-1.6</sup> M, detection limit of 1.6 × 10<sup>-7</sup> M, response time of 16 s, lifetime of five months, and good response reversibility. The proposed sensor has demonstrated good selectivity for Pb(II) over other monovalent, divalent and trivalent interfering ions, and could be used in a pH range of 3.62–5.22. The Pb(II) sensor has been successfully applied for the determination of Pb(II) concentration in real-world samples and also as an indicator electrode for potentiometric titration of lead ions.

**KEYWORDS:** potentiometric Pb(II) sensors, polysulfoaminoanthraquinone, solid ionophore, combinatorial screening

## INTRODUCTION

With the rapid development of modern industry, lead ions are ubiquitous in the natural environment as one of the most toxic heavy metals because of their nonbiodegradability and accumulation in organisms. Many analytical techniques, such as inductively coupled plasma mass spectrometry, atomic fluorescence, and absorption spectrometries, can be used to quantitatively analyze lead ions. However, these methods are usually limited to the laboratory because of the high cost of the appropriate equipment and the requirement for professional skills of an operator. In contrary, potentiometric sensors are characterized by simple operation, fast response, low cost, and nontoxic operation and are, therefore, particularly suitable for outdoor operations and online monitoring of lead ions in their solutions.<sup>1,2</sup>

For potentiometric sensors or ion selective electrodes (ISEs), ionophores embedded in the sensing membrane largely determine the selectivity and sensitivity of the sensor toward lead ions.<sup>3,4</sup> While many ionophores have been developed for the selective coordination of Pb(II) including macrocyclic compounds such as crown ethers,<sup>5</sup> calixarenes with the right cavity size,<sup>5–7</sup> nitrogen-containing compounds,<sup>8,9</sup> and O/S

atom-enriched organic compounds,<sup>10</sup> most require sophisticated synthetic procedures and are therefore not well suited to wide practical application.

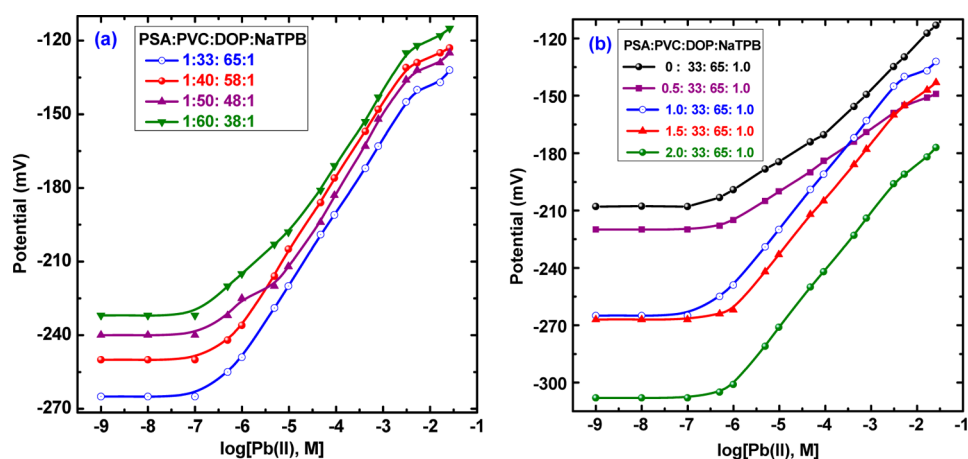
Recent investigations have demonstrated that some electrically conducting homopolymers<sup>11–13</sup> or copolymers<sup>14,15</sup> show strong interactions with metal ions. Polysulfoaminoanthraquinone (PSA),<sup>16</sup> a new semiconducting fused-ring polymer synthesized in our laboratory, has four types of functional groups including imino (–NH– and –N=), carbonyl (–C=O), and sulfonic groups (–SO<sub>3</sub><sup>–</sup>H<sup>+</sup>), which may all contribute to such binding. In addition, the PSA chains may provide rigid, nonpolarized ring cavities with the right size to accommodate Pb(II) ions. We therefore believe that the development of PSA as an ionophore of Pb(II)-ISE deserves systematic research.

To achieve Donnan exclusion of salt from the fixed charge (ionic sites) inside a sensing membrane, some counterions should be confined to the sensing membrane. Although neutral-ionophore-based membranes may work properly even when

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**Figure 1.** Variation of the potentiometric response curves of Pb(II)-sensor or Pb(II)-ISE membranes with changes in (a) DOP plasticizer and (b) PSA ionophore contents with a thickness of  $\sim 150 \mu\text{m}$  with an inner solution of  $1.0 \times 10^{-4} \text{ M Pb(NO}_3)_2$ .

**Table 1.** Characteristics of Pb(II)-Sensors Containing Different Amount of DOP Plasticizer and PSA Ionophore with a Sensing Membrane Thickness of  $\sim 150 \mu\text{m}$  with Inner Solution of  $1.0 \times 10^{-4} \text{ M Pb(NO}_3)_2$

PSA/PVC/DOP/NaTPB (weight ratio)	linear fitting range (M)	fitting equation	correlation coefficient, R	slope (mV decade <sup>-1</sup> )	detection limit (M)
1.0:60:38:1.0	$10^{-5.0}$ – $10^{-2.0}$	$E = -54.8 + 28.8 \log a$	0.9987	28.8	$6.3 \times 10^{-7}$
1.0:50:48:1.0	$10^{-5.0}$ – $10^{-2.0}$	$E = -60.9 + 30.3 \log a$	0.9983	30.3	$1.3 \times 10^{-6}$
1.0:40:58:1.0	$10^{-6.0}$ – $10^{-2.0}$	$E = -58.4 + 29.5 \log a$	0.9990	29.5	$3.2 \times 10^{-7}$
1.0:33:65:1.0	$10^{-6.0}$ – $10^{-2.0}$	$E = -71.8 + 29.5 \log a$	0.9999	29.5	$2.5 \times 10^{-7}$
0:33:65:1.0	$10^{-6.0}$ – $10^{-2.3}$	$E = -90.5 + 18.7 \log a$	0.9930	18.7	$5.0 \times 10^{-7}$
0.5:33:65:1.0	$10^{-6.0}$ – $10^{-2.3}$	$E = -119 + 16.2 \log a$	0.9995	16.2	$5.0 \times 10^{-7}$
1.5:33:65:1.0	$10^{-6.0}$ – $10^{-2.0}$	$E = -88.4 + 28.9 \log a$	0.9999	28.9	$6.3 \times 10^{-7}$
2.0:33:65:1.0	$10^{-6.0}$ – $10^{-2.0}$	$E = -122.1 + 29.8 \log a$	0.9998	29.8	$6.3 \times 10^{-7}$

there are only a very small amount of ionic sites (e.g., as impurities) in the membranes, the addition of a lipophilic ion-containing salt is advisable and beneficial to diminish electrostatic effects and achieve stable and quick responses. Some salts like sodium tetraphenylborate (NaTPB), potassium tetrakis(4-fluorophenyl)borate, tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (TFPB), and tetrakis(4-chlorophenyl)borate (TCIPB), have currently been used as ion exchangers or anion repulsive agents in Pb(II)-ISE. The chemical stability of these anionic additives is limited to some extent, especially in the presence of acids, oxidants, and light. For example, the phenyl on lipophilic borate is easily attacked by  $\text{H}^{+17}$  and  $\text{Hg(II)}^{18}$  to cause decomposition of  $\text{TPB}^-$  and  $\text{TCIPB}^-$  in aqueous solutions, a serious problem when lead and mercury ions are present together in the same sample. Additionally, some anion repulsive agents such as TFPB are generally expensive.

