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1-Hexyl-3-methylimidazolium hexafluorophosphate as new component of polymeric membrane of lead ion-selective electrode

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ABSTRACT

The ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate is used as a new lipophilic ionic additive in the polymeric membrane of a solid contact type lead ion-selective electrode. The membrane is deposited on an internal glassy carbon electrode with poly(3-octyl)thiophene as an intermediate layer. The sensor exhibits good analytical parameters: low detection limit of $3.5 \times 10^{-9}\,\mathrm{mol\,L^{-1}}$, Nernstian response slope of 29.8 mV/decade, a wide concentration range of 1×10^{-8}–$1 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$, short response time of 7 s, and relatively long lifetime of 100 days. The proposed sensor has a working pH range of 4.0–6.9 and excellent selectivity for Pb(II) ions over a wide variety of other metal ions. The efficiency of the proposed sensor was demonstrated by its application for direct determination of Pb^{2+} ions in real water samples.

Keywords: Ionic liquid; Ion-selective electrode; Solid contact; Lead determination

1. Introduction

Lead is an important environmental pollution due to its application in various industrial products. Furthermore, this metal presents a serious threat to the health of people and animals. The toxicity is related to its involvement in interactions with enzymes and nucleic acid where inhibition of biochemical pathways often constitutes the source of symptomatic physiological aberrations [1,2]. In the environment, it is generally present as inorganic Pb^{2+} which can be readily detected and quantified using lead ion-selective electrodes (ISEs).

Potentiometric ISEs are an established instrument for direct determination of activity of many analytes [3–6]. Solid internal contact electrodes refer to a type of ISEs in which the internal reference electrode is in direct contact with the electroactive membrane requiring no internal solution. The elimination of the internal solution permits fabrication of sensors with considerable design flexibility and potential operation in high pressure environments where conventional ISEs might otherwise be damaged. Furthermore, this type of electrode allows for a particularly low detection limit attributed to the absence of transmembrane ion fluxes [7].

Ionic liquids (ILs) are salts which are liquid at or just above room temperature. They are composed entirely of ions and possess unique properties, including, low volatility, tunable viscosity, high conductiv-

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ity, large electrochemical window, and low toxicity. These properties make ILs suitable for many applications including extraction [8], chromatography [9], capillary electrophoresis [10], mass spectrometry [11], electrochemistry [12], and chemical sensors [13,14].

The potentiometric behavior of ISEs with a liquid or polymeric membrane depends strongly on extraction and ion-exchange processes between the aqueous and organic phases [15–17]. It is known that the nature and amount of the lipophilic additive strongly affect the response of the membrane ion-selective sensors, for instance by reducing the membrane resistance [18,19] and improving the response behavior and selectivity [20,21]. In some cases, where membrane extraction capability is poor, addition of a lipophilic additive can improve sensor sensitivity by improving exchange properties. Lipophilic ionic additives can even induce membrane response when little or no ionophore is present in the membrane [22]. Recently, it has been reported that ILs can replace commonly used lipophilic ionic additives (e.g. phenyl borates) in the polymeric membrane of ISEs [23–25]. In recent years, 1-alkyl 3-methyl imidazolium hexafluorophosphate has been used as an extraction solvent for the preconcentration of lead [26–29]. On the basis of these extraction results and my experience in construction of ISEs, I have decided to prepare a new solid contact lead ion-selective electrode using 1-hexyl-3-methylimidazolium hexafluorophosphate as a lipophilic additive to the polymeric membrane.

2. Experimental

2.1. Reagents

Bis(1-butylpentyl) adipate (BBPA) (Fluka), Poly (vinyl chloride) low molecular weight (PVC) (Aldrich), *tert*-butylcalix [4]arene-tetracis(N,N-dimethylthioacetamide (lead ionophore IV) (Fluka), 1-hexyl-3-methylimidazolium hexafluorophosphate ($HMImPF_6$) (Fluka) and poly(3-octyl)thiophene (POT) (Aldrich) were used as received. Other reagents were purchased from Fluka and used as received.

