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Determination of the leaching of polymeric ion-selective membrane components by stripping voltammetry

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ABSTRACT

This paper focuses on the quantitative determination of the loss of the components from plastic membranes of ion-selective electrodes (ISEs) during contact with aqueous bathing solutions. The leaching processes, which affect the ISE responses, are rarely characterized by independent methods. For this purpose, differential pulse cathodic stripping voltammetry (DP CSV) is used. This method, owing to its high sensitivity, acceptable recovery and accuracy, is a good tool to characterize the kinetics of leakage of the lipophilic salts. Sodium tetraphenylborate (NaTPB) leakage from the PVC-based sodium-selective membrane containing two different plasticizers, *o*-nitrophenyl octyl ether (*o*-NPOE) or di(2-ethylhexyl) sebacate (DOS) is presented. Correlation between the rate of leaching of the lipophilic salt and dielectric constants of the plasticizers is observed. The data obtained by DP CSV correlate well with potentiometric and electrochemical impedance responses. The observed outflow of TPB^- is associated with decreasing potentiometric sensitivity to sodium and increasing bulk membrane resistance.

1. Introduction

Potentiometric ion sensors based on polymeric membranes with highly selective neutral or charged ionophores are widely used for the routine assessments of many important inorganic and organic ions. In conventional designs of polymeric membranes poly(vinyl chloride) (PVC), containing a neutral carrier/ion-exchanger, lipophilic salt and the plasticizer, are used [1,2].

The relative proportion of the components affects the membrane properties, and consequently the ISE response characterized by the electrode slope, the selectivity, the response time and life-time. A typical cationic-sensitive plastic membrane contains 33 wt% poly(vinyl chloride) (PVC), 66 wt% plasticizer, and 1 wt% selective carrier [3,4]. To greatly improve the characteristics of cation-sensitive membranes, lipophilic anions are added [3]. They support obtaining Nernstian responses [5], improve the ISE selectivity [6], and last but not least, reduce the co-ion interference and in this way help to maintain the slope by preventing Donnan exclusion failure [7]. The leaching of lipophilic additive over the ISE life-time brings adverse effects [8]. Unfavourable changes in the electrode sensitivity, even a slope conversion from cationic to anionic and reduced detection limits have been reported [9–12]. However, quantitative data on the influence of leaching of lipophilic salt on ISE response are rare and scattered. Consequently, a fundamental understanding of the role of leaching in ISE signal formation is far from complete.

A lipophilic anion in the cation-sensitive membranes is routinely introduced by using alkali metal salts of tetraphenylborate derivatives. One of them is sodium tetraphenylborate (NaTPB) [8,13] which is often employed, e.g. in the membranes of electrodes sensitive to lithium [14], mercury(II) [15], lead(II) [16], Yb(III) [17], and cobalt(II), cadmium(II) or nickel(II) ions [18–20], in spite the fact of insufficiently hydrophobic properties.

In this paper NaTPB is used as a model lipophilic salt and a marker of the leaching process. We apply differential pulse cathodic stripping voltammetry (DP CSV), with the hanging mercury drop electrode (HMDE) as the working electrode, to determine leaching of sodium tetraphenylborate from sodium-sensitive PVC-based membranes. To exert influence on the leaching process, the membranes contain different plasticizers—*o*-nitrophenyl octyl ether (*o*-NPOE) and di(2-ethylhexyl) sebacate (DOS).

2. Experimental

2.1. Chemicals

High molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), *o*-nitrophenyl octyl ether (*o*-NPOE),

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lipophilic salt—sodium tetraphenylborate (NaTPB) and sodium ionophore III—ETH 2120 were obtained from Fluka (Buchs, Switzerland) of selectophore grade. Tetrahydrofuran (THF) from Fluka (Buchs, Switzerland) was distilled twice before use. The salt NaCl was of analytical grade from Fluka (Buchs, Switzerland).

For all experiments, the aqueous solutions were prepared with doubly distilled and freshly deionized water obtained with Milli-Q, Millipore, Austria (resistivity 18.2 MΩ cm).

2.2. Potentiometric measurements

The potentials were measured using a 16-channel mV-meter (Lawson Labs, Inc., Malvern, PA). The reference electrode was an Ag/AgCl electrode with 3 M KCl solution in a bridge cell. The measurements were carried out at 22 ± 1 °C.