In this study, PSA, synthesized by chemically oxidative polymerization of ammonium 5-sulfonate-1-aminoanthraquinone (SA) monomer, was chosen as a novel solid ionophore for the construction of a Pb(II)-ISE sensor. Oleic acid (OA) was selected as an ion-exchanger to replace the often used lipophilic borate to form an ionic site. The ionophore content, plasticizer, pH, ionic site, membrane thickness, inner filling ion species, and its concentration were systematically optimized for the fabrication of the sensor with the maximal performance. The sensors have been practically applied to analyze Pb(II) concentration in four types of real-world samples included human saliva, tap water, tea leaves, and river water. Finally, the sensor was also investigated as an indicator electrode in the potentiometric titration of Pb(II) with EDTA.

## RESULTS AND DISCUSSION

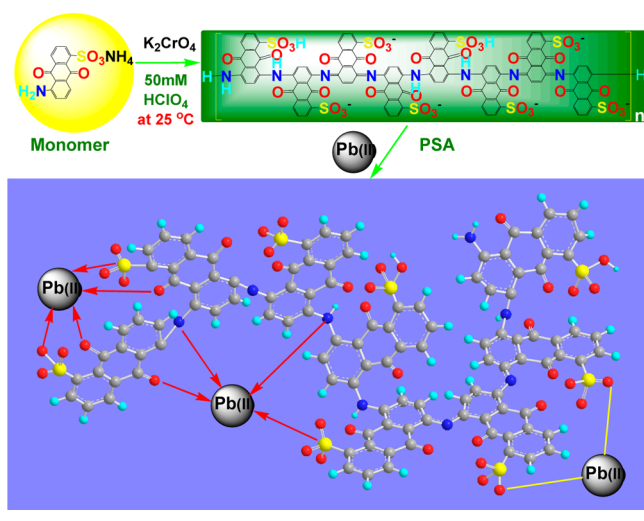
**Plasticizer Content in the Sensing Membranes.** The plasticizer used in a sensing membrane can influence the mobility of the ionophore molecules and the state of the metal-binding ligands, and therefore have a great effect on the potential response characteristics.<sup>19</sup> A good plasticizer should have a low tendency of exudation from the matrix, high capacity to dissolve other additives in the membrane, and adequate dielectric constant. Therefore, sensing membrane compositions were carefully optimized by varying the plasticizer content. Dioctyl phthalate (DOP) was selected as the plasticizer because of its most outstanding plasticizing properties in conducting polymeric ionophore.<sup>11</sup> Historically plasticized PVC membranes for Pb(II)-sensor fabrication contain about 50 to 67% plasticizer. These PVC films have advantageous physical properties including a low glass transition temperature (below room temperature). As shown in Figure 1a and Table 1, we found that the Nernstian slopes and linear range of the sensing membranes to be significantly affected by DOP content. Electrodes with PSA/PVC/DOP/NaTPB weight ratios of 1.0:60:38:1.0 and 1.0:50:48:1.0 showed the poorest comprehensive performance, presumably because at the lowest DOP contents, the mobility of NaTPB across the membranes was reduced and consequently the specific membrane resistance was greatly increased. Only the electrode with PSA/PVC/DOP/NaTPB (1.0:33:65:1.0) having the highest DOP content demonstrated the optimal potential response with a Nernstian slope of  $29.5 \text{ mV decade}^{-1}$ , a detection limit of  $2.5 \times 10^{-7} \text{ M}$ , and linear range between  $10^{-6.0}$  and  $10^{-2.0} \text{ M}$ . The use of more DOP than 65.0% led to high Pb(II) diffusion through the

membranes and high trans-membrane ion flux and thus inferior detection limits, and also low membrane strength. Therefore, the plasticizer content could not be too low or too high. In summary, the optimal DOP content in the plasticized PVC-based sensing membranes was found to be 65 wt %.

#### PSA Ionophore Content in the Sensing Membranes.

The ionophore (also referred to as the ion carrier or ligand) is the most important sensing component in an ion-selective membrane. It selectively binds the target ion (commonly referred to as primary ion) while discriminating against interfering ions. This selectivity results from proper complexation of primary ions shown in Scheme 1, and weak or minimal

**Scheme 1. Chemical Oxidative Polymerization of Ammonium 5-Sulfonate-1-aminoanthraquinone for the Synthesis of Polysulfoaminoanthraquinone (PSA) Particles Having Molecular Components for Complexation and Ion Exchange (Indicated by Red Arrows and Yellow Lines, Respectively) for Pb(II) Ions**



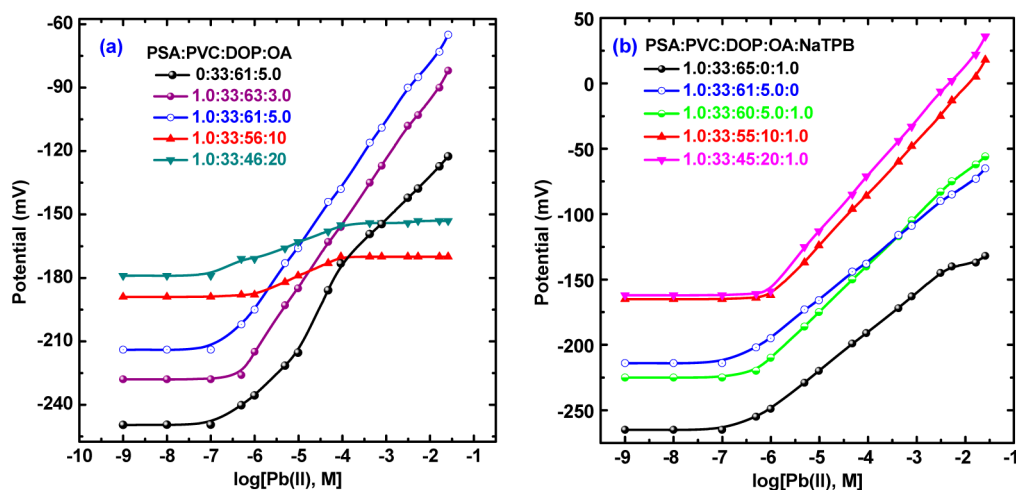
complexation of interfering ions. The known excellent adsorption of Pb(II) and Hg(II) onto the PSA nanoparticles suggested that the PSA-based ISE could have Nernstian responses to both ions.<sup>16</sup> However, the Hg(II) ion is inclined

to hydrolyze and the interaction between PSA and Hg(II) is affected by both complexation and redox reactions, while the interaction between PSA and the chemically inert Pb(II) ion only reflects complexation effects (Scheme 1).<sup>16</sup> As a result, the PSA was used as the ionophore of Pb(II)-ISE for the first time.