All aqueous solutions were prepared with salts of the highest purity available (i.e. pure pro analysis) using freshly deionized water. Buffer solutions pH 2–8 (for the study of effect of pH) were prepared by mixing the corresponding amounts of $0.02\,\mathrm{mol\,L^{-1}}$ potassium phthalate monobasic, with $0.02\,\mathrm{mol\,L^{-1}}$ HCl or NaOH (pH = 2–3.8), $0.02\,\mathrm{mol\,L^{-1}}$ CH_3COOH with $0.02\,\mathrm{mol\,L^{-1}}$ NaOH (pH 4–8).

2.2. Preparation of the electrode

The composition of the lead ion-selective membrane was as follows (% wt.): 33% PVC, 60% BBPA, 6% $HMImPF_6$, and 1% ionophore (*tetr*-butylcalix [4] arene-tetrakis (N,N-dimethylthio-acetamide); 100 mg of mixture of membrane components was dissolved in 1 mL of THF to give the membrane cocktail. The internal electrode was a glassy carbon disk. Before the electrode preparation, the glassy carbon electrode was polished with 0.3 μm Al_2O_3 powder and rinsed well with water and THF. Next, POT was applied on the electrode surface by drop-casting 10 μL of 25 mM chloroform solution (respective monomer). The film was left to dry for at least 1 h. Then, an average amount of $2 \times 25\,\mu\mathrm{L}$ of the membrane cocktail was cast on the top of the POT layer and left to dry. After overnight THF evaporation, the obtained solid contact electrode was conditioned for at least 24 h in $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ $Pb(NO_3)_2$ to saturate PVC membrane in the primary ions and then for at least 24 h in the appropriate conditioning solution before potentiometric measurements. Concentrations of conditioning solutions were as follows: $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$, $1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$, $1 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$, and $1 \times 10^{-9}\,\mathrm{mol\,L^{-1}}$. All conditioning and sample solutions have the same background $5 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ acetate buffer.

2.3. The measurement of the electromotive force

The measurement of the electromotive force (EMF) of the system: lead electrode—reference electrode Orion 90-02 was carried out at room temperature in a solution stirred with a mechanical stirrer by means of potentiometric system consisting of a 16-channel data acquisition system (Lawson Labs. Inc., USA) and an IBM PC computer. A multifunction computer meter CX-741 (Zabrze Mikulczyce, Poland) and an Orion 81–72 glass electrode were used for pH measurement. Sequential dilutions of stock solutions were performed using the 700 Dosino and 711 Liquino pump systems (Metrohm, Switzerland).

2.4. The measurement of lifetime

The electrode lifetime was tested by measuring the characteristic slope and the detection limit of electrode kept in conditioning solution—$1 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ $Pb(NO_3)_2 + 5 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$acetate buffer. The measurements were made systematically, usually every 7 days, in freshly prepared $Pb(NO_3)_2$ solution. The correct working time of the electrode was determined up to this moment, until they showed the deviation ± 10% from the Nernstian characteristic slope.

2.5. The measurement of membrane resistance

The resistance of the cell containing the studied electrodes was determined by measuring the time loading of condenser from 100 up to 500 mV voltage by constant current flowing through the studied electrode. The electrode resistance is directly proportional to the time of the condenser loading. The measurement system was previously calibrated by using the following precisor resistors: 150 kΩ, 500 kΩ, 1 MΩ, 11.7 MΩ, 23 Ω, and 47.9 Ω.