2.3. Composition and preparation of ion-selective membrane

The ion-selective membranes were cast by dissolving the membrane components in 1.2 mL of THF and pouring the cocktail onto a glass plate surrounded by a glass ring of inside diameter 16.2 mm. The solution was allowed to evaporate overnight. Disks (5 mm in diameter) were cut from the membranes with a cork borer (the weight of each membrane was 19.8 ± 0.3 mg) and after a certain soaking time in 2 mL 10^{-3} M NaCl they were placed inside conventional Philips ISE bodies (Fluka). The inner solution compartment was filled with 10^{-3} M NaCl.

All the membranes were separately conditioned and stored. For each membrane composition at least three identical membranes were examined. Two groups of sodium-selective membranes were studied. In the first one (*series* a), PVC membranes were plasticized with polar *o*-nitrophenyloctyl ether (*o*-NPOE), and in the second one (*series* b) with non-polar bis(2-ethylhexyl) sebacate (DOS). Each group was represented by two membranes with different amounts of sodium (ETH 2120) ionophore (*series* I: 0 wt% and *series* II: 2 wt% of ETH 2120). All membranes contained (0.5 wt%) of NaTPB.

2.4. Voltammetry

A multipurpose Electrochemical Analyzer M161 with the electrode stand M164 (both MTM-ANKO, Poland) was used for all the voltammetric measurements. The classical three-electrode quartz cell (volume 20 mL) was used, consisting of the Hanging Mercury Drop Electrode M163 (MTM-ANKO), a double-junction reference electrode Ag/AgCl/(3 M KCl) with replaceable outer junction (0.02 M NaCl) (Mineral, Poland) and a platinum wire as an auxiliary electrode. Stirring was performed during the preconcentration time using a magnetic bar rotating at approximately 500 rpm.

Quantitative measurements were performed using DP CSV voltammetry and the standard addition procedure (three additions of NaTPB) in the supporting electrolyte: 0.05 M NaCl (total volume 10 mL) contained in a voltammetric cell. The potential of the electrode was changed in the following sequence: accumulation potential (E_{acc}) equal to 90 mV and accumulation time (t_{acc}) was in the range of 15–45 s. During the accumulation step, NaTPB was adsorbed while the solution was being stirred. Then, after a rest period of 5 s a differential pulse voltammogram was recorded in the cathodic direction from 90 mV to −600 mV. The other experimental parameters were as follows: step potential, 3 mV; pulse amplitude, ΔE −20 mV; time step potential, 40 ms ((t_{w}) 20 ms waiting plus (t_{p}) 20 ms probing time). The measurements were carried out in deaerated solutions.

All experiments were carried out at 22 ± 1 °C.

Table 1
Membrane compositions in wt%.

Membrane no.	Plasticizer	PVC	ETH 2120	NaTPB
Ia	67.5 *o*-NPOE	33	–	0.5
Ib	67.5 DOS	33	–	0.5
IIa	67.5 *o*-NPOE	31	2	0.5
IIb	67.5 DOS	31	2	0.5

2.5. Electrochemical impedance spectroscopy (EIS)

The impedance measurements were performed using an Autolab General Purpose Electrochemical System and Autolab Frequency Response Analyzer System (AUT20.FRA2-AUTOLAB, Eco Chemie, B.V., The Netherlands) connected to a one-compartment, three-electrode cell where the PVC electrode was connected as the working electrode. The reference electrode was an Ag/AgCl/(3 M KCl) electrode, and the auxiliary electrode was a glassy carbon rod. The temperature was adjusted to 22 °C with a temperature controller connected to a thermostat. The accuracy of the preset temperature was ±0.25 °C.

3. Results and discussion

3.1. Potentiometric response of PVC membranes used

In the first step, the potentiometric response of the ISE membranes was tested. The effect of the plasticizer was studied by using *o*-NPOE and DOS in the membranes. The compositions of the membranes used in this study are listed in Table 1.

Because all membranes were loaded with NaTPB, from the beginning they contained primary (sodium) ions. The potentiometric responses of all the membranes were studied in the chloride salts of primary ions in the concentration range from 10^{-1} M to 10^{-6} M after different soaking times. Examples of the calibration curves for all membranes after 1 h, 24 h and 92 h conditioning in 10^{-3} M NaCl are shown in Fig. 1.

The potentiometric responses observed for the membranes do not contain ionophore (*series* I) plasticized with *o*-NPOE (*series* Ia) and are quite unlike those seen for the membranes containing DOS (*series* Ib). This difference is dictated by the influence of the plasticizer's polarity, and characterized by dielectric permittivity (ε_{r}), which is $\varepsilon_{\mathrm{r}} = 3.9$ for DOS and $\varepsilon_{\mathrm{r}} = 23.9