It is known that the sensitivity and selectivity of ISEs toward target ions depend significantly on the nature of the ionophore.<sup>1</sup> Optimization of sensing performance of Pb(II)-ISEs versus PSA ionophore content is compared in Figures 1b and 2a and Tables 1 and 2. Two PSA-free electrodes showed the lowest correlation coefficients and a shallow slope because of the absence of PSA sensing materials. The electrode with a membrane of PSA/PVC/DOP/NaTPB (0.5:33:65:1.0) composition exhibited the lowest slope (the poorest response) because of both low ionophore content, and the sub-Nernstian sensitivity of 16.2 mV decade<sup>-1</sup>, indicative of low electrode sensitivity. A high ionophore content of 2.0 wt % was also unfavorable to the stable transportation of ions across the membrane for a different reason: because so many PSA particles could not be homogeneously dispersed,<sup>20a</sup> pinholes can be generated in the membrane giving an increased ion flux, ultimately leading to performance deterioration. Only the electrode with an intermediate ionophore concentration (for example, PSA/PVC/DOP/NaTPB (1.0:33:65:1.0)), resulting in a presumed optimal amount of PSA dispersed homogeneously in the membrane, demonstrated the optimal response.

#### Oleic Acid Content in the Sensing Membranes.

Because oleic acid (OA) possesses high lipophilicity, low vapor pressure, and high capacity to dissolve the substrate and other additives present in the membrane, OA was chosen to partly replace the plasticizer DOP. As shown in Figure 2b and Table 2, electrode in which OA partially replaced DOP (with total OA + NaTPB content of greater than 5 wt %) showed super-Nernstian response, perhaps because high ionic strength within the membrane may lead to high ion concentration in the sensing membrane surface. This was supported by the observation that the super-Nernstian response was suppressed by lowering the ion exchanger concentration within the membrane, thereby reducing the ionic strength.<sup>20b</sup> Therefore, even the replacement of DOP with OA was harmful to the improvement of the electrode performance, and incorporation of both OA and NaTPB was not advantageous to overall



**Figure 2.** Potentiometric response curves of Pb(II)-ISE based on the sensing membrane having different DOP/OA ratios (a) in the absence of NaTPB and (b) in the presence of NaTPB with a thickness of  $\sim 150 \mu\text{m}$  with inner solution of  $1.0 \times 10^{-4} \text{ M Pb}(\text{NO}_3)_2$ .

**Table 2.** Characteristics of Pb(II)-Sensors Based on PSA Ionophores with Different Oleic Acid Content ( $\sim 150 \mu\text{m}$  Thickness, Inner Solution Concentration of  $1.0 \times 10^{-4} \text{ M Pb(NO}_3)_2$ )

PSA/PVC/DOP/OA/NaTPB (weight ratio)	fitting range (M)	fitted equation	correlation coefficient, R	slope (mV decade <sup>-1</sup> )	detection limit (M)
0:33:61:5.0:0	$10^{-6.3}$ – $10^{-1.6}$	$E = -76.8 + 26.2 \log a$	0.9931	26.2	$2.5 \times 10^{-7}$
1.0:33:63:3.0:0	$10^{-6.3}$ – $10^{-1.6}$	$E = -33.9 + 30.1 \log a$	0.9997	30.1	$3.2 \times 10^{-7}$
1.0:33:61:5.0:0	$10^{-6.3}$ – $10^{-1.6}$	$E = -18.8 + 29.3 \log a$	0.9997	29.3	$1.6 \times 10^{-7}$
1.0:33:56:10:0	$10^{-6.0}$ – $10^{-4.0}$	$E = -133.4 + 9.1 \log a$	0.9997	9.1	$7.9 \times 10^{-7}$
1.0:33:46:20:0	$10^{-6.0}$ – $10^{-4.0}$	$E = -122.8 + 8.1 \log a$	0.9986	8.1	$1.3 \times 10^{-7}$
1.0:33:65:0:1.0	$10^{-6.0}$ – $10^{-2.0}$	$E = -71.8 + 29.5 \log a$	0.9999	29.5	$2.5 \times 10^{-7}$
1.0:33:60:5.0:1.0	$10^{-6.0}$ – $10^{-2.0}$	$E = 7.3 + 36.4 \log a$	0.9999	36.4	$4.0 \times 10^{-7}$
1.0:33:55:10:1.0	$10^{-6.0}$ – $10^{-1.8}$	$E = 78.1 + 40.4 \log a$	0.9995	40.4	$1.0 \times 10^{-6}$
1.0:33:45:20:1.0	$10^{-6.0}$ – $10^{-1.8}$	$E = 99.5 + 42.6 \log a$	0.9997	42.6	$7.9 \times 10^{-7}$

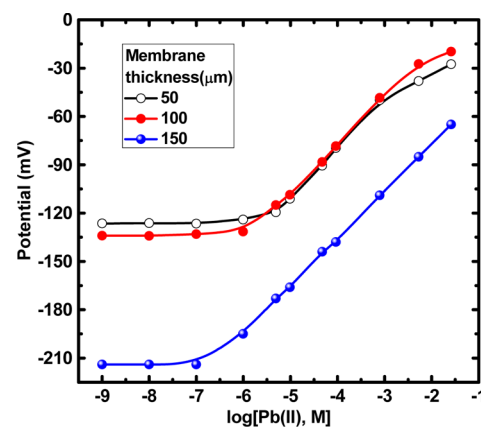
sensitivity. This is an important issue since electrochemical sensors are generally considered to be less sensitive than fluorescent assays,<sup>1,21</sup> and this is certainly true in the present case. Table 2 shows that the detection limit ( $1.6 \times 10^{-7} \text{ M}$ ) of the present potentiometric assay is  $\sim 1000$  times higher than that of the previous fluorescent assay.<sup>16</sup> This is expected since the complexation of Pb(II) with solid PSA in the potentiometric sensor would be less sensitive than the complexation and simultaneous quenching magnifying effect of Pb(II) with PSA molecules in solution in the fluorescent chemosensor.

A proper ion-exchanger in an ion-membrane sensor is required to enhance the electrical conductivity of the membrane and reduce the interference of lipophilic counterions, and thus quicken response and improve the selectivity, respectively. Without such additives, the electrodes hardly ever respond properly to target ions. The ion-exchanger such as different tetraphenyl borate salts and their lipophilic derivatives including sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), and fatty acids, such as OA<sup>22–29</sup> as lipophilic additives shown in Supporting Information Scheme S1 are widely used for the fabrication of ISEs. These anionic additives can ionize in plasticizers to give TPB<sup>-</sup>, TCIPB<sup>-</sup>, TFPB<sup>-</sup>, and C<sub>18</sub>H<sub>33</sub>O<sub>2</sub><sup>-</sup>, which can greatly reduce the anionic interference. Therefore, the ion-exchangers play an important role in elevating permselectivity to PVC-based sensors.<sup>30a</sup> In our tests, the addition of 5.0 wt % OA as a lipophilic additive replacing 1.0 wt % NaTPB showed better Nernstian response, superior detection limit of down to  $10^{-6.8} \text{ M}$  and wider linear range of  $10^{-6.3}$ – $10^{-1.6} \text{ M}$  at the same time (Figure 2a and Table 2). While it appears that OA helps suppress NaTPB leakage, a further increase in the OA content up to 20 wt % did not further enhance the sensing performance. Rather, it gave much lower sensitivity, since too much OA may also leak from the sensing membrane. An OA concentration of 5.0 wt % was chosen as the optimum amount of ion-exchanger for the following study, reflecting its balanced role as both a phase transfer catalyst and a contributor to the complexation mechanism and the dielectric constant of the membrane.<sup>29</sup>

This type of effect has been observed by others. For example, the optimized detection limit and response slope of acetophenone-plasticizing PVC-based Al(III)-ISE were found to be  $5.0 \times 10^{-7} \text{ M}$  and  $17.5 \text{ mV decade}^{-1}$ , respectively, if adding 5 wt % OA to replace part of the plasticizer acetophenone.<sup>25</sup> Although calcium and magnesium oleates have low water solubility (40 mg/100 mL and 24 mg/100 mL, respectively), we observed no precipitates when OA was dropped into aqueous Ca(NO<sub>3</sub>)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> at  $1.0 \times 10^{-3} \text{ M}$ , with the OA still forming oil phase droplets on water.