3. Results and discussion

3.1. Potential response

The potential response of prepared sensor was determined in lead nitrate solutions of the concentration 1×10^{-1}–1×10^{-10} mol L^{-1}. The analytical sensor characteristics are summarized in Table 1. It is well established that in the case of solid contact electrodes the conditioning procedure used can significantly affect both the detection limit and selectivity coefficients [30,31]. Therefore, the effect of conditioning solution on the electrode response was studied in detail (see Fig. 1) and we showed that the lead ion concentration in the conditioning solution indeed impacts electrode response. The electrode conditioned in 1×10^{-3} mol L^{-1} Pb(NO$_3$)$_2$ exhibits the highest detection limit of 3.2×10^{-7} mol L^{-1}. The high lead concentration in the conditioning solution results in a high accumulation of lead ions in the membrane which can then leach into the sample during measurements in dilute samples resulting in an increased detection limit. The detection limit of electrode decreases considerably if the lead concentration in the conditioning solution is being diminished to 1×10^{-7} mol L^{-1} due to the more limited outward leaching flux from the membrane. Further decreasing the lead concentration does not improve sensor response; therefore, 1×10^{-7} mol L^{-1} lead concentration in the conditioning solution was optimal.

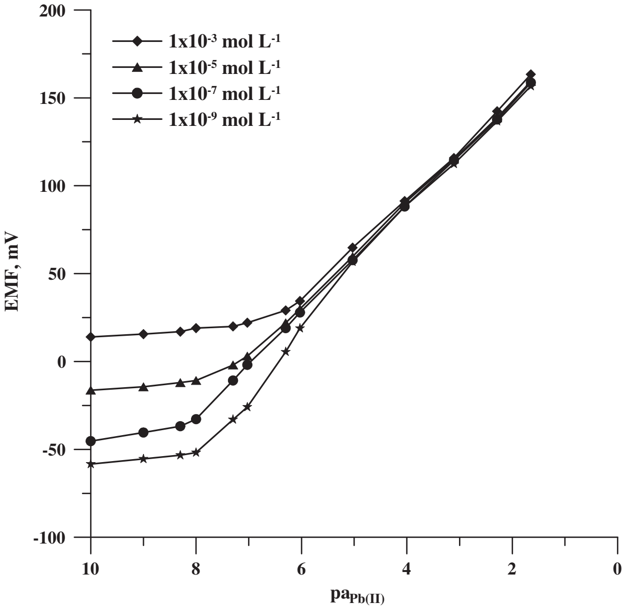

Fig. 1. Lead electrode response after conditioning in various lead solutions.

3.2. Selectivity

The most important parameter of any ion-selective electrode is the sensor response towards the primary ion in the presence of other interfering ions. The selectivity of the studied sensors was evaluated by determining selectivity coefficients against interfering ions by the separate solution method (SSM) (by extrapolating the response functions to $a_i = a_j = 1$ mol L^{-1}) [32], as well as by the fixed interference method (FIM) [33] (interfering ions concentration 1×10^{-1} mol L^{-1} and 1 mol L^{-1}). The values of selectivity coefficient log $K^{pot}{}_{Pb/M}$ obtained by both the methods are shown in Table 2. As detailed in Table 2, the proposed sensor is very selective to lead over all the interfering ions examined (i.e. $\log K^{pot}_{Pb/M} \leq -5$).

A comparison of the proposed sensor with others using the same ionophore is given in Table 3 indicating that the selectivity coefficients of the proposed

Table 1
Effect of life time on the properties of the proposed lead sensor

Life time (days)	Slope (mV/decade)	Detection limit (mol L^{-1})	Measuring range (mol L^{-1})	Intercept E_0 (mV)
3	29.8	3.5×10^{-9}	1.0×10^{-8}–1.0×10^{-1}	207.6
10	29.8	3.5×10^{-9}	1.0×10^{-8}–1.0×10^{-1}	206.4
20	29.8	3.5×10^{-9}	1.0×10^{-8}–1.0×10^{-1}	201.8
60	29.4	3.8×10^{-9}	1.0×10^{-8}–1.0×10^{-1}	195.1
100	28.9	6.3×10^{-9}	1.5×10^{-8}–1.0×10^{-1}	186.8
120	27.0	1.0×10^{-8}	4.0×10^{-8}–1.0×10^{-1}	184.6
150	25.1	1.5×10^{-8}	5.5×10^{-8}–1.0×10^{-1}	176.8
180	20.5	5.0×10^{-8}	1.0×10^{-7}–1.0×10^{-1}	166.6

