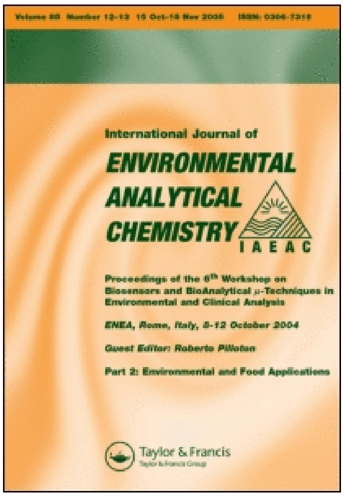

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Ionic liquids as new lipophilic additives to the membrane of lead ion-selective electrodes with solid contact

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Ionic liquids as new lipophilic additives to the membrane of lead ion-selective electrodes with solid contact

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The potentiometric properties of lead-selective electrodes with solid contact containing in the polymeric membrane addition of ionic liquids (ILs) were investigated. The studies were carried out with plasticised PVC membranes doped with alkylmethyl imidazolium chlorides. The electrode basic analytical parameters, such as detection limit, linear range, slope characteristic, response time and dependence of the electrode potential on pH as well as selectivity coefficients in relation to some inorganic cations were determined. As follows from the studies, the addition of ILs to the membrane phase improved the analytical parameters of the studied electrodes, especially the improvement in selectivity was notable. The best results were obtained for electrode having membrane dopped with 1-butyl-3-methylimidazolium chloride (BMImCl).

Keywords: lead ion-selective electrode; ionic liquids; solid contact

1. Introduction

The use of ion-selective electrodes in the analysis and monitoring of environmental, clinical, and industrial ions and gases has been continuously expanding [1–4]. Solid internal contact electrodes refer to a type of ISEs in which the internal reference electrode is in direct contact with the electroactive membrane and contains no internal solution. These electrodes will have certain advantages such as their small size, lower cost of production and ability to operate in high pressure environments where conventional ISEs might be damaged. Furthermore, such electrodes has allowed for low detection limit, which has been attributed to the absence of transmembrane ion fluxes [5].

Ionic liquids (ILs) form a new class of solvents. They are not volatile or inflammable and conduct the electric current [6]. They are gaining worldwide attention among academics and are used in industry as replacements for organic solvents in catalyses, syntheses and separations [7–9]. Among ILs applications, the use of IL/water two-phase system is one of the most promising for electroanalytical chemistry and extraction [10]. In the literature the application of ILs to the extraction of many ionic and non-ionic species was described successfully [11–14].

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Haixia *et al*. [15] as well as Zaijun *et al*. [16] used ILs as extraction solvents for the preconcentration of lead by dithizone. They obtained unprecedentedly high values of enrichment factor in comparison to those obtained with the conventional extraction system.

The mechanism of the potential formation of ion selective electrodes (ISEs) with a liquid or pseudoliquid (polymeric) membrane depends strongly on extraction and ion-exchange processes between the aqueous and organic phases [17–21]. It is known that the nature and amount of the lipophilic additive strongly influence the response of the membrane ion-selective sensors, such as reducing the membrane resistance [22,23], improving the response behaviour and selectivity [24,25] and in some cases, where the extraction capability is poor, increase the sensitivity of the membrane sensors [26]. Therefore, I have decided to use ILs as components of the polymeric membrane of ISE selective to lead ions, and it was with great joy that I obtained an electrode better characterising the analytical parameters.

The aim of this research was to create ion-selective electrodes sensitive to lead ions (ISE-s) with solid contact based on a PVC membrane phase containing an ionic liquid as an additional component. It seems that ILs can replace commonly used lipophilic ionic additives (phenyl borates) in the membrane phase, which are introduced to the membrane to reduce the anion interference and to lower the membrane resistance. Additionally, chloride ILs keep constant concentration of chloride ions in the membrane phase what guarantee potential stability of internal Ag/AgCl electrode.

2. Experimental

2.1 *Reagents*

2-Nitrophenyl octyl ether (NPOE) (Fluka), bis(1-butylpenthyl) adipate (BBPA) (Fluka), tributyl phosphate (TBP) (Merck), Poly(vinyl chloride) low molecular weight (PVC) (Aldrich), Potassium tetrakis (p-chlorophenyl) borate (KTpClB) (Fluka), *tetr*-butylcalix[4] arene-tetracis(N,N-dimethylthioacetamide (lead ionophore IV) (Fluka).

All ionic liquids (ILs) (purum; $\geq$97) and other reagents were purchased from Fluka.

All aqueous solutions were prepared with salts of the highest purity available (pure pro analysis) using freshly distilled deionised 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 ($\mathrm{pH} = 2$–3.8), $0.02\,\mathrm{mol\,L^{-1}}$ CH_3COOH with $0.02\,\mathrm{mol\,L^{-1}}$ NaOH (pH 4–8).

2.2 *Ionic liquids (ILs)*

The ILs used in this work were: 1-ethyl-3-methylimidazolium chloride(EMImCl), 1-butyl-3-methylimidazolium chloride (BMImCl), 1-hexyl-3-methylimidazolium chloride (HMImCl). These ionic liquid are known to be immiscible in water but soluble in majority plasticisers.

2.3 *Preparation of the membrane of solid contact electrode*

The electrode membrane phase consists of two layers placed in a Teflon holder: the inner layer containing plasticised PVC doped with the lipophilic additive (IL or KTpClB) in which the Ag/AgCl electrode is placed, and the outer layer contacting with the tested solution and containing an ionophore apart from the inner layer components. In order to prepare the inner layer membrane components: lipophilic additive, PVC and membrane solvents were weighed, respectively. The components were mixed and the mixture was de-aerated. The Teflon holder was filled with the mixture so that the silver-silver chloride electrode was immersed in it. Then the mixture was gelated at 80°C for 30 min. In order to prepare the outer layer, the active substance (ionophore) was dissolved in a plasticiser (the same as the inner layer) with PVC and IL or KTpClPB. The mixture was de-aerated, placed on the inner layer and gelated at 80°C for 10 min. Then the mixture was cooled to room temperature. The electrode was conditioned for 3 h before the measurements in the $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ $Pb(NO_3)_2$ solution. After that time, the potential of the electrodes was stable. During the last 5 minutes of the 3 h conditioning time the potential drift was 0.1 to $0.5\,\mathrm{mV\,min^{-1}}$. The quantitative and qualitative composition of electrode membranes is given in Table 1.

The construction of the electrode was described in earlier papers [21,27]. The schematic diagram of the electrode is shown in Figure 1. The construction of the two-layer membrane phase permits one to economise expensive ionophore without changing the electrode properties [21]. In order to examine the inner membrane phase/outer membrane phase interface potential the following cell D was constructed:

Cell D: Ag/Ag/CI/ inner membrance phase/outer membrane phase/Ag/AgCI

The composition of the inner membrane phase of the cell D corresponds to the composition of the inner membrane phase electrode 2C and analogously the composition of the outer membrane phase corresponds to the composition of the outer membrane phase electrode 2C.

2.4 *Preparation of the membrane of liquid contact electrode*

In order to compare the electrode with internal filing solution was also studied.

The membranes of classical electrodes (nos. 5A, 5B, 5C in Table 1) were prepared by mixed membrane components by means of ultrasounds. The obtained mixture was dissolved in THF (1 mL of THF per 0, 1g of the mixture) and poured into a glass ring (34 mm diameter) on a glass plate and covered for 1 day in order to slow down the process of THF evaporation. Then the substance was dried at 30° C for 0.5 hour. The membranes of 5 mm diameter were cut out and installed in a Teflon sensor (IS 561 type, Phillips). The internal reference electrode is Ag/AgCl electrode. It is placed in a solution of internal electrolyte composed of $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ $Pb(NO_3)_2$ sat. AgCl. Before measurements the electrodes were conditioned for 1 day in internal electrolyte. Between measurements the electrodes were stored in a solution of internal electrolyte.

2.5 *The measurement of the electromotive force*

The measurement of the electromotive force of the system: lead electrode–reference electrode Orion 90-02 was carried out at room temperature in a solution stirred with a mechanic stirrer by means of potentiometric system consisting of a 16 channel data acquisition system (Lawson Labs. Inc., USA) and IBM PC computer. An Orion 81-72 glass electrode was used for pH measurement.

Table 1. Composition of electrode membranes and sensors performance.

	Membrane composition, %wt.									
No. electrode	Ionophore, %wt.	PVC, %wt.	Plasticizer, %wt.	Lipophilic additive,%wt.	Limit detection, mol L^{-1}	Slope, mV/decade	Linear range, mol L^{-1}	pH range	Response time, s	Resistance MΩ
1A	1	33	TBP, 63	EMImCl, 3	2.3×10^{-5}	30.8	1.0×10^{-4}–2.2×10^{-2}	3.6–6.9	3–5	2.5 ± 0.1
2A	1	33	TBP, 63	BMImCl, 3	6.1×10^{-5}	26.7	1.0×10^{-4}–2.2×10^{-2}	3.8–6.9	3–5	3.0 ± 0.1
3A	1	33	TBP, 63	HMImCl, 3	6.1×10^{-5}	24.2	1.0×10^{-4}–2.2×10^{-2}	3.8–6.9	3–5	2.5 ± 0.1
4A	1	34	TBP, 64.75	KTpClB, 0.25	2.3×10^{-5}	28.0	1.0×10^{-4}–5.0×10^{-3}	3.8–6.9	5–10	4.0 ± 0.15
5A	1	34	TBP, 64.75	KTpClB, 0.25	3.0×10^{-6}	24.9	1.0×10^{-5}–5.0×10^{-3}	3.8–6.9	3–8	2.5 ± 0.1
1B	1	33	NPOE, 63	EMImCl, 3	2.1×10^{-6}	23.9	1.0×10^{-5}–5.0×10^{-3}	2.2–7.3	3–5	0.4 ± 0.02
2B	1	33	NPOE, 63	BMImCl, 3	4.8×10^{-7}	28.8	1.0×10^{-6}–5.0×10^{-3}	2.2–7.2	3–5	0.8 ± 0.02
3B	1	33	NPOE, 63	HMImCl, 3	1.3×10^{-6}	31.6	1.0×10^{-5}–5.0×10^{-3}	4.4–7.3	3–5	0.75 ± 0.02
4B	1	34	NPOE, 64.75	KTpClB, 0.25	6.6×10^{-7}	34.1	2.5×10^{-5}–5.0×10^{-3}	4.3–6.7	5–10	2.0 ± 0.15
5B	1	34	NPOE, 64.75	KTpClB, 0.25	6.6×10^{-6}	25.7	1.0×10^{-5}–5.0×10^{-3}	4.6–7.3	3–8	0.50 ± 0.02
1C	1	33	NPOE, 31.5 BBPA, 31.5	EMImCl, 3	1.1×10^{-6}	25.3	1.0×10^{-5}–2.2×10^{-2}	3.9–7.1	3–5	1.8 ± 0.1
2C	1	**33**	**NPOE, 31.5 BBPA, 31.5**	**BMImCl, 3**	$\mathbf{4.8 \times 10^{-7}}$	29.0	$\mathbf{1.0 \times 10^{-6}}$**–**$\mathbf{2.2 \times 10^{-2}}$	**3.5–7.3**	**3–5**	1.7 ± 0.1
3C	1	33	NPOE, 31.5 BBPA, 31.5	HMImCl, 3	1.8×10^{-6}	23.9	1.0×10^{-5}–2.2×10^{-2}	3.7–7.1	3–5	1.9 ± 0.15
4C	1	34	NPOE, 32.38 BBPA, 32.38	KTpClB, 0.25	4.0×10^{-6}	36.5	1.0×10^{-5}–2.2×10^{-2}	4.7–7.1	5–10	4.0 ± 0.15
5C	1	34	NPOE, 32.38 BBPA, 32.38	KTpClB, 0.25	1.8×10^{-6}	22.2	1.0×10^{-5}–5.0×10^{-3}	4.8–6.1	3–8	1.7 ± 0.15
1C*	–	33	NPOE, 32 BBPA, 32	EMImCl, 3	4.0×10^{-5}	9.5	1.0×10^{-4}–2.2×10^{-2}			
2C*	–	33	NPOE, 32 BBPA, 32	BMImCl, 3	1.7×10^{-6}	11.4	1.0×10^{-5}–2.2×10^{-2}			
3C*	–	33	NPOE, 32 BBPA, 32	HMImCl, 3	1.5×10^{-5}	6.3	1.0×10^{-4}–2.2×10^{-2}			

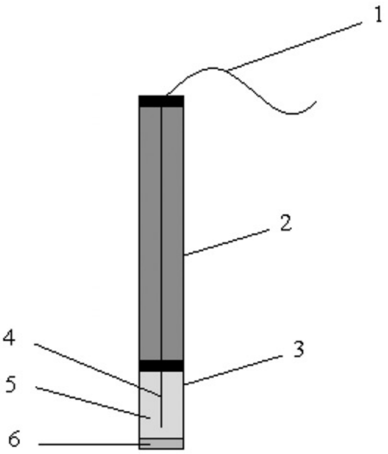

Figure 1. Scheme of lead electrode: 1 – cable, 2 – body, 3 – Teflon sensor, 4 – Ag/AgCl electrode, 5 – inner of membrane phase layer, 6 – outer of the membrane phase layer.

2.6 *The measurement of the electrode 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. Previous calibration of measurement system is necessary. The following precisor resistors were used for calibration procedure: 150 kΩ, 500 kΩ, 1 MΩ, 11.7 MΩ, 23 Ω, 47.9 Ω.

3. Results and discussion

In this work I have investigated membranes containing three ionic liquid: EMImCl, BMImCl HMImCl as well as commonly used KTpClPB. Their concentration in the membrane phase was 204.6 mmol kg^{-1} for EMImCl, 171.8 mmol kg^{-1} for BMImCl, 146.6 mmol kg^{-1} for HMImCl and 5 mmol kg^{-1} for KTpClPB. Three plasticisers, TBP (electrodes signed A), NPOE (electrodes signed B) and BBPA + NPOE (1 : 1 wt/wt) (electrodes signed C), were used for membrane preparation. The concentration of ionophore is 1% (9.5 mmol kg^{-1}).

In order to evaluate the effect of the addition of ILs to the electrode membrane phase, basic analytical parameters of electrodes containing them in the membrane phase were determined and compared with the parameters of electrodes without ILs but with traditional ionic additive KTpClPB in the membrane phase.

3.1 *Electrode response*

The potentials of the cell setup of lead electrodes having a membrane with or without IL were measured in lead nitrate solutions of the concentration 1×10^{-1}–1×10^{-7} mol L^{-1} and plotted in Figures 2–4. The values of electrodes potential after 10 min of equilibration are taken to plots. The analytical parameters of individual sensors such as limit of detection, the working concentration range, the slope of the linear section of the response curve and

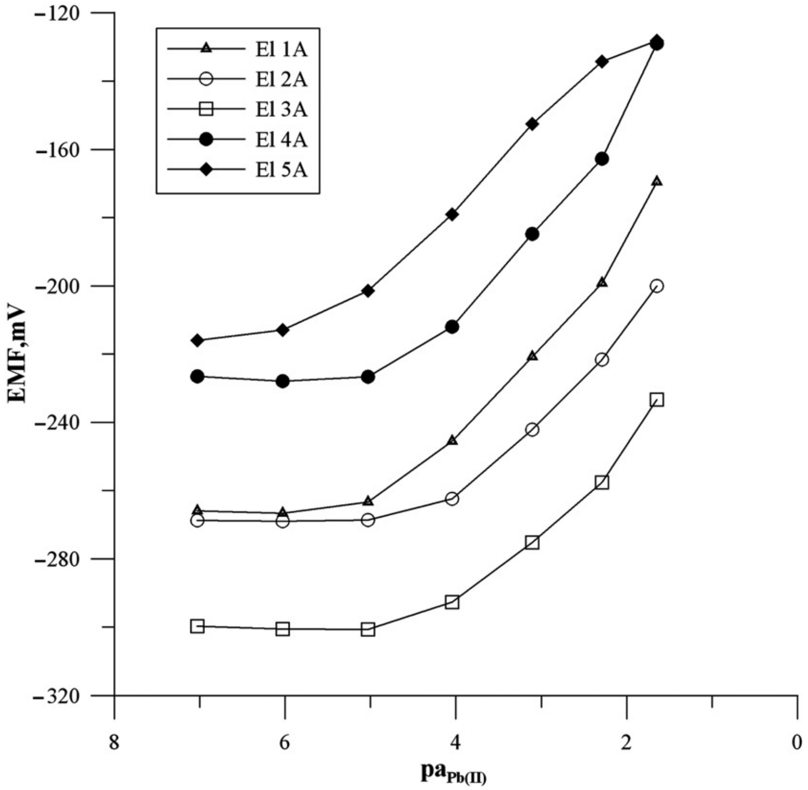

Figure 2. Effect of addition of ILs to the membrane phase on lead electrode response based on TBP.

response time were determined from the results of these measurements and are summarised in Table 1.

All obtained electrodes exhibit cationic response to Pb^{2+} ions with Nernstian, near Nerstian or sub Nerstian slope, both these with conventional lipophilic additive as well as with ILs. This may be rather surprising because the applied ILs contain lipophilic cation and hydrophilic anion – conversely than commonly used for cationic electrodes phenylborates. On the other hand, many electrodes work correctly without addition ionic sites due to the presence of anionic impurities in the polymeric materials such as PVC [28]. Therefore the addition of ionic sites is not necessary but advantageous.

It is well established that the polarity and chemical structure of the membrane plasticiser can have a significant influence on the selectivity and dynamic response range of ISEs [29]. The kind of plasticiser influences both the dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex [26,30].

It is clear from analysis of Table 1 and Figures 2–4 that o-NPOE and BBPA are more effective plasticisers than TBP in preparing the lead ISEs. The response of sensors having a membrane based on plasticiser TBP is rather poor (relatively high limit of detection and narrow linear range). This is observed both for sensors containing ionic liquid in the membrane as well for electrode with phenyl borate. Whereas the linear part of the

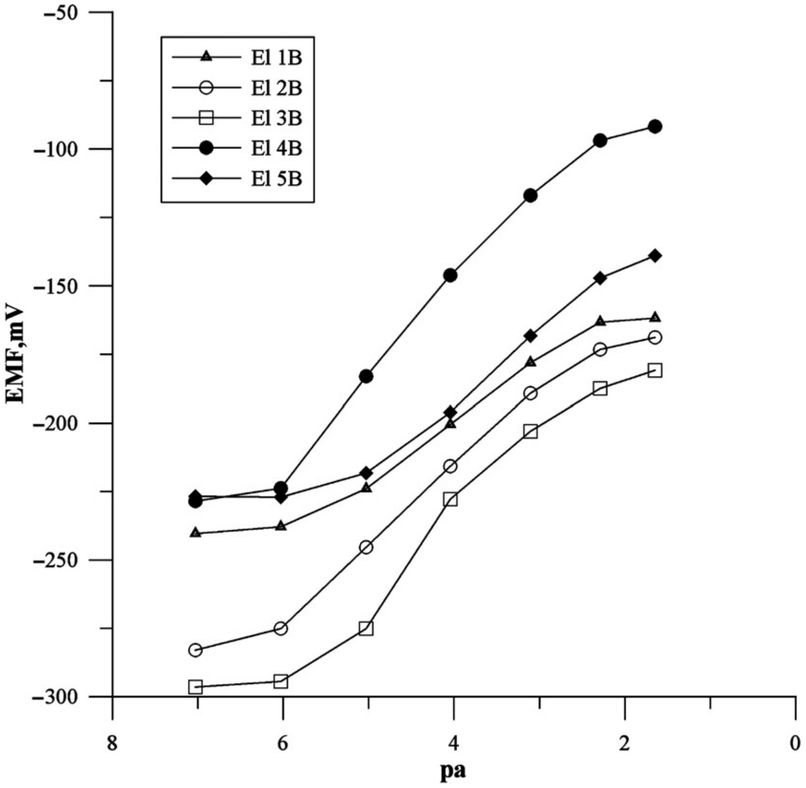

Figure 3. Effect of addition of ILs to the membrane phase on lead electrode response based on NPOE.

calibration curve of the electrodes with NPOE and BBPA + NPOE is longer and the detection limit is improved compared to the electrodes with TBP.

The effect of the addition of ILs to the membrane phase of studied electrodes depends on the plasticiser. For electrodes based on non-polar plasticiser TBP any essential differences in the analytical parameters between electrodes containing ionic liquid and electrode containing KTpClPB in the membrane are observed. These electrodes are characterising by similar detection limit, linear range and pH range.

Completely different situation exist for electrodes prepared with polar plasticiser o-NPOE. The electrodes 1B, 2B and 3B containing in the membrane 3 wt% ionic liquids: EMImCl, BMImCl and HMImCl, respectively, are characterised by a decreased detection limit, better characteristic slope (only electrode 2B and 3B 28.8 and 31.6 mV/decade, respectively), shorter response time (3–5 s) and wider pH range in comparison with the electrode 4B and 5B with the same composition of the membrane but with conventional lipophilic additive KTpClPB.

It is similar in the case of the third plasticiser BBPA + o-NPOE 1 : 1 wt/wt. For electrodes having membranes doped with ILs (especially BMImCl – electrode 2C) an improvement of the analytical parameters was observed – theoretical value of the characteristic slope 29.0 mV/decade, a decrease of detection limit 4.8×10^{-7} mol L^{-1}, wider pH range and reduced response time.

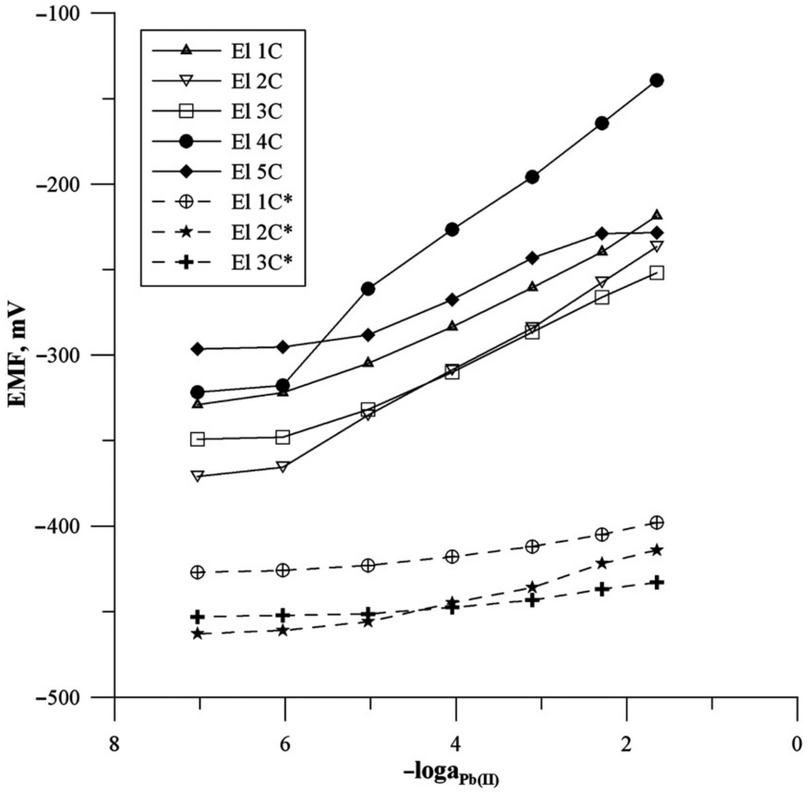

Figure 4. Effect of addition of ILs to the membrane phase on lead electrode response based on BBPA + NPOE 1 : 1 mixture.

In order to verify the hypothesis that ILs can act as ion-exchanger, the selected eletrodes containing IL in the membrane but without ionophore were also studied. The electrodes 1C*, 2C*, 3C* having the membrane of a composition corresponding to the composition of electrodes 1C, 2C and 3C respectively, were constructed. The potential response of those electrodes is presented in Figure 4 and in Table 1. The response of electrodes 1C*, 2C*, 3C* in the Pb^{2+} is cationic but slope of characteristic is poor being only few mV/decade. These results show that ILs do not act as ion exchanger and they do not compete with the ionophore in the formation of membrane potential.

Figure 5 shows the potential of the cell D measured during two weeks after preparation. Cell D consists of two halves. The membrane phase with ionophore and other membrane composition as the outer layer of electrode 2C and internal reference electrode Ag/AgCl was one half. The other reference half was the membrane phase which did not contain ionophore as the inner layer of the electrode 2C with the same Ag/AgCl electrode. As follows from the course of curve in Figure 5, the potential at the inner membrane phase/outer membrane phase interface is established during few hours after preparation. After this time it is stable with small fluctuation 0.5 mV. The obtained results confirm that the potential of the internal reference Ag/AgCl electrode is stable and it is determined by Cl^- ions originating from IL added to the membrane phase. For the given composition

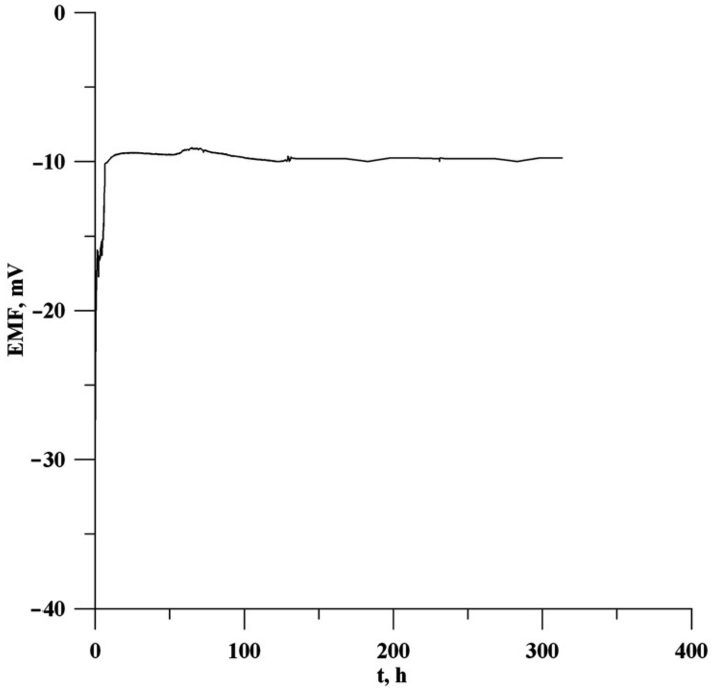

Figure 5. Potential of the cell D measured during two weeks after preparation.

of membrane phase constant concentration of IL keeps constant the concentration of chloride ions.

As follows from the results obtained for the cell D, the potential of studied lead electrodes depends on the concentration of Cl^- in the membrane which is constant for a given membrane and inner layer/outer layer interface potential which is constant, as well as on the lead concentration in the sample solution.

3.2 *Response time and resistance*

The response time of the examined electrodes was established by injecting concentrated standard solutions into a stirred $Pb(NO_3)_2$ solution. Simultaneously, EMF changes of the system: lead electrode-reference electrode were recorded. The response time was determined as the time which elapses between the instant when a studied ion-selective electrode and reference electrode are brought into contact with a sample solution at which the activity of the Pb^{2+} ions is changed and the first instant at which the $\Delta E/\Delta t$ becomes equal to 0.4 mV/min [31].

A comparison of values of membrane resistance of electrodes without lipophilic additives which are equal 58 MΩ, 42 MΩ, 51 MΩ for membranes based on TBP, NPOE and BBPA + NPOE, respectively and values of membrane resistance given in Table 1, clearly revealed that the addition of ILs to the membrane phase of the studied electrodes cause a decrease of membrane resistance and consequently shortens the response time of the electrodes. Electrodes 1A, 2A and 3A with solid contact have shorter response time in comparison with electrode 4A (the same construction but containing KTpClPB) and the same response time as electrode 5A with internal filing solution. This effect is also observed in the case of B- and C-series electrodes.

The response time of all electrodes depends on lead concentration in the solution and it is longer in diluted solutions. In Table 1 are given limited values of response time obtained for the concentration of Pb^{2+} ions $1 \times 10^{-2}\,mol\,L^{-1}$ and $1 \times 10^{-5}\,mol\,L^{-1}$, respectively.

The resistance of membrane containing IL is smaller than resistance of membrane containing KTpClPB but the same order magnitude. On the other hand, the concentration of ILs in the membrane is greater than concentration of KTpClPB. On the basis of these results, I can conclude that ILs dissociated partially in the membrane phase and degree of dissociation of ILs depends on polarity of plasticiser used for membrane preparation.

3.3 *Selectivity*

The most important parameter of any ion-selective electrode is its response to the primary ion in the presence of other ions. This is usually described in terms of the selectivity coefficients. The selectivity coefficients were determined by the separate solution method (by extrapolating the response functions to $a_i = a_j = 1\,mol\,L^{-1}$) [32]. For selectivity measurements, freshly prepared electrodes were used. They were conditioned in a discriminated ion solution, $1 \times 10^{-2}\,mol\,L^{-1}$ $NaNO_3$. As described by Bakker [33,34], this has a beneficial effect because it avoids any possibility of primary ion leaching from the membrane. For each interfering ion, the EMF was determined at four concentrations (1×10^{-1} to $1 \times 10^{-4}\,mol\,L^{-1}$). The experimental slopes, which were found to be close to Nerstian in all cases.

The obtained results are presented in Figures 6–8. A comparison of the values of selectivity coefficients clearly revealed that the addition of ILs to the membrane phase also improves the selectivity of the studied lead electrodes. This effect was observed for almost all the studied electrodes and is the strongest for the electrodes based on o-NPOE and BBPA + O-NPOE mixture containing in the membrane 1-butyl-3-methylimidazolium chloride (BMImCl). Electrodes 2B and 2C exhibit excellent selectivity and they are characterised by very good values of selectivity coefficients ($\log K^{pot}{}_{Pb/M} \leq -5$).

3.4 *Dependence of EMF on pH*

The dependence of the electrode potential on pH was investigated using $1 \times 10^{-3}\,mol\,L^{-1}$ $Pb(NO_3)_2$ solution over the pH range 2.0–8.0. Adjustment of pH was carried out using universal buffer solutions. From the obtained results the working pH range in which the potential of electrodes is almost constant (±2mV) was determined and given in Table 1. As follows from the research, the effect of the addition of ILs to the membrane phase is also dependent on the plasticiser. All electrodes based on TBP have the same working pH range. However, for electrodes having membranes with plasticiser o-NPOE and BBPA + o-NPOE mixture a positive role of the presence ILs in the membrane is evident (Table 1). Electrodes 1B, 2B, 3B as well as 1C, 2C, 3C are characterised by a wider working pH range in comparison with the electrode 4B, 5B and 4C, 5C, respectively. Figure 9 provides an example of the dependence of EMF on pH of C-series electrodes.

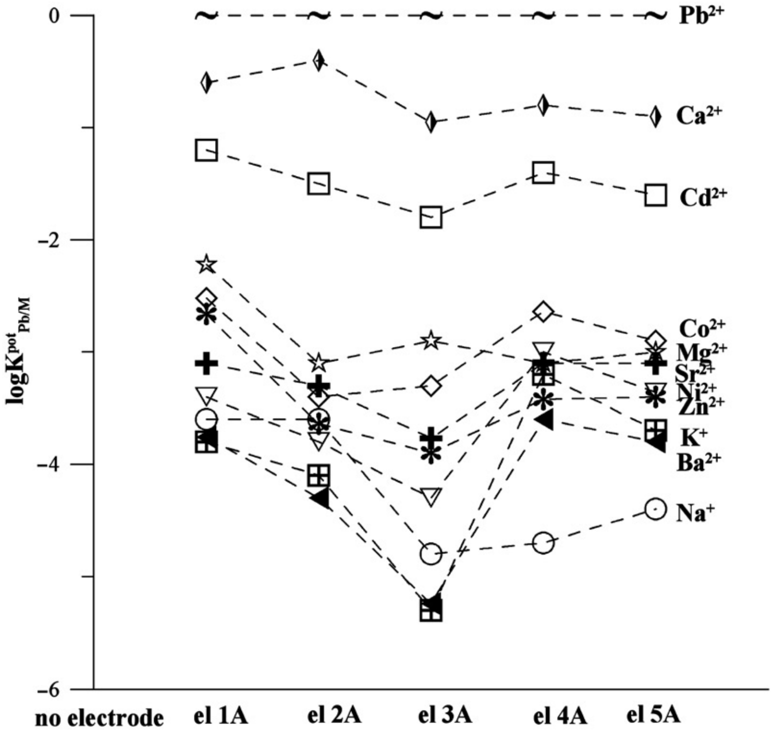

Figure 6. Selectivity coefficients ($\log K^{pot}{}_{Pb/M}$) determined by separate solution method for electrodes based on TBP.

4. Conclusion

The research has found that the properties of the Pb^{2+}ion-selective electrode can be significantly improved by the addition of 3%wt, of ILs to the membrane phase. This effect was found to depend both on the kind of plasticiser used for the preparation of the membranes as well as on the kind of IL.

The comparison of the structure of ILs used for membrane preparation shows that the effect of ILs on electrode properties also depends on the kind of substituent in position R^1 of the imidazole ring. The IL with R^1 = butyl cause a more positive change in the properties of electrodes containing them in the membrane phase than the ILs having as R^1 = ethyl or hexyl.

The best analytical parameters are exhibited by electrode 2C containing 1-butyl-3-methylimidazolium chloride in the membrane phase based on mixed plasticiser BBPA + NPOE. The characteristic slope of this electrode is 29.0 mV/decade, the limit of detection is 4.8×10^{-7} mol L^{-1}, the linearity range 1.0×10^{-6}–2.2×10^{-2} mol L^{-1} and values of selectivity coefficients are beneficial $\log K^{pot}{}_{Pb/M} \leq -5$.

ILs act as very promising solid contact of ISE with polymeric membrane because they connect two functions in one membrane component. On the one hand, ILs keep constant concentration of chloride ions in the membrane phase what guarantee the stability of potential of internal Ag/AgCl reference electrode. On the other hand, they lower the membrane resistance and reduce anion interference, altogether improving

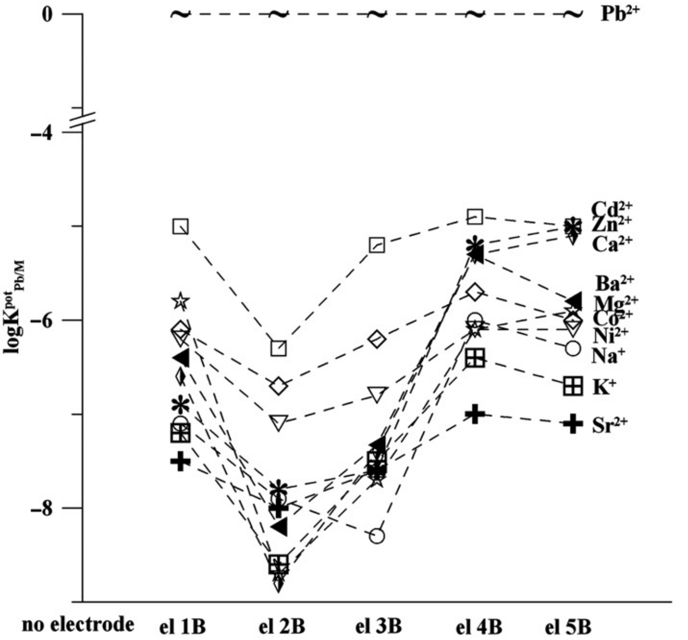

Figure 7. Selectivity coefficients ($\log K^{\mathrm{pot}}{}_{\mathrm{Pb/M}}$) determined by separate solution method for electrodes based on NPOE.

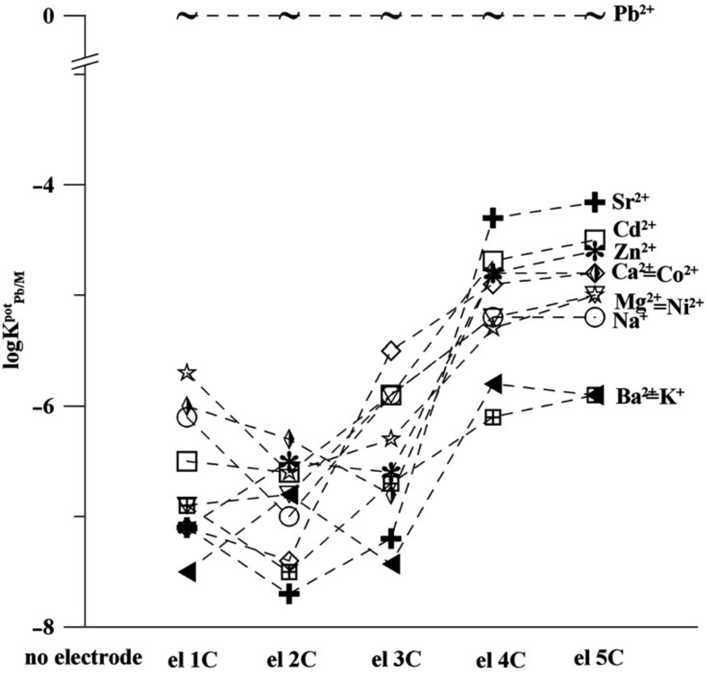

Figure 8. Selectivity coefficients ($\log K^{\mathrm{pot}}{}_{\mathrm{Pb/M}}$) determined by separate solution method for electrodes based on BBPA + NPOE 1 : 1 mixture.

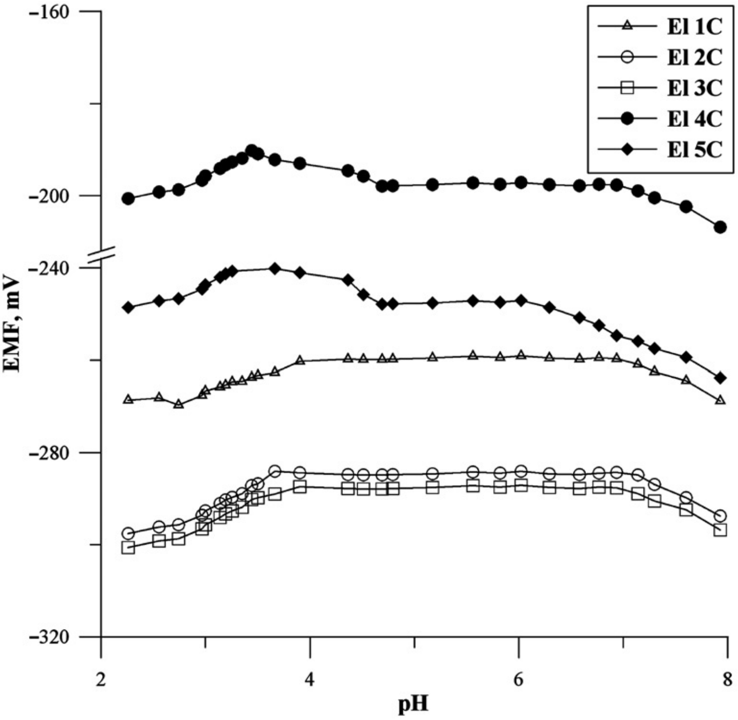

Figure 9. The dependence of the potential of C-series electrodes on pH.

the analytical parameters of the electrode such as detection limit, measuring range, working pH range and selectivity.

The obtained results confirm an important role of extraction in the process of the formation of membrane potential and can be useful in the preparation of an ion-selective membrane sensitive to other ions, but in order to recognise the role of ILs in the ion-selective membrane further research is required concerning a wider group of ILs, ionophores and plasticisers.

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