Insoluble oleate salts with Ca(II) or Mg(II) ions will form when sodium oleate meets Ca(NO<sub>3</sub>)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> at 90 °C or higher temperature. Therefore, no precipitate formed when OA-containing electrode meets aqueous Ca(II) and Mg(II) under ambient conditions. Furthermore, OA is not degraded by mercury ions, which often coexist with lead ions, whereas mercury may degrade tetraphenyl borate and TCIPB salts.<sup>18</sup> TFPB salts are in any case too expensive to realize industrial applications.

**Optimization of Sensing Membrane Thickness.** The sensing membranes of PSA/PVC/DOP/OA (1.0:33:61:5.0) with three thicknesses from 50 to 150  $\mu\text{m}$  were tested, with the results shown in Figure 3 and Table 3. With increasing the



**Figure 3.** Potentiometric responses of the Pb(II)-ISEs based on different membrane thicknesses at PSA/PVC/DOP/OA of 1.0:33:61:5.0 with the same inner filling solution of  $1.0 \times 10^{-4} \text{ M Pb(NO}_3)_2$  and the same conditioning process.

thickness, the response slope of  $29.3 \text{ mV decade}^{-1}$  became closer to the theoretical Nernstian slope of  $29.6 \text{ mV decade}^{-1}$  and the detection limit improved for the thickest material, possibly due to less transmembrane defects. However, we suspect that membranes thicker than 150  $\mu\text{m}$  would suffer from slower response and much longer conditioning times, so 150  $\mu\text{m}$  was chosen as the thickness for final fabrication and testing of a Pb(II) sensor.

**Optimization of Inner Filling Ion Species.** Five ions [H<sup>+</sup>, Na(I), Mg(II), Ni(II), and Zn(II)] known to be generally less interfering to the formation and performance of conducting aniline-derivative polymers<sup>11,15</sup> were chosen as inner filling ions and conditioning ions. In these experiments, the sensing membranes did not contain the primary ion of Pb(II) when these ions were used. As seen in Figure 4a and Table 3, the

Table 3. Characteristics of Pb(II) Ion Sensors Based on Solid PSA Ionophores

sensing membrane thickness ( $\mu\text{m}$ )	inner filling ions			fitted equation	R	response slope (mV decade <sup>-1</sup> )	detection limit (M)
	species	concentration (M)	fitting range (M)				
150	Pb(II)	$10^{-4}$	$10^{-6.3}$ – $10^{-1.6}$	$E = -18.8 + 29.3 \log a$	0.9997	29.3	$1.6 \times 10^{-7}$
100	Pb(II)	$10^{-4}$	$10^{-6.0}$ – $10^{-2.3}$	$E = 38.1 + 28.8 \log a$	0.9983	28.8	$1.3 \times 10^{-6}$
50	Pb(II)	$10^{-4}$	$10^{-5.3}$ – $10^{-3.1}$	$E = 48.0 + 31.7 \log a$	0.9995	31.7	$3.2 \times 10^{-6}$
150	H <sup>+</sup>	$10^{-4}$	$10^{-5.0}$ – $10^{-1.6}$	$E = 29.9 + 31.8 \log a$	0.9996	31.8	$3.2 \times 10^{-7}$
150	Na(I)	$10^{-4}$	$10^{-6.0}$ – $10^{-1.6}$	$E = 80.0 + 45.3 \log a$	0.9966	45.3	$7.9 \times 10^{-7}$
150	Mg(II)	$10^{-4}$	$10^{-6.0}$ – $10^{-4.0}$	$E = 7.4 + 33.4 \log a$	0.9978	33.4	$1.0 \times 10^{-6}$
150	Ni(II)	$10^{-4}$	$10^{-6.0}$ – $10^{-4.0}$	$E = 24.1 + 35.1 \log a$	0.9989	35.1	$1.0 \times 10^{-6}$
150	Zn(II)	$10^{-4}$	$10^{-5.0}$ – $10^{-1.6}$	$E = 120.0 + 53.8 \log a$	0.9959	53.8	$4.0 \times 10^{-6}$
150	Pb(II)	$10^{-5}$	$10^{-5.3}$ – $10^{-2.3}$	$E = 66.0 + 35.6 \log a$	0.9985	35.6	$7.9 \times 10^{-7}$
150	Pb(II)	$10^{-3}$	$10^{-5.3}$ – $10^{-1.6}$	$E = 17.1 + 30.7 \log a$	0.9987	30.7	$2.0 \times 10^{-6}$

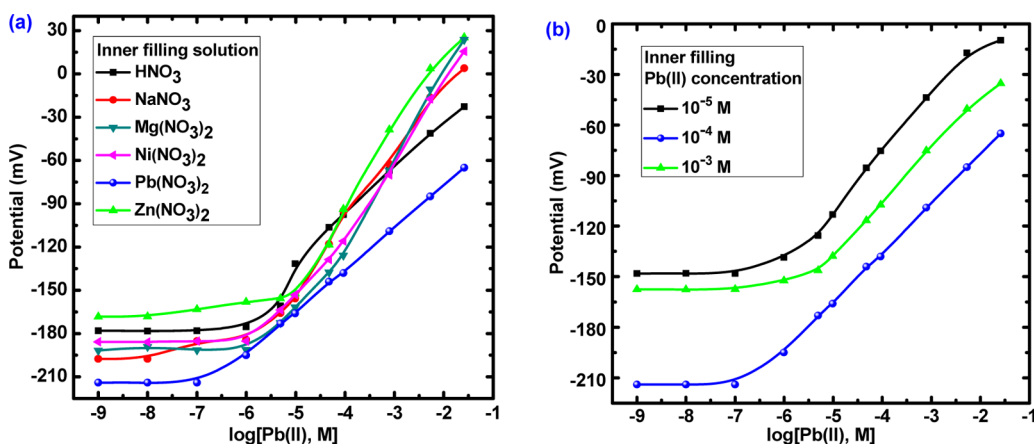


Figure 4. Response curve of Pb(II)-ISE based on 150  $\mu\text{m}$ -thick membrane of PSA/PVC/DOP/OA (1.0:33:61:5.0) with (a) different inner filling ions under 24 h-condition in respective ion solutions at the same ion concentration of  $1.0 \times 10^{-4}$  M and (b) effect of the inner filling Pb(II) activity on the response potential.

