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Poly(n-butyl acrylate) based lead (II) selective electrodes

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ABSTRACT

Poly(n-butyl acrylate) membranes for potentiometric ion-selective electrodes were developed and studied on example of lead-selective sensors. A novel approach resulting in Nernstian responses of tested sensor was proposed. Introduction of 5% (w/w) hydroxyethyl methacrylate into n-butyl acrylate moiety resulted in significant improvement of sensor analytical parameters. For the latter membrane material linear responses were obtained within lead activities range from 10^{-2} to 10^{-9} mol/dm^3, while for poly(n-butyl acrylate) based membranes pretreated in the same manner super-Nernstian behavior was obtained in a parallel experiment. Electrochemical impedance spectroscopy studies did not reveal significant differences between these two membranes, also similar lead ions diffusion coefficients were determined using inductively coupled plasma mass spectrometry with laser ablation.The difference between two kinds of membranes was found to concern higher Pb(II) ions contents in the surface part of the membrane with hydroxyethyl methacrylate, resulting in balanced Pb ions fluxes from/to the membrane.

1. Introduction

Polyacrylate based ion-selective membranes have attracted recently significant attention and are studied in different research groups (e.g. [1–8]). Possibility of elimination of plasticizer from the membrane composition or of chemical binding of ionophore or liphophilic salt to the membrane matrix is attractive for many applications requiring long term stability of the membrane [6,9]. Polyacrylate membranes can be prepared by photopolymerization carried out directly on an electrode support [5,7]. Alternatively thermally initiated polymerization can be performed, yielding insoluble polymers that have to be transferred as such to internal-solution sensors [8] or more advantageously leading to solution processable polyacrylate polymers [1–4,6,9–11], that can be applied on any sensor configuration. In the latter case the obtained polymers can be dispersed in a suitable solvent and mixed with ionophore and/or ion-exchanger to obtain membrane cocktails that can be cast in similar way as poly(vinyl chloride) ones.

Important features of polyacrylate ion-selective membranes are usually much lower ion diffusion coefficients compared to poly(vinyl chloride) counterparts. As a result, for sensors with polyacrylate membranes usually more favorable, lower, detection limits are obtained [1,5]. On the other hand, lower ions diffusion coefficients of polyacrylate based membranes lead to higher electrical resistance of obtained sensors and longer conditioning time required to obtain desired saturation of the membrane and stable responses. Thus, for some applications, tailoring of sensors responses and affecting resistivity of the membrane in other way than adding plasticizer to the composition, is important. Taking the advantage of compatibility of different acrylate compounds, this can be achieved by using copolymers or even composites instead of acrylate-homopolymers [7,10]. Potentially many different acrylate copolymers can be used to tailor ion-transport properties of polyacrylate membranes, and thus to affect analytical parameters of resulting sensors just by choosing different monomers. A good example is introduction of acrylonitrile into izodecylacrylate based polymer membrane [6,8].

Recently we have reported on using poly(n-butyl acrylate) composite with methylmethacrylate end capped poly(3,4-ethylenedioxythiophene) polymer to obtain stable detection limit calcium-selective electrodes [7]. Incorporation of conducting polymer into the membrane phase has resulted in change of membrane resisitivity of the photopolymerized polymer [7].

Among different sensors with polyacrylate based membranes that have been reported, to authors best knowledge only two works dealing with polyacrylate based lead-selective electrodes have been published [8,11]. In a recent report Lewenstam and co-workers [8] have studied internal-solution lead-selective electrodes with membranes containing ETH 295 ionophore in copolymer of izodecylacrylate, acrylonitrile and 1,6-hexanediol diacrylate. Ion mobility in this membrane was studied by means of electrochemical impedance spectroscopy and was found to be much lower than in plasticized poly(vinyl chloride) membrane. Polyacrylate

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membranes studied in that report were characterized with nearly Nernstian slope and detection limit close to 10^{-6} M [8].

