Studies on a Pb\textsuperscript{2+}-selective electrode with a macrocyclic liquid membrane. Potentiometric determination of Pb\textsuperscript{2+} ions

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Abstract: This paper presents experimental and theoretical data regarding the design, characterization and analytical applications of a non-expensive, liquid-membrane ion-selective electrode for Pb\textsuperscript{2+} ions. The membrane is a solution of the active complex formed by Pb\textsuperscript{2+} ions with dibenzo-18-crown-6-ionophore (DB\textsubscript{-[18]-C-6}) extracted in propylene carbonate (PC). The successful application of the developed electrode for the determination of Pb\textsuperscript{2+} ions in aqueous solution samples by direct potentiometry and potentiometric titration is presented. For the presented analytical results, there are insignificant systematic errors between the direct potentiometric method with the developed ion-selective electrode and atomic absorption spectrometry.

Keywords: dibenzo-18-crown-6, liquid membrane electrode, lead, potentiometric determination.

INTRODUCTION

Macrocyclic ligands are known as efficient and selective ion-carriers through liquid membranes. The use of macrocyclic ligands as complexing agents offers the possibility of designing ligands with a wide range of functional groups and, consequently, different abilities to complex cations. Due to these properties, crown ethers have been used in last the years to develop ion-selective electrodes for the determination of lead\textsuperscript{1-3} and other transition metals.\textsuperscript{4-9}

The response of the ion selective electrode has been attributed to an exchange process of Pb\textsuperscript{2+} ions between the analyzed aqueous solution and the organic solution of the membrane in propylene carbonate. The equilibrium of the system is achieved when the electrochemical potentials of Pb\textsuperscript{2+} ions in the two phases are equal and the Pb\textsuperscript{2+} ions in the aqueous phase do not influence the activity of the ions in the organic phase. This electrode has been successfully used for direct potentiometric determination and potentiometric titrations of Pb\textsuperscript{2+} ions in aqueous solutions.

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EXPERIMENTAL

Construction of the electrode

The body of the electrode consisted of a 127 mm long capron tube (1) with an inner diameter of 14 mm. At the lower end, it was closed with a 10 mm long and 10 mm thick, micro-porous alumina rod (2) mounted in a detachable cap (3). The alumina rod was impregnated with a solution of the active substance and plays the role of both electrical and mechanical support for the liquid membrane.

The internal reference electrode was eliminated by introducing a 140 mm long stainless steel wire (4) with an inner diameter of 1 mm directly inside the micro-porous alumina rod, which makes contact with the connection terminal (7) of the measuring instrument.

The internal reference solution (5) contains the ionic pair formed by the Pb\(^{2+}\) ions with DB-\([18]\)-C-6 ionophore, 10\(^{-2}\) mol L\(^{-1}\), extracted in a mixture of propylene carbonate and toluene (9/1 vol/vol). To prevent evaporation of the internal solution, the electrode was equipped at the top with a detachable screwed capron stopper (6), which was penetrated by a stainless steel wire, and allows filling with the organic solution, the system being perfectly airtight.

![Schematic representation of the electrode.](image)

Electrode employed

The values of the stability constant were calculated and the extractability properties of the formed ionic pair in the organic solvent were studied earlier.\(^{10-13}\) The structure of the active substance is shown in Fig. 2.

Earlier characterized microporous alumina\(^{14,15}\) was used as the membrane support. The microporous alumina, after calcination at 750 °C, had a specific surface area of 198 m\(^2\) g\(^{-1}\) and a porous volume of 0.34 cm\(^3\) g\(^{-1}\).

The proportion of pores having a diameter less than 37.5 Å was 74 % and the density of this membrane support material was 1.65 g cm\(^{-3}\). The good mechanical properties proved that this material could be used as a membrane support for the newly developed ion-selective electrode.

The direct measurements of the electrode potential were made in a solution of Pb\(^{2+}\) (Merck) at pH 5.6. The determinations of the electromotive force were made with a digital FASTECHO 763 pH
meter, versus a saturated calomel electrode (Radiometer). For the AAS measurements, a digital GBC AVANTA PM atomic absorption spectrometer was used.

RESULTS AND DISCUSSIONS

Response of the electrode to the concentration of Pb$^{2+}$ ions

The variation of the electrode potential versus the saturated calomel electrode (SCE) at 25 °C and ionic strength $\mu = 0.3$ provided with Sr(NO$_3$)$_2$, 0.1 mol L$^{-1}$ (which does not influence the electrode potential), as a function of $-\log [\text{Pb}^{2+}]$ in aqueous solutions is presented in Fig. 3.

The values of the potential slope $\Delta E/\Delta \log [\text{Pb}^{2+}]$, presented in Fig. 3, were statistically calculated through the linear regression method. The values of the electrode slope were obtained with CH$_3$COO$^-$ as the coupling anion. The range of the linear response of the electrode is between $10^{-2} - 10^{-6}$ mol L$^{-1}$.