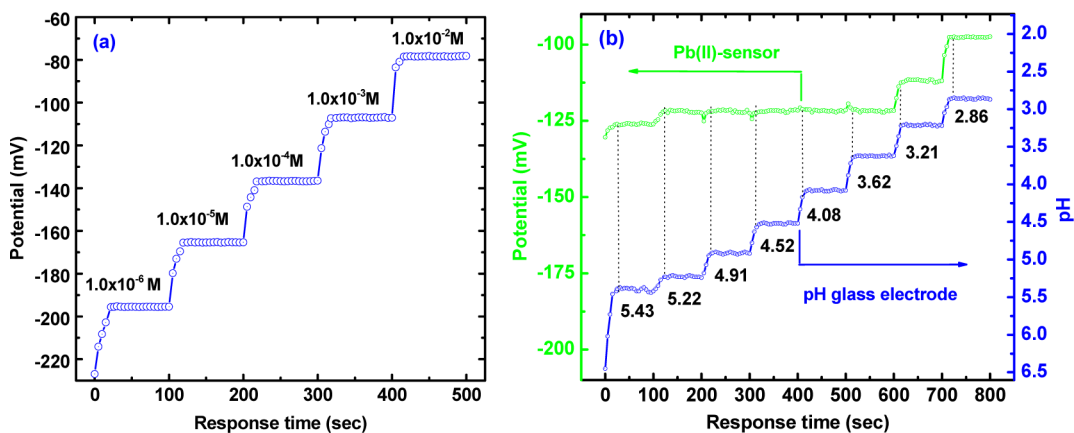


Figure 5. (a) Dynamic response time profile of the Pb(II) sensor based on membrane with PSA/PVC/DOP/OA weight ratio of 1.0:33:61:5.0. (b) Effect of pH on the response potential at  $1.0 \times 10^{-3}$  M Pb(II) concentration of the same sensor.

response curves exhibited similar response times (20–30 s) and higher slopes, but inferior detection limits. This could be related to the ion exchange between nonprimary ions in the membranes and primary Pb(II) ions in the sample solution. Different degrees of ion exchange are expected to cause changes in sensitivity to Pb(II), and nonprimary ions with higher atomic weight tend to give higher slopes owing to greater complexation with the ionophore (more ion exchange resulting in greater sensitivity). Note also that Na(I) yields higher slope than Mg(II) and Ni(II) partly due to its greater theoretical

slope according to the Nernst equation. Overall, however, we conclude that Pb(II) is the best inner filling and conditioning ion for the fabrication of Pb(II) sensors, achieving the best detection limit of  $1.6 \times 10^{-7}$  M.

**Optimization of Inner Filling Pb(II) Concentration.** In the case of plasticized sensing membranes, it is known that Pb(II) leakage from the inner filling Pb(II) solution at higher concentrations (up to  $1.0 \times 10^{-3}$  M) leads to inferior detection limits. Contrariwise, Pb(II) depletion at the membrane surface in sample solutions at higher Pb(II) concentrations causes the

super-Nernstian effect,<sup>30b</sup> in the case of inner filling Pb(II) solution at  $1.0 \times 10^{-5}$  M, as summarized in Figure 4b and Table 3. Therefore, an inner filling Pb(II) ion concentration of  $1.0 \times 10^{-4}$  M is optimal for these Pb(II) sensors, giving ideal Nernstian slope and superior detection limit. This concentration matches well with the linearly sensitive Pb(II) concentration range of  $1.0 \times 10^{-6}$ – $2.5 \times 10^{-2}$  M.

**Dynamic Response Time of the Sensor.** For conventional plasticized PVC membrane-based ISEs, the potentiometric response is controlled by the phase-boundary potential that results from the sample and membrane interface when activity changes occur in either surface layer.<sup>31a</sup> Figure 5a shows that the dynamic response time of the optimized sensor, measured as the time required to reach equilibrium response, was approximately 22 s for Pb(II) concentration of  $1.0 \times 10^{-6.0}$  M. On elevating the Pb(II) concentration from  $1.0 \times 10^{-6.0}$  to  $1.0 \times 10^{-2.0}$  M, the response time shortened steadily from 22 to 16 s. Thus, the response time was found to be sensitive to the Pb(II) concentration, probably because of accelerating exchange kinetics of complexation–decomplexation of Pb(II) at more concentrated Pb(II) solution/membrane interface.

**Working pH Range of the Sensor.** The influence of solution pH on the potential response of the Pb(II) sensor was tested in  $1.0 \times 10^{-3}$  M Pb(II) over pH range between 2.6 and 5.4, adjusted by addition of 1.0 and 0.10 M HNO<sub>3</sub> or 0.10 M NaOH. As seen in Figure 5b, the potential remained substantially constant from pH 3.62 to 5.22. Increased potential at pH < 3.62 is consistent with the expected protonation of the ligands in the membrane phase, diminishing their ability bind Pb(II) ions. At higher pH, the potential drop may be due to the formation of hydroxyl complexes of Pb(II) ions in solution and the deprotonation of OA as an organic acid. The optimal working pH range of the sensor was therefore established as 3.62–5.22.

**Sensor Selectivity.** The selectivity coefficient is one of the key parameters of the sensor, determining whether a reliable measurement in target sample is possible. Selectivity coefficients ( $K_{Pb,M}^{pot}$ ) of the proposed sensor are listed in Supporting Information Figure S1 and Table 4. With the

**Table 4. Logarithmic Selectivity Coefficients for the Pb(II)-ISE by a Fixed Interference Method at an Interfering Ion Concentration of  $1.0 \times 10^{-3}$  M**

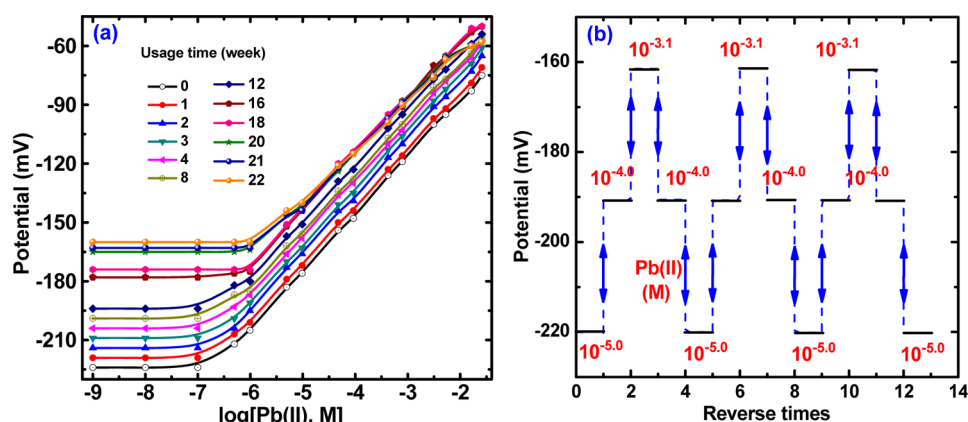
compound	interfering ion	detection limit $a'_{pb}$ (M)	selectivity coefficient log $K_{Pb,B}^{pot}$
AgNO <sub>3</sub>	Ag(I)	$10^{-5.4}$	0.6
NaNO <sub>3</sub>	Na(I)	$10^{-5.5}$	0.5
NH <sub>4</sub> NO <sub>3</sub>	NH <sub>4</sub> (I)	$10^{-5.5}$	0.5
KNO <sub>3</sub>	K(I)	$10^{-5.8}$	0.2
Ca(NO <sub>3</sub> ) <sub>2</sub>	Ca(II)	$10^{-5.5}$	−2.5
Mg(NO <sub>3</sub> ) <sub>2</sub>	Mg(II)	$10^{-5.8}$	−2.8
Ba(NO <sub>3</sub> ) <sub>2</sub>	Ba(II)	$10^{-5.5}$	−2.5
Cu(NO <sub>3</sub> ) <sub>2</sub>	Cu(II)	$10^{-5.4}$	−2.4
Zn(NO <sub>3</sub> ) <sub>2</sub>	Zn(II)	$10^{-5.6}$	−2.6
Mn(NO <sub>3</sub> ) <sub>2</sub>	Mn(II)	$10^{-5.8}$	−2.8
Co(NO <sub>3</sub> ) <sub>2</sub>	Co(II)	$10^{-5.6}$	−2.6
Ni(NO <sub>3</sub> ) <sub>2</sub>	Ni(II)	$10^{-6.0}$	−3.0
CdCl <sub>2</sub>	Cd(II)	$10^{-5.4}$	−2.4
Hg(NO <sub>3</sub> ) <sub>2</sub>	Hg(II)	$10^{-3.5}$	−0.5
AlCl <sub>3</sub>	Al(III)	$10^{-5.6}$	−3.6
Cr(NO <sub>3</sub> ) <sub>3</sub>	Cr(III)	$10^{-5.4}$	−3.4
FeCl <sub>3</sub>	Fe(III)	$10^{-5.8}$	−3.8