Table 2
Selectivity coefficient values determined by SSM method and FIM method

Ion	$\log K^{pot}_{Pb,Me}$	
	SSM method	FIM method
Cd^{2+}	−5.5	−5.3
Cu^{2+}	−4.2	−4.0
Zn^{2+}	−6.0	−5.7
Co^{2+}	−6.4	−6.6
Ni^{2+}	−6.4	−6.6
Ca^{2+}	−7.2	−7.2
Ba^{2+}	−6.6	−6.2
Mg^{2+}	−8.1	−7.9
Sr^{2+}	−6.4	−6.3
Li^{+}	−6.5	−6.6
K^{+}	−8.6	−8.5
Na^{+}	−10.4	−8.5

sensor are better than those reported for liquid contact electrode [34], and are comparable to those reported for solid contact electrodes [24].

3.3. Dependence of EMF on pH

The influence of the pH on the response of studied electrode was investigated using $1\times10^{-4}\,mol\,L^{-1}$ $Pb(NO_3)_2$ solution over the pH range 2.0–8.0. The pH was adjusted using universal buffer solutions (described in the experimental section) and the working pH range was determined as where the potential of the electrode was nearly constant (±2 mV) (see Fig. 2). Based on this analysis, the working pH range is 4.0–6.9. Beyond this range, a more gradual change in the potential was detected. The decrease of the potential at higher pH values can be attributed to the formation of some hydroxy complexes of Pb^{2+} in solution and in more acidic media, the hydrogen ions affect the equilibrium of the complex formation between lead ions and the ionophore leading again to the lower electrode potential.

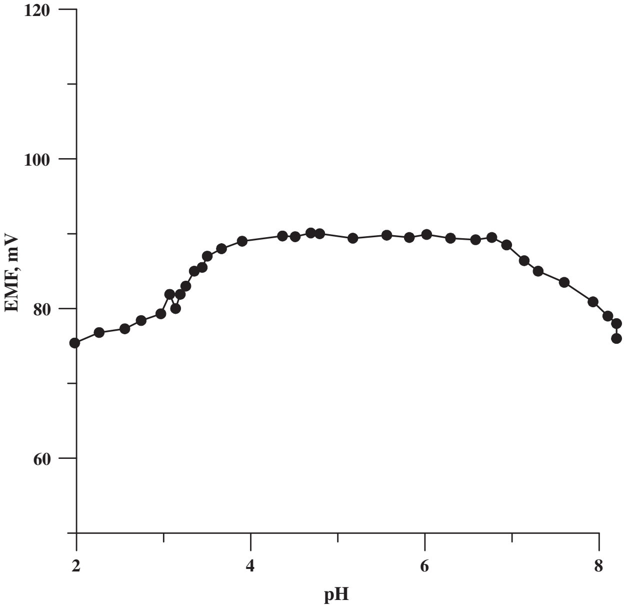

Fig. 2. Effect of pH on the electrode response.

3.4. Response time and membrane resistance

The response time of the examined electrode was established by injecting concentrated standard solutions into a stirred $Pb(NO_3)_2$ solution and simultaneously monitoring EMF changes of the lead electrode–reference electrode system. The response time was determined as the elapsed time from the moment when the studied ion-selective electrode and reference electrode are brought into contact with a sample solution with a changed activity of the Pb^{2+} ions to the time when the $\Delta E/\Delta t$ becomes equal to 0.4 mV/min [35]. Using this approach, the response time of the electrode was very short (7s) and is attributed to a low membrane resistance of $0.7\pm0.1\,M\Omega$. Membrane resistance is proportional to ionic strength of the membrane phase. Thus, the increase of the ionic strength here by adding an ionic liquid has a beneficial effect for the equilibration time.