![Fig. 2. The structure of the active ionic pair of the ion-selective membrane (a) and of the propylene carbonate solvent (b).](image)

![Fig. 3. The response of the electrode potential (vs. SCE) as a function of $-\log [\text{Pb}^{2+}]$ for Pb(CH$_3$COO)$_2$ at 25 °C, pH 5.6, $\mu = 0.3$.](image)
The influence of pH on the response of the Pb²⁺-selective electrode was studied in the pH range 2 – 9 using citric acid/Na⁺ citrate, 0.01 mol L⁻¹, (for the pH range 2 – 6.5) and boric acid/Na⁺ borate, 0.01 mol L⁻¹ (for the pH range 6.5 – 9) buffer solutions. From Fig. 4, it can be observed that a pH variation between 3.6 and 7 does not affect the electrode potential.

The decrease of the electrode potential in alkaline media can be explained by the formation of lead hydroxide in the aqueous solution, and at lower values of pH by the protonation of the ionophore in the membrane solution.

**Selectivity of the electrode**

The constructed electrode was tested for a series of cations, which could interfere with the Pb²⁺ ions in the ionic exchange equilibrium in the membrane. For these cations, the selectivity coefficients were determined using the mixed solution and the separate solution method. The values of the selectivity coefficients are presented in Table I. The strong interference of K⁺ ions can be avoided by adding 2 mL tartric acid, 0.1 mol L⁻¹, which precipitates the K⁺ ions in the analyzed aqueous samples. Even if the values of the selectivity coefficients determined through the separate solution method are smaller, the mixed solution method represents the condition and properties of the real samples better, especially for strongly interfering ions.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Mixed solution method</th>
<th>Separate solution method</th>
<th>RSD/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>2.59·10⁻³</td>
<td>2.53·10⁻³</td>
<td>1.1718</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>1.29·10⁻³</td>
<td>1.18·10⁻³</td>
<td>4.4534</td>
</tr>
</tbody>
</table>

Fig. 4. The influence of the pH on the response of the Pb²⁺-selective electrode at 25 °C and μ = 0.3.

The decrease of the electrode potential in alkaline media can be explained by the formation of lead hydroxide in the aqueous solution, and at lower values of pH by the protonation of the ionophore in the membrane solution.
Dynamic response and reproducibility of the electrode response

The response characteristics of the newly developed Pb$^{2+}$-selective electrode were evaluated during a period of 28 days, after conditioning the electrode in a 0.01 mol L$^{-1}$ solution of Pb(CH$_3$COO)$_2$ for 48 h.

The response time of the electrode in dilute solutions (10$^{-4}$ – 10$^{-6}$ mol L$^{-1}$) were about 1 min, while in more concentrated solutions (10$^{-2}$ – 10$^{-3}$ mol L$^{-1}$), the electrode potential reached an equilibrium value in a few seconds. A magnetic stirrer was used during all potential measurement. The reproducibility of the electrode response was tested over 4 weeks, during which time the electrode potential changed only by ± 2 mV, without modifying the value of the electrode slope. In order to evaluate the stability of the electrode response, the detection limit (LD), the quantization limit (LQ) and the drift of the measured potential, a 1 × 10$^{-3}$ mol L$^{-1}$ Pb$^{2+}$ solution was used. The characteristics of the electrode are summarized in Table II.

Analytical applications

The validation of the constructed electrode was checked by determining the Pb$^{2+}$ ions in both synthetic samples, prepared for the construction of the calibration curve, and also in natural aqueous samples by direct potentiometry and potentiometric titration. For the direct potentiometric determinations, a calibration curve was used, constructed according to the data presented in Fig. 3.
The expression of the regression equation for the calibration graph shown in Fig. 4 is $Y = -28381X + 270.29$, where $X$ represents the function $-\log [\text{Pb}^{2+}]$ and $Y$ represents the value of the electromotive force of the electrode (mV) versus SCE, the value of the correlation coefficient being $R^2 = 0.9998$.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Initial Pb$^{2+}$ (SAA)/mg·L$^{-1}$</th>
<th>Addition of Pb$^{2+}$/mg·L$^{-1}$</th>
<th>Theoretical total/mg·L$^{-1}$</th>
<th>Experimental Pb$^{2+}$-selective electrode/mg·L$^{-1}$</th>
<th>S.D.</th>
<th>RSD/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4.140</td>
<td>6.216</td>
<td>10.356</td>
<td>10.310</td>
<td>0.0325</td>
<td>0.2225</td>
</tr>
<tr>
<td>2.</td>
<td>8.280</td>
<td>6.216</td>
<td>14.496</td>
<td>14.450</td>
<td>0.0325</td>
<td>0.1589</td>
</tr>
<tr>
<td>3.</td>
<td>10.360</td>
<td>6.216</td>
<td>16.576</td>
<td>16.520</td>
<td>0.0395</td>
<td>0.1692</td>
</tr>
<tr>
<td>4.</td>
<td>15.540</td>
<td>2.072</td>
<td>17.612</td>
<td>17.560</td>
<td>0.0367</td>
<td>0.2090</td>
</tr>
<tr>
<td>5.</td>
<td>20.720</td>
<td>2.072</td>
<td>22.792</td>
<td>22.730</td>
<td>0.0438</td>
<td>0.1361</td>
</tr>
<tr>
<td>6.</td>
<td>41.440</td>
<td>2.072</td>
<td>43.512</td>
<td>42.470</td>
<td>0.7368</td>
<td>1.2188</td>
</tr>
</tbody>
</table>