exception of the oxidizable Hg(II), PSA was found to be selective toward Pb(II) against all divalent or trivalent interfering ions examined, with logarithmic selectivity coefficients smaller than −2. This indicates that these divalent or trivalent interfering ions would not significantly disturb the response of the sensors toward Pb(II). We also tested an optimized membrane formulation (PSA/PVC/DOP/OA = 1.0:33:61:5.0) an ionophore in the presence of five common oxidizing species [Hg(II), Ag(I), Cu(II), Fe(III), and H<sub>2</sub>O<sub>2</sub>] in a wide concentration range from  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M. As shown in Supporting Information Figure S2, neither Hg(II) nor H<sub>2</sub>O<sub>2</sub> induced a significant response, Ag(I) and Cu(II) were detected with much lower response slopes (14.2 and 13.0) than the Nernstian slopes (59.6 and 29.8) of the other monovalent and divalent metal ions respectively, and Fe(III) was detected with a response slope of up to 33.0, much higher than the Nernstian slope (14.9) expected of trivalent metal ions. Because of these varying outcomes and the potential for additional redox reactions between the PSA and the five oxidizing species, we judge PSA to be not the ideal ionophore for sensing these types of oxidizing species.

The concentration of Ca(II) ions in most environmental water samples is much higher than Pb(II) concentrations,<sup>31b</sup> and Ca(II) ions did not strongly interfere with the measurement of Pb(II), since there is almost no interaction between Ca(II) ions and the conducting polymer particles. This is supported by a quantitative recovery of Pb(II) ions from the real environmental water samples containing different interferents including Ca(II)/Mg(II) ions at respective 50/26 times higher concentration than Pb(II) ions demonstrated below. The comparison of selectivity coefficients is not meaningful among interfering ions with different charges, although the direct comparison of the selectivity coefficients should be significant for evaluating interference among the same valent ions. Supporting Information Figure S1 shows that the interferences are comparable for the Pb(II)-ISE in the presence of  $1.0 \times 10^{-3}$  M monovalent or divalent interfering ions, even though their selectivity coefficients differ ( $10^{0.5}$  or  $10^{-2}$ , respectively). This superior selectivity of PSA may be ascribed to its rigid preorganized structure with the right cavity size to match with Pb(II).

**Sensor Lifetime and Reversibility.** The lifetime of the sensors was evaluated by periodically and repetitively recalibrating the potential response to Pb(II) ions in their standard solutions. Figure 6a and Supporting Information Table S1 show that the lifetime was about 21 weeks (5 months), much longer than that of other Pb(II)-sensors with lower detection limits superior to  $2.0 \times 10^{-6}$  M listed in Supporting Information Table S2. Such long lifetimes are an expected benefit of the sensor design, since the solid PSA ionophore cannot be lost during long-term usage regardless of possible loss of the liquid plasticizer. In addition, the partly water-soluble borate was completely replaced by water-insoluble OA.

The reversibility of the potential response of the Pb(II) ion-selective electrode with PSA/PVC/DOP/OA weight ratio of 1.0:33:61:5.0 toward Pb(II) solutions at three typical concentrations was determined as illustrated in Figure 6b. The potential response changed very little for variation in Pb(II) concentration from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-3.1}$  M, repetitively, showing good reversibility of the potential response of the sensors to Pb(II).



**Figure 6.** (a) Nernstian response curves with usage time of Pb(II)-ISE based on membrane with a thickness of  $\sim 150 \mu\text{m}$  with inner filling solution of  $1.0 \times 10^{-4} \text{ M Pb(NO}_3)_2$ . (b) Reversibility of the potential response of the Pb(II) ion-selective electrode with PSA/PVC/DOP/OA weight ratio of 1:33:61:5 toward Pb(II) solutions at three concentrations.

**Table 5. Simulated and Calculated Values Obtained by the Electrochemical Impedance Spectra of the PSA-Based Sensing Membranes with the Same Thickness and Area of  $150 \mu\text{m}$  and  $1.0 \text{ cm}^2$  Having Respective OA and NaTPB Ion Exchangers**

membrane composition	conditioned in $1.0 \times 10^{-4} \text{ M Pb(NO}_3)_2$	bulk resistance $R_b$ ( $\text{M}\Omega$ )	geometric capacitance $C_g$ (pF)	membrane conductivity $\sigma$ ( $\text{S cm}^{-1}$ )	Warburg impedance coefficient $\sigma_w$ ( $\Omega\text{-s}^{-1/2}$ )
PSA/PVC/DOP/OA = 1.0:33:61:5.0	no	10.0	59.7	$1.50 \times 10^{-9}$	
	yes	41.9	69.0	$3.58 \times 10^{-10}$	
PSA/PVC/DOP/NaTPB = 1.0:33:66:1.0	no	3.73	107	$4.02 \times 10^{-9}$	$3.65 \times 10^5$
	yes	6.66	86.8	$2.25 \times 10^{-9}$	$5.49 \times 10^5$

**Bulk Impedance of PSA Membranes.** Electrochemical impedance spectra (EIS) of PSA-containing sensing membranes with OA ion exchanger (Supporting Information Figures S3a and b) all showed single nearly nondepressed semicircles throughout the frequency scope in the complex impedance plane plot (Nyquist plot) because of the absence of additional salts. Considering that the contacting interface between membrane and electrode is copper, both double layer capacitance and charge-transfer resistance are ignored, and the nondepressed semicircles are largely ascribed to the bulk resistance  $R_b$  of the membrane.<sup>32</sup> From the diameter of the semicircles, the  $R_b$  is found to be  $10.0 \text{ M}\Omega$  for virgin membrane and  $40.9 \text{ M}\Omega$  for the conditioned one (Table 5). The increase in resistance after conditioning may result from new interfaces formed between the copper sheet and the conditioning aqueous solution at lower Pb(II) concentration ( $1.0 \times 10^{-4} \text{ M}$ ) adsorbed on the membrane surface. Based on the  $R_b$ , the membrane conductivity is estimated at  $1.50 \times 10^{-9}$  and  $3.58 \times 10^{-10} \text{ S cm}^{-1}$ , respectively.