3.5. Lifetime and long-term stability

The usefulness of analytical time of the prepared electrode was tested over a period of 6 months (Table 1) where the electrode was continuously stored (except during testing) in conditioning solution. Potentiometric measurements were conducted every week for at least 5 h in freshly prepared $Pb(NO_3)_2$ solutions in order to determine the slope and detection limit. The proposed sensor behaved normally over a period of one hundred days without observing any significant change in the detection limit, working concentration range, or response slope. After that period, a slight change in the response slope and detection limit was observed Furthermore, the electrode potential was relatively stable over time with a drift of 0.2 mV per day.

Table 3
Comparison of the properties of various Pb^{2+} selective electrodes based on lead IV ionophore

Ref.	Slope (mV/ decade)	pH range	Limit detection (mol L^{-1})	Response time (s)	logK^{pot}	Contact
[34]	28.7	3.0–6.0	3.1×10^{-7}	<10	logK^{pot} > −4: Cu^{2+},Cd^{2+},Na^+,Li^+ logK^{pot} > −5; NH_4^+, K^+, Ca^{2+}, Ba^{2+} logK^{pot} > −6; Mg^{2+}, Na^+, Co^{2+}	Liquid
[36]	29.2	Not reported	1.0×10^{-7}	Not reported	Not reported	Liquid
[36]	29.2	Not reported	1.0×10^{-7}	Not reported	Not reported	Solid
[37]	28.7	Not reported	1.1×10^{-8}	Not reported	Not reported	Solid
[24]	29.8	3.5–7.3	4.3×10^{-9}	5–7 s	logK^{pot} > -4: – logK^{pot} > −5; – logK^{pot} > −6; Cu^{2+}, Cd^{2+}, $Mg^{2+}K^+$, Li^+, Na^+ logK^{pot} > −7: Ca^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}	Solid
This work	29.8	4.0–6.9	3.5×10^{-9}	7 s	logK^{pot} > −4: – logK^{pot} > −5; Cu^{2+}, logK^{pot} > −6; Cd^{2+}, logK^{pot} > −7: K^+, Li^+, Na^+, Ba^{2+}, Sr^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} logK^{pot} > −9: K^+, Na^+, Mg^{2+}, Ca^{2+}	Solid

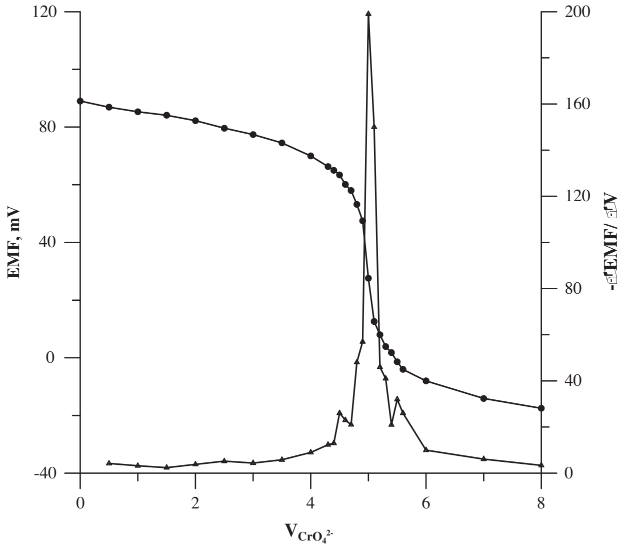

Fig. 3. Potentiometric titration curve and first derivative curve of 50 mL of 1.0×10^{-4} mol L^{-1} $Pb(NO_3)_2$ solution (pH = 4.8 acetate buffer) with 1.0×10^{-3} mol L^{-1} K_2CrO_4 using the proposed sensor as an indicator electrode.