TABLE IV. The results of the Pb$^{2+}$ ions determination in natural water samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Experimental with Pb$^{2+}$-selective electrode/mg·L$^{-1}$</th>
<th>AAS/mg·L$^{-1}$</th>
<th>S.D.</th>
<th>RSD/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>8.13</td>
<td>8.14</td>
<td>0.0141</td>
<td>0.1228</td>
</tr>
<tr>
<td>2.</td>
<td>7.89</td>
<td>7.86</td>
<td>0.0212</td>
<td>0.1904</td>
</tr>
<tr>
<td>3.</td>
<td>8.01</td>
<td>8.05</td>
<td>0.0282</td>
<td>0.2490</td>
</tr>
<tr>
<td>4.</td>
<td>4.11</td>
<td>4.15</td>
<td>0.0282</td>
<td>0.4842</td>
</tr>
<tr>
<td>5.</td>
<td>4.13</td>
<td>4.15</td>
<td>0.0141</td>
<td>0.2415</td>
</tr>
<tr>
<td>6.</td>
<td>4.18</td>
<td>4.15</td>
<td>0.0212</td>
<td>0.3601</td>
</tr>
<tr>
<td>7.</td>
<td>2.85</td>
<td>2.88</td>
<td>0.0212</td>
<td>0.5235</td>
</tr>
<tr>
<td>8.</td>
<td>2.83</td>
<td>2.80</td>
<td>0.0212</td>
<td>0.5328</td>
</tr>
<tr>
<td>9.</td>
<td>2.89</td>
<td>2.91</td>
<td>0.0141</td>
<td>0.3448</td>
</tr>
</tbody>
</table>

The validity of the direct potentiometric determination of Pb$^{2+}$ ions using the new Pb$^{2+}$-selective electrode was also checked by the standard addition method, the experimental data being presented in Table III. The electrode was then used for the determination of Pb$^{2+}$ ions in real water samples coming from several natural water sources. The results obtained by direct potentiometric measurement with the newly developed Pb$^{2+}$-selective electrode (presented in Table IV) are in accordance with these obtained by the AAS method.

The newly developed sensor was also successfully employed as an indicator electrode for the titration of synthetic Pb$^{2+}$ solutions with EDTA solution.

For this, a 100 mL Pb(CH$_3$COO)$_2$, 0.01 mol L$^{-1}$ was titrated with EDTA, 0.01 mol L$^{-1}$ solution (Fig. 5a) and 100 mL Pb(CH$_3$COO)$_2$ × 10$^{-4}$ mol L$^{-1}$ was titrated with a EDTA, 1 × 10$^{-3}$ mol L$^{-1}$ solution (Fig. 5b). It can be observed that on the ad-
dition of EDTA, the concentration of Pb\(^{2+}\) ions decreased, causing a decrease in the potential.

The potential rose by 66 mV for the titration curve a) (Fig. 5a) and by 36 mV for titration curve b) (Fig. 5b). However, the curves have a sharp break point which corresponds to the stoichiometry of the reaction. After the end-point, the sensor potential remains almost constant because it does not respond to small changes in the Pb\(^{2+}\) ions concentration. This method proved that the amount of Pb\(^{2+}\) ions can be accurately determined with the newly developed electrode.

**CONCLUSIONS**

A non-expensive, ion-selective electrode with a liquid membrane for Pb\(^{2+}\) ions has been developed, characterized and used for the determination of Pb\(^{2+}\) ions in natural water samples. The present results regarding the range of linear response, the nearly Nernstian cationic response (28.38 mV), pH dependence, dynamic properties and stability prove the good analytical performances of the constructed electrode. The electrode exhibited fairly good selectivity towards the nominated cations over each others. The successful analytical applications of the electrode for the determination of lead both by direct potentiometry and by potentiometric titration were described. The developed method has shown itself to be simple, accurate and precise, and not affected by systematic errors.
ИЗВОД

ИСПИТИВАЊЕ Pb²⁺-СЕЛЕКТИВНЕ ЕЛЕКТРОДЕ СА МАКРОЦИКЛИЧНОМ ТЕЧНОМ МЕМБРАНОМ. ПОТЕНЦИОМЕТРИСКО ОДРЕЂИВАЊЕ Pb²⁺ ЈОНА

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У раду су дати експериментални и теоријски подаци који се односе на дизајн, карактеризацију и аналитичку примењу јон-селективне електроде са течном мембраном за Pb²⁺ јона. Мембрана је раствор активног комплекса Pb²⁺ јона и дiben-зо-18-курука-6- jonofora (DB-18-C-6) екстахованог пропилекarbonатном (PC). Приказана је успешна примена овакве електроде за потенциометрију и потенциометријску титрацију Pb²⁺ јона у воденим растворима. Презентовани аналитички резултати показују незнатну систематску разлику (и грешку) директне потенциометријске методе са овом електродом у односу на атомску абсорпцију спектрометрију.


REFERNCES