The Nyquist plots of the membrane containing NaTPB as ion exchanger are linear at low frequency and slightly depressed semicircles at high frequency, implying a limitation including mass transport. The depressed semicircles are related to dispersion effect, and these systems can be represented by an equivalent circuit in Supporting Information Figure S4b comprising series one parallel RC element and one Warburg impedance  $Z_w$ . Again, the  $R_b$  of the conditioned membrane is larger than that of virgin one, and the membrane conductivity was estimated as  $(4.02\text{--}2.25) \times 10^{-9} \text{ S cm}^{-1}$  in Table 5. On the other hand, the straight Warburg line becomes an arc due to concentration polarization of NaTPB. Their fitting lines of the Warburg resistance (only  $Z_{re}$ ) vs (angular frequency) $^{-1/2}$  are shown in Supporting Information Figure S5. From the intersection and slope of the lines, both bulk resistance  $R_b$

and Warburg coefficient  $\sigma_w$  are found to coincide with those deduced from the diameter of semicircles in Supporting Information Figure S3c and d. The diffusion coefficient  $D$  was estimated to be on the order of  $10^{-9} \text{ cm}^2\text{-s}^{-1}$  on the basis of the  $\sigma_w$  on the assumption that Na(I) ions from NaTPB are the main mobile sites in the bulk membrane; almost no Pb(II) ions are trapped in either the virgin or conditioned membrane.

From Bode form in Supporting Information Figure S6, it is found that the  $|Z|$  value is almost constant, and the phase angle is close to zero in the frequency range from 0.05 to 50 Hz for membranes with OA as ion exchanger in virgin state, indicating that the capacitive response hardly ever changes and the impedance of  $10.6 \text{ M}\Omega$  results from the pure resistance of the system. The total impedance is about 2.7 times larger than that with NaTPB. The semiconducting PSA ionophore-based sensing membrane without NaTPB can sense lead ions in the same way.

Another result of OA taking the place of NaTPB in the sensing membrane is that there are no linear segments at low frequency in the Nyquist plot (Supporting Information Figure S3a and b), signifying no ion diffusion in membrane bulk even after conditioning in  $1.0 \times 10^{-4} \text{ M Pb(NO}_3)_2$ . In other words, the conditioning process did not bring detectable Pb(II) ions into the bulk membrane, and thus primary ion leakage can be suppressed substantially. The electronic conductivity does not suffer since both semiconducting ionophore and about  $10^{-3} \text{ M H}^+$  dissociated from OA are present in the membrane. As a result, such a semiconducting polymer ionophore having complex functionality in solid state has distinguished itself from the traditional PVC membrane with soluble ionophores in molecular scales.

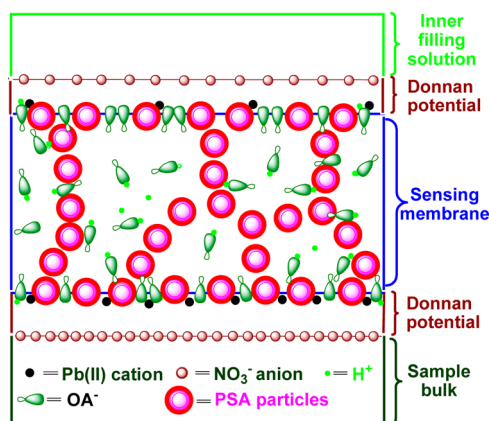
#### Potentiometric Responsive Mechanism of the Sensor.

The membrane potential consists of three types of potentials, that is, the bulk membrane potential, the Donnan potentials at

two sides of the membrane. For the sensing membrane PVC/DOP/OA/PSA without NaTPB, the electrical conductivities determined by electrochemical impedance spectroscopy, including both electronic and ionic conductivities, were the same as the electronic-only conductivity revealed by multimeter. In contrast, the conductivity tested by the electrochemical impedance spectroscopy for the sensing membrane PSA/PVC/DOP/NaTPB with NaTPB was almost 1 order of magnitude larger than that determined by multimeter. Since in the former case there are no Pb(II) ions within the membrane bulk, and thus no primary ion flux or diffusion across the membrane, these results suggest that the membrane can conduct electricity via the large  $\pi$ -conjugated electrons on the PSA macromolecular chains rather than the Pb(II) ions. This is quite different from the potentiometric responsive mechanism of the sensing membrane containing liquid ionophores. Very low diffusion coefficients of Pb(II) ions across membranes containing intrinsically conducting nanoparticles of solid copolyaniline as ionophores have also been reported, further supporting the absence of conduction by primary ions within the membrane bulk.<sup>15</sup> For these reasons, the Pb(II)-sensor reported here, containing solid electrically conducting PSA ionophore and OA, possesses long lifetime and strong sensitivity or superior lower detection limits. Good selectivity is thought to arise from a fortuitous match between the metal-binding groups on the PSA chains and the relatively large size of the Pb(II) ion.

Scheme 2 illustrates the proposed potentiometric responsive mechanism of the sensing membranes, comprised of two

**Scheme 2. Potentiometric Responsive Mechanism of the Sensing Membrane Containing Electrically Conducting PSA Particles As Ionophores in the Pb(II)-Sensor after Conditioning in  $1.0 \times 10^{-4}$  M  $\text{Pb}(\text{NO}_3)_2$**



contributing factors: (1) electric conductance through the network formed by PSA particulate ionophores within the bulk membrane of DOP plasticizing PVC helps to conquer the low electric conductance of the NaTPB-free sensing membrane and (2) significant and selective complexation of Pb(II) ions onto the PSA particles on the active surface of the membrane.

**Comparison of the Pb(II) Sensor with Others.** Figure 7a, Table 6, and Supporting Information Table S2 list some key parameters (slope, pH range, linear range, detection limit, and lifetime) of the Pb(II) sensor developed in this study compared to other Pb(II)-ISEs obtained commercially and described in the literature.<sup>11,33–46</sup> The Pb(II) sensor based on PSA-nanosized ionophore demonstrates a relatively wide fitting

range, superior detection limit, and long lifetime,<sup>47</sup> but its response time and pH range are not always better than others.

**Potentiometric Titration As Indicator Electrode.** The optimized Pb(II)-ISE sensor was tested as an indicator electrode in the potentiometric titration of Pb(II) at  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4}$  M with  $1.0 \times 10^{-3}$  M EDTA. During this titration no pH or ionic strength adjustments were made. As presented in Figure 7b, the observed titration curves accurately represented the amount of lead ions in the test solutions.

**Real Sample Assay.** Four samples from real-world sources (tap water, river water, black tea, human saliva) were analyzed with the optimized PSA-based sensor, and no Pb(II) was detected. These fluids were then spiked with  $\text{Pb}(\text{NO}_3)_2$  to a Pb(II) concentration of approximately 1 mg/L ( $5.0 \times 10^{-6}$  M), and analyzed by standard atomic absorption spectroscopy (AAS), as well as with our sensor. The two methods agreed quite well (Table 7), showing that quantitation of Pb(II) ions in the presence of different potentially interfering species is feasible. The type of Pb(II)-ISE described here should therefore be useful for outdoor operations and online detection of potential Pb(II) contamination with fast response, low cost and simple operation.