3.6. Analytical application of electrode

3.6.1. Potentiometric titration

The proposed electrode was found to work well under laboratory conditions where it was compared with the potentiometric titration of 50 mL of 1.0×10^{-4} mol L^{-1} $Pb(NO_3)_2$ solution (pH = 4.8 acetate buffer) with 1.0×10^{-3} mol L^{-1} K_2CrO_4 solution. The obtained potentiometric titration curves are shown in Fig. 3. As can be seen, the amount of lead ions in the solution can be accurately determined with the proposed solid contact electrode. The end point of the titration was determined using the first derivative method. The relative standard deviation in the determination of five replicate samples was 1.3%.

3.6.2. Determination of lead in real water samples

The practical usefulness of the membrane sensor was determined by measuring of the lead ions concentrations in tap water, river water, and waste water samples. The analysis was performed by the standard addition technique. The results are summarized in Table 3. As can be seen, the obtained results are comparable with those obtained by the anodic stripping voltammetry (ASV) analysis. Thus, the electrode

Table 4
Determination of Pb^{2+} by the proposed electrode in water samples

Sample	Added lead ($mg\,L^{-1}$)	Found lead by ISE[a], ($mg\,L^{-1}$)	Recovery (%)	Found lead by ASV ($mg\,L^{-1}$)
Tap water	0.104	0.101 ± 0.002	97.1	0.106
	0.145	0.146 ± 0.002	100.7	0.147
	0.186	0.184 ± 0.003	98.9	0.186
	0.207	0.209 ± 0.003	101.0	0.209
River water	0.104	0.108 ± 0.002	103.8	0.039
	0.145	0.147 ± 0.003	101.4	0.105
	0.186	0.189 ± 0.003	102.2	0.166
	0.207	0.206 ± 0.005	99.5	0.208
Waste water	–	0.058 ± 0.003	–	0.060
	0.104	0.164 ± 0.003	101.2	0.163
	0.145	0.207 ± 0.005	102.0	0.206
	0.186	0.240 ± 0.005	98.3	0.246
	0.207	0.261 ± 0.007	98.5	0.266

[a] Results are based on five measurements.

provides a good alternative for the environmental monitoring of Pb^{2+}.

3.7. Comparison of the proposed electrode with other Pb-ISE

In Table 3, the properties of the studied electrode are compared with other previously reported lead electrodes based on the same ionophore. The electrode is superior to other sensors in terms of detection limit and selectivity while comparable with regard to other parameters such as slope, pH range, and response time.

The comparison of studied electrode and electrode described in [24] is interesting because both contain ionic liquid in the membrane but they have different constructions. The proposed electrode has membrane containing 1-hexyl-3-methylimidazolium hexafluorophosphate which is thinly deposited on internal glassy carbon electrode. The electrode in Ref. [24] has a bulk membrane containing another ionic liquid 1-butyl-3-methylimidazolium chloride in which internal Ag/AgCl electrode is immersed. The studied electrode is characterized by slightly better detection limit and improved selectivity over K^+, Na^+, Mg^{2+}, and Ca^{2+} ions in comparison to previously reported electrode [24].

It is worth noting that both electrodes containing ionic liquid in the membrane regardless of construction are characterized by better detection limit and improved selectivity than other electrodes based on the same ionophore. This fact confirms that presence of ionic liquid in the polymeric membrane has a beneficial effect on the parameters of lead-selective electrode (Table 4).

4. Conclusion

The application of the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate instead of a conventional lipophilic additive in a solid contact type ISE has been demonstrated resulting in obtaining an excellent lead sensor. The ionic liquid assures low membrane resistance, which in turn leads a short response time and a small potential drift of 0.2 mV per day. Furthermore, the presence of ionic liquid in the membrane phase expediently affects the equilibrium of lead extraction thus the presented electrode is characterized by good analytical parameters: low detection limit, wide measuring range, wide pH range, and superlative selectivity.

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