The aim of this work was to compare analytical properties of lead-selective membranes prepared from linear poly(n-butyl acrylate), solution processable polymer in course of chemical polymerization, in all-solid-state arrangement. The polymerization process applied utilized both photoinitiation by UV lamp and thermal polymerization. The possibilities of tailoring sensors responses by using linear copolymers of n-butyl acrylate with hydroxyethyl methacrylate (HEMA) were also studied. The poly(hydroxyethyl methacrylate) is usually used as internal pseudo-solid layer and it is known to retain electrolyte within the polymeric phase. The idea behind making copolymers of n-butyl acrylate with relatively small addition of hydroxyethyl methacrylate was to achieve linear responses of the sensor within broad acitivities range during typical conditioning regime (i.e. about 20 h in mM solution of primary ions).

Potentiometric characteristic of prepared solid-state sensors were supported with ion diffusion coefficients determination from the data obtained by inductively coupled plasma mass spectrometry with laser ablation (LA–ICP–MS) [12]; the sensors were also characterized using electrochemical impedance spectroscopy.

2. Experimental

2.1. Apparatus, electrodes and measurements procedures

In the potentiometric experiments a multi-channel data acquisition setup and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) was used. The pumps systems 700 Dosino and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solution.

Glassy carbon (GC) electrodes of area 0.07 cm^2 were used. The substrate electrodes were polished with Al_2O_3, 0.3 μm and rinsed well in water.

In volatmmetric experiment galvanostat–potentiostat CH-Instruments model 660A (Austin, TX, USA) and conventional three-electrode cell, with platinum sheet as counter electrode, were used.

The double junction silver/silver chloride reference electrode with 1 M lithium acetate in the outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used. The recorded potential values were corrected for the liquid junction potential calculated according to the Henderson approximation.

An inductively coupled plasma mass spectrometer ELAN 9000 (PerkinElmer, Germany) equipped with the laser ablation system LSX-200+ (CETAC, USA) was used. The LSX-200+ combines a stable, environmentally sealed 266 nm UV laser (Nd-YAG, solid-state, Q-switched) with a high sampling efficiency, variable 1–20 Hz pulse repetition rate and maximum energy up to 6 mJ/pulse. Samples were inserted in a cell on X, Y, Z-translation stage. The exact position of the sample was observed with a CCD camera as a viewing system under PC control. The LSX-200+ was centrally controlled by Cetac Windows software what allows selective ablation of chosen areas of investigated samples. The applied laser energy was 3.2 mJ/pulse, repetition rate was 5 Hz, spot size was 100 μm. The distribution of lead within the ion-selective membrane thickness was followed by monitoring the signal intensities for two lead isotopes ^{206}Pb and ^{208}Pb. This approach allows additional confirmation of the element profile within the target and elimination of "side-effects". The distribution of lead within target thickness for different membranes was compared. Note that the quantitative analysis of the membranes' components was not aimed. The penetration depth was estimated taking into account actual thickness of LA–ICP–MS target (determined post-experiment) and time of LA–ICP–MS analysis of the membrane.

The mean ion activities were calculated according to Debye-Hückel theory [13].

All experiments were performed at ambient temperature (23 °C).

2.2. Reagents

Lead-selective ionophore—IV (tert-butylcalix[4]arene-tetrakis (N,N-dimethylthioacetamide), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), tetrahydrofuran (THF), were from Fluka AG (Buchs, Switzerland), 2,2′-azobis(2-methylpropionitrile) (AIBN), n-butyl acrylate and hydroxyethyl methacrylate were from Aldrich (Germany).

Doubly distilled and freshly deionised water (resistance 18.2 M Ω cm, Milli-Qplus, Millipore, Austria) was used throughout this work. All salts used were of analytical grade and were obtained from POCh (Gliwice, Poland).

2.3. The general procedure for synthesis of acrylate polymers

A portion of n-butyl acrylate monomer (to yield pBA polymer) or n-butyl acrylate monomer containing 5 wt.% of hydroxyethyl methacrylate (to yield pBA-HEMA) containing 1 wt.% of AIBN was irradiated for 15 min under UV lamp and then heated under nitrogen for 8 h in a water bath (100 °C). Then a new portion of AIBN (again, 1 wt.%) was added and the mixture was heated for another 8 h under above stated conditions. Finally, the reaction mixture was heated for 1 h (100 °C) under diminished pressure (water pump). The yield of the polymerization was 96–98% (calculated taking into account mass of monomers used and mass of resulting polymer).

2.4. Lead-selective membranes

Lead membrane cocktails contained (by weight): 0.7% of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, 1.3% of lead ionophore and 98% of acrylic polymer or copolymer, the total 200 mg of mixture was dissolved in 0.6 ml of THF.

2.5. All-solid-state sensors

As a solid contact poly(octylthiophene), POT was used [14]. POT as obtained, i.e. in neutral, semiconducting, ion-free form, was dissolved in chloroform to achieve concentration of 2 mg/ml. 10 μl POT solution was applied on the surface of GC electrode, placed in up side down position and left to dry in laboratory atmosphere, yielding POT layer.

Total 20 μl of the membrane cocktail (in 10 μl portions) was applied on the top of a GC electrode previously coated with POT, placed in up side down position and left for THF evaporation for overnight. The thickness of the membrane, measured using micrometer, was close to 200 μm.

A target for LA–ICP–MS was prepared by applying 10 μl of membrane cocktail on the acetate transparency sheets, and then the aliquot was left in laboratory atmosphere until THF evaporation.

Water uptake by polymers was estimated using polymer layers (as synthetized polymer, free from ionophore or ion-exchanger) obtained on polyacetate sheets (polymer applied as THF solution), dried (to constant mass in the laboratory atmosphere) soaked in deionised water for 90 min and tissue dried. Recorded polymer mass increase was attributed to water uptake and was expressed in % relative to the polymer mass.

The obtained sensors and LA–ICP–MS targets were conditioned before measurements for 18 h in 10^{-3} M lead nitrate solutions. In-between measurements electrodes were stored in this solution, too.

3. Results and discussion

3.1. Potentiometric studies

Application of polymeric membranes obtained from alkilo-acrylic monomers for potentiometric sensors allows elimination of plasticizer from membrane composition [1,2]. Often photopolymerization is the simplest method of membrane preparation, allowing deposition of the membrane e.g. directly on a solid-state arrangement transducer. However, sometimes it is more advantageous to separate polymerization process from membrane application; this issue is especially important when photopolymerization process can be disturbed by other components of the membrane cocktail. Thus, in our opinion, it is worth looking at chemically polymerized linear acrylic polymers in the context of application for ion-selective membrane preparation, especially that these polymers are solution processable, what makes membrane application significantly easier [1–4,6,9–11].

Fig. 1 presents responses of lead-selective electrodes containing poly(n-butyl acrylate) membranes without or with addition of 5 wt.% HEMA, recorded in $Pb(NO_3)_2$ solutions. The pronounced difference in potentiometric responses obtained for pBA and pBA-HEMA membranes was observed after the same pretreatment. For pBA membrane linear potential dependencies were recorded within the Pb^{2+} ions activities range from 0.1 to 10^{-5} M with slope close to Nernstian, equal to 26.6 ± 1.6 mV/dec ($R^2 = 0.990$). For lead ions activities range from 10^{-5} to 10^{-7} M abrupt potential decrease was observed followed by only small potential changes for even lower activities. This type of responses is not unusual for polyacrylate based membranes [7]; taking into account the onset of super-Nernstian slope, it is rather related to insufficient saturation of the polyacrylate membrane with analyte ions during overnight conditioning and eager incorporation of Pb(II) ions during calibration.

A significantly different potentiometric response pattern was obtained for pBA-HEMA based membrane, linear responses within the $Pb(NO_3)_2$ activity range from 10^{-2} to 10^{-9} M were obtained with slope close to Nernstian and equal to 26.2 ± 0.3 mV/dec ($R^2 = 0.999$). The value obtained is well comparable with literature data obtained for membranes based on copolymer of methylmethacrylate–dodecylmethacrylate applied also on poly(octylthiophene) support [11]. $Pb(NO_3)_2$ activity change from 0.1 to 10^{-2} M for pBA-HEMA membrane was accompanied with only 15 mV potential increase, similarly as usually observed for membranes not characterized with super-Nernstian slopes, e.g. poly(vinyl chloride) lead-selective membranes [15]. Interestingly, introduction of 5 wt.% HEMA to n-butyl acrylate polymer resulted in significantly more useful potentiometric responses of the sensor; most probably due to more enhanced, compared to pBA, retention of some of analyte ions within the copolymer phase or higher rate of ions uptake. The estimation of water uptake by studied polymers (free from ion-selective cocktail components) in fact revealed higher water uptake in the case of pBA-HEMA—ca 60% relative to polymer mass compared to ca 40% obtained for pBA. Although obtained values are estimation only and more detailed studies are required to explain water uptake mechanism, the significant difference between values obtained suggests much higher water contents in the case of pBA-HEMA membrane. Thus, due to higher water uptake, the conditioning enhances incorporation of primary ions leading to Nernstian potentiometric responses in the case of pBA-HEMA, after the same conditioning time that is leading to super-Nernstian responses for pBA membrane.

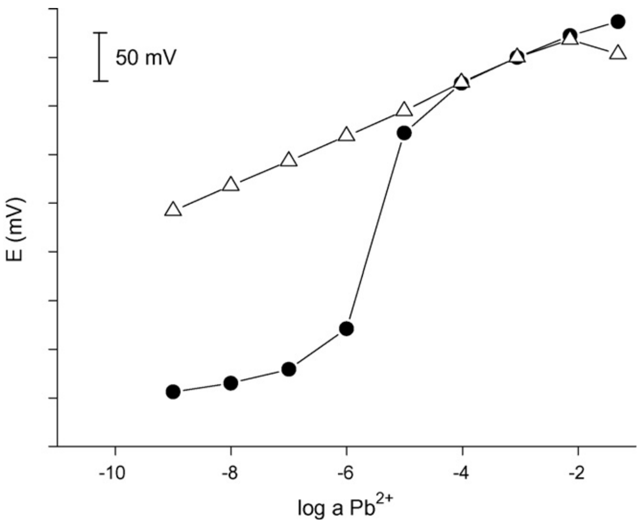

Fig. 1. Open circuit potentiometric responses of lead-selective electrodes prepared using different acrylic polymers or copolymer, symbols denote membranes polymer: (●) pBA and (△) pBA-HEMA. For easy comparison all curves were shifted to give equal potential at log *a* $Pb^{2+} = -3$.

Comparison of stability of responses in time of sensors prepared using pBA or pBA-HEMA polymer matrix did not reveal significant differences within higher activity region (>10^{-5} M). The potential stability within activity range from 10^{-1} to 10^{-5} M over three days calibrations (recorded within activities range from 0.1 to 10^{-9} M) was close to ± 5 mV for both pBA and pBA-HEMA membranes. For pBA based membrane pronounced differences in potentiometric responses were revealed in lower activates range, where gradual change of potentiometric response pattern was observed—change from super-Nernstian responses to linear potentiometric dependencies. The pBA-HEMA based membrane was characterized with unchanged response pattern, however, as usually when testing sensor within broad electrolyte activities range, potential stability in the region of low activities (10^{-7}–10^{-9} M) was worse than in relatively high concentrations and it was close to ±10 mV.

Table 1 presents potentiometric selectivity coefficients determined for studied membrane for chosen model interfering ions. The comparison of values obtained for pBA and pBA-HEMA shows that lower $\log K_{\mathrm{Pb,J}}^{\mathrm{pot}}$ were obtained for pBA-HEMA membrane. Nevertheless, the slopes of dependencies recorded in interfering ions solutions were close to Nernstian for both membrane materials, although closer to Nernstian slopes were obtained for pBA membrane (as expected for membrane characterized with super-Nernstian type responses). Selectivity coefficients obtained for the tested membranes were, except K^+ interferences, well comparable with (pBA) or even better (pBA-HEMA) than the values reported for poly(vinyl chloride) membrane [16].

3.2. Electrochemical impedance spectroscopy studies

Fig. 2 presents results (in the form of Bode plots) of electrochemical impedance spectroscopy studies conducted for tested sensors at potential equal to 300 mV, using amplitude 100 mV

Table 1
Mean potentiometric selectivity coefficients, $\log K_{\mathrm{Pb,J}}^{\mathrm{pot}} \pm \mathrm{SD}$ obtained within the activities range from 10^{-2} to 10^{-4} mol/dm^3, separate solution method, for lead-selective electrodes with different membrane matrixes, for $\log K_{\mathrm{Pb,J}}^{\mathrm{pot}}$ calculation experimental electrode slopes in primary ions solutions were used.

Ion J	$\log K_{\mathrm{Pb,\,J}}^{\mathrm{pot}} \pm$ SD and slope (mV/dec) between 10^{-2} and 10^{-4} M for sensor with membrane	
	pBA	pBA-HEMA
K^+	-4.3 ± 0.1 (61.6)	-5.5 ± 0.3 (55.3)
Na^+	-5.2 ± 0.1 (56.9)	-6.6 ± 0.3 (55.3)
H^+	-5.6 ± 0.4 (46.3)	-6.4 ± 0.1 (50.3)

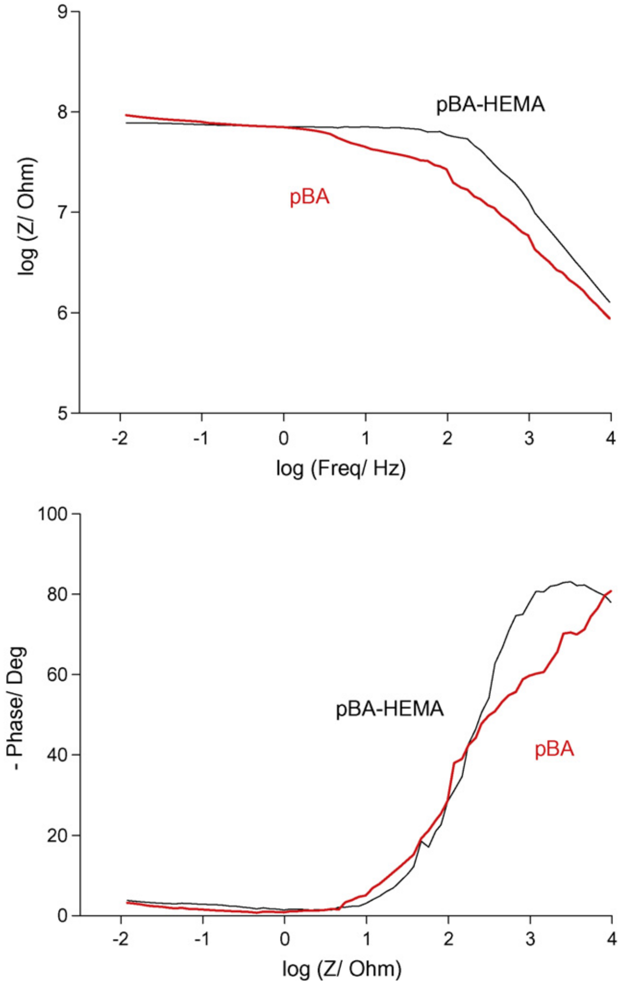

Fig. 2. Bode plots-results of electrochemical impedance spectroscopy studies conducted in 10^{-3} M $Pb(NO_3)_2$ for tested sensors at 300 mV using amplitude 100 mV within frequency range 0.01–10^4 Hz.

within frequency range 0.01–10^4 Hz in 10^{-3} M $Pb(NO_3)_2$. The high amplitude was used to obtain sufficiently high signal to noise ratio for highly resistive polyacrylate membranes. The data for both kinds of membranes did not differ significantly. In the range of lower frequency, from 10^{-3} to 10^2 Hz (pBA-HEMA) or 10^1 Hz (pBA) the impedance value is practically independent of frequency applied. Taking into account that the phase angle is close to 0, the impedance value represents the ohmic resistance of the membrane, close to $10^8\,\Omega$. For higher frequencies, significant decrease in the impedance was observed and in the same time decrease in the phase angle down to -90° was recorded. This suggests growing role of capacitance related phenomena.

Similar results were also reported earlier for other polyacrylate based membranes, e.g. [17]. The obtained impedance data were analyzed by a simplified model of parallel connection of resistance (corresponding to the membrane resistance) and capacitance (representing geometric capacitance of the membrane). From the impedance value recorded for high frequency (10^4 Hz), where the impedance is determined by the capacitance part, the geometric capacitance could be estimated as $\sim 10^{-10}$ F, consistent with literature data for other compositions of poly n-butyl acrylate based membranes [17].

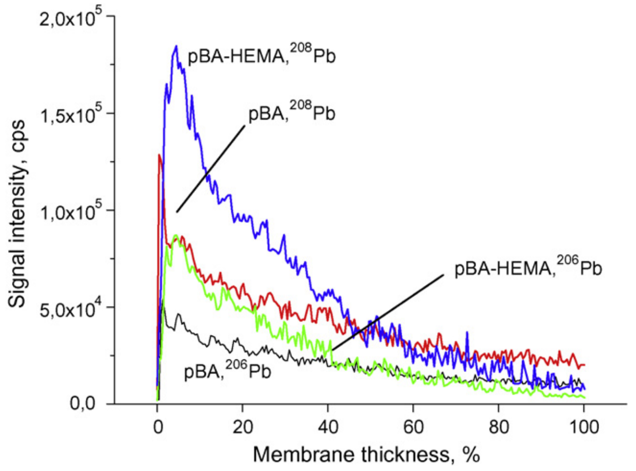

Fig. 3. Intensity of the measured signal as a function of laser ablation penetration depth obtained for tested lead-selective membranes: pBA or pBA-HEMA based membrane.

3.3. Inductively coupled plasma mass spectrometry with laser ablation

The membrane properties were also studied by means of LA–ICP–MS technique. Fig. 3 presents lead signal intensities as a function of target depth recorded for pBA and pBA-HEMA based membranes, respectively. Note that both membranes were conditioned overnight in 10^{-3} M $Pb(NO_3)_2$. The distribution of lead within the thickness of investigated targets revealed some difference between the two membranes.

For pBA the highest lead signal intensities were recorded at the membrane surface that was in contact with conditioning solution. With increasing penetration depth the gradual decrease in the signal of both isotopes, ^{208}Pb and of ^{206}Pb, was observed. The obtained dependence is pointing not to complete saturation of the membrane, being in good accordance with potentiometric results (super-Nernstian slope) presented in Fig. 1.

From the recorded Pb profile, relating to lead ions–ionophore complex, diffusion coefficient within the membrane can be estimated. In the calculations we used data related to the membrane part close to the surface, to avoid possible errors related to conical crater formation within the membrane upon laser beam irradiation, especially occurring for deeper parts of the membrane. In such a case, equation describing semi-infinite linear diffusion can be applied.

$$c(x,t) = c(0,t)\left[1 - \operatorname{erf}\left(\frac{x}{2D^{1/2}t^{1/2}}\right)\right] \qquad (1)$$

where D is diffusion coefficient of Pb^{2+}–ionophore complex in the membrane, $c(0, t)$ and $c(x, t)$ are Pb(II) concentrations in the membrane, close to surface and for the distance x from the surface, respectively; erf is error function. The ratio of concentrations ($c(x, t)$ and $c(0, t)$) is equal to the ratio of appropriate signal intensities. For the pBA membrane the diffusion coefficient equal to $(2.5 \pm 1)\cdot 10^{-10}$ cm^2/s was obtained, i.e. over one order of magnitude higher than reported for poly(n-butyl acrylate) cross-linked, photopolymerized membranes [4].

For pBA-HEMA based membrane a similar profile of lead signals intensities across the membrane was observed, with increasing penetration depth the values of signal intensities decrease gradually to reach signals recorded for pBA at about 40% of the membrane thickness, both for ^{208}Pb and ^{206}Pb. Using Eq. (1) the diffusion coefficient of Pb^{2+}–ionophore complex in the pBA-HEMA membrane was estimated to be $(3 \pm 1)\cdot 10^{-10}$ cm^2/s, i.e. similar to the value obtained for pBA membrane, within limits of experimental error. This similarity of diffusion coefficients in both membranes is consistent with low difference in electrochemical impedance spectroscopy data.

On the other hand, the signals recorded at the pBA-HEMA membrane surface were about two times higher compared to those recorded for pBA polymer. Assuming that the area under the signal trace (for defined isotope) can be used to estimate lead contents in the membranes prepared using similar matrix, the lead contents – especially in the membrane surface region – are significantly higher in the case of pBA-HEMA compared to pBA. This is in good agreement with potentiometric studies results, Fig. 1. The lack of super-Nernstian slope can be explained by lower rate of Pb ions spontaneous extraction to the membrane (compared to that for pBA membrane), resulting from higher concentration of primary lead ions in the surface part of the membrane. Therefore, for the pBA-HEMA membrane advantageous balance of ion fluxes (from/to the membrane) was established, resulting in observed extended range of linear potentiometric responses.

Taking into account potentiometric, electrochemical impedance data and LA–ICP–MS results it seems quite probable that incorporation of HEMA in the pBA matrix results in relatively small but important change in membrane properties—they are most probably still dominated by n-butyl acrylate moiety (resulting in small difference in diffusion coefficients and membrane resistance); however, inclusion of hydrophilic HEMA units facilitates more pronounced incorporation of analyte ions (and water) in the surface membrane part in course of overnight conditioning, yielding higher saturation of the membrane and Nernstian responses.

Additionally, the above results of LA-ICP-MS studies point out that depending on composition of polyacrylate based membrane different loading with primary ions can be obtained within the same preconditioning procedure.

4. Conclusions

Lead-selective, all-solid-state, electrodes have been prepared using membranes based on linear n-butyl acrylate polymers. It was shown that introduction of a small amount (5 wt.%) of hydroxyethyl methacrylate units to n-butyl acrylate moiety was leading to significant improvement of sensor performance: low activity detection limits were obtained without using time consuming conditioning procedures; moreover, this was achieved with some improvement in sensor selectivity. Although the lead ions diffusion coefficients determined for both kinds of membranes are similar and are close to 10^{-10} cm/s^2, in the case of copolymer, pBA-HEMA, significantly higher contents of lead in the membrane were revealed. The effect of introduction of HEMA units to the polymer is most probably related to improved incorporation of electrolyte to the membrane, due to hydrophilicity of HEMA component; nevertheless is not impairing the stability of potentiometric responses.

The results obtained also show the crucial role of primary ions amount in the surface part of the membrane for the shape of potentiometric characteristics.

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