## CONCLUSION

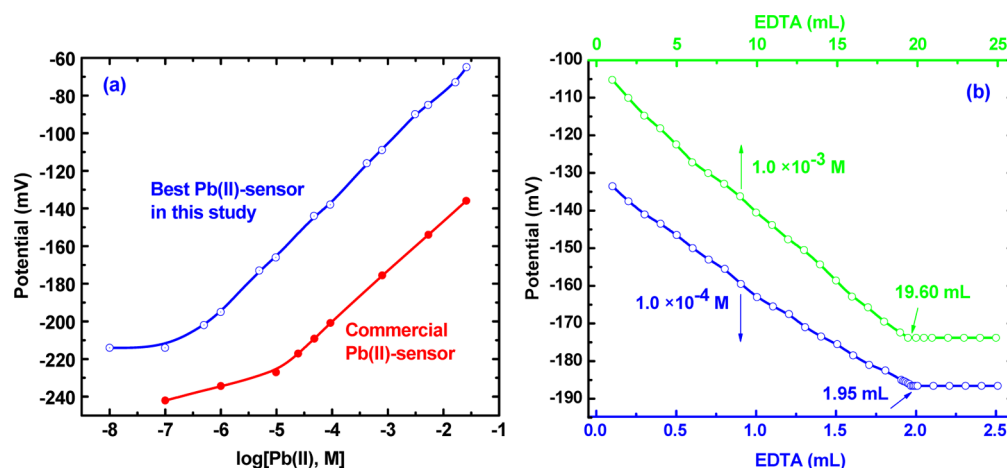
Polysulfoaminoanthraquinone (PSA) nanoparticles are a suitable ionophore for construction of a PVC-based membrane selective electrode for the determination of Pb(II) ions in aqueous solution. The factors of sensing membrane composition, oleic acid (OA) additive, dioctyl phthalate (DOP) plasticizer, membrane thickness, inner filling ion species, and concentration were systematically optimized. Compared to the conventional dissolved ionophore, the inherent advantages of the optimized sensor include simple operation, precise results, low cost, fast response, wide dynamic range, long lifetime, and good selectivity over other metal ions. The proposed sensor was successfully applied for the analysis of Pb(II) content in aqueous solutions and for online monitoring Pb(II) in real world samples containing various interferents. The novel nature of our optimizing combinatorial approach is that both sensing membrane ingredient and the sensor fabrication can be optimized comprehensively. The Pb(II) sensor optimized thus is better than the most sensitive and selective sensors known.

## EXPERIMENTAL PROCEDURES

**Preparation of Polysulfoaminoanthraquinone Particles.** Polysulfoaminoanthraquinone (PSA) nanoparticles were synthesized by oxidative polymerization of ammonium 5-sulfonate-1-aminoanthraquinone in aqueous medium containing the oxidant  $\text{K}_2\text{CrO}_4$ , as shown in Scheme 1.<sup>16</sup> The virgin PSA powder thus obtained was composed of irregular grainy nanoparticles with a diameter 50–190 nm, and was insoluble in both water and THF. A stable dispersion was achieved in PVC/NaTPB/OA/DOP solution in THF,<sup>16</sup> as well as in the resulting sensing membrane.

**Fabrication of Sensing Membrane and Ion Selective Electrode.** The general procedure to prepare the PVC membrane was as follows: 195 mg of DOP, 99 mg of PVC, 3 mg of PSA, and 3 mg of NaTPB or 15 mg of OA were mixed thoroughly in 5 mL of THF. The mixture was stirred at 25 °C for 2 h with ultrasonic treatment to promote the dispersion of the PSA particulate. The resulting viscous solution was cast into





**Figure 7.** (a) Potentiometric response curves of the Pb(II)-sensors fabricated in this study and obtained commercially (type pPb-1-01). (b) Potentiometric titration plots of  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4}$  M Pb(II) solution (20.0 mL) with  $1.0 \times 10^{-3}$  M EDTA.

**Table 6.** Characteristics of PSA electrode and commercial Pb(II)-ISEs

sensors	fitting range (M)	fitting equation	correlation coefficient, R	slope ( $\text{mV decade}^{-1}$ )	detection limit (M)	response time (s)
optimal Pb(II) sensor in this study	$10^{-6.3}$ – $10^{-1.6}$	$E = -18.8 + 29.3 \log a$	0.9997	29.3	$1.6 \times 10^{-7}$	16–20
commercial Pb(II) sensor pPb-1-01	$10^{-5.0}$ – $10^{-1.6}$	$E = -93.1 + 26.8 \log a$	0.9999	26.8	$2.8 \times 10^{-6}$	30–50
Orion Pb(II)-sensor 9682BNWP	$10^{-5}$ – $10^{-1}$	NA	NA	23–29	$\sim 10^{-6}$	$\leq 10$

**Table 7.** Determination of Lead Concentration in Spiked Real-World Samples at  $1.04 \text{ mg L}^{-1}$  by the Proposed Pb(II) Sensor and Comparison against a Reference AAS Method

real-world samples	AAS ( $\text{mg L}^{-1}$ )	ISE-standard addition ( $\text{mg L}^{-1}$ ) <sup>a</sup>	relative standard deviation (%)	relative error (%)
tap water	0.95	1.03 ( $\pm 0.05$ )	$\pm 4.9$	8.4
river water	1.16	1.05 ( $\pm 0.05$ )	$\pm 4.8$	9.5
black tea	0.96	1.04 ( $\pm 0.04$ )	$\pm 3.8$	8.3
human saliva	1.0	1.04 ( $\pm 0.05$ )	$\pm 4.8$	4.0

<sup>a</sup>Average of six-times replicate measurements ( $\pm$ standard deviation).

a 28 mm diameter glass ring affixed onto a glass plate. After the solvent evaporation at room temperature for 24 h, the membrane discs of 14-mm diameter were glued onto a 10-mm inner diameter plastic tube.

**Potential Measurements.** All response potentials were examined by varying the  $\text{Pb}(\text{NO}_3)_2$  concentration in a range between  $1.0 \times 10^{-9}$  and  $1.0 \times 10^{-1}$  M.<sup>11,15</sup> Potentials were measured with a PHS-3C potentiometer (Shanghai Leici Instruments Factory, China) with a sensitivity of 0.6 mV and an input resistance of greater than  $1.0 \times 10^{12} \Omega$ . The potential readings were recorded after the response potential kept a stable value with a drift of less than 1 mV/10 min. The potential response curves were plotted as a logarithmic function of Pb(II) activity. The activities of the primary ions were based on activity coefficient, which was calculated according to Debye–Huckel equation. 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. The dynamic response time required for the proposed Pb(II) sensor to reach a steady potential within  $\pm 1$  mV of the final equilibrium value was measured after successive additions of concentrated primary

Pb(II) ion solution (1.0 mL) over a fixed initial volume of 100 mL.

## ■ ASSOCIATED CONTENT

### Supporting Information

Reagents, Debye–Huckel equation, selectivity/lifetime/bulk membrane impedance measurements, conductivity/diffusion coefficient equations, real sample testing, the molecular structural formulas of anionic lipophilic additives, characteristics of Pb(II) sensors with time, comparison of Pb(II) sensors in PVC matrix based on PSA ionophores and other ionophores in the literature, potentiometric response curves of the Pb(II) sensor by a fixed interference method, potential response of the Pb(II) sensor toward respective five oxidizing species, Nernstian response curves of Pb(II) sensor with time, reversibility of the potential response of the Pb(II) sensor, Nyquist and Bode form diagrams of electrochemical impedance spectra of the sensing membranes, and plot of real resistance  $Z_{re}$  as function of angular speed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [huangmeirong@tongji.edu.cn](mailto:huangmeirong@tongji.edu.cn).

\*E-mail: [adamxgli@yahoo.com](mailto:adamxgli@yahoo.com).

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### Notes

The authors declare no competing financial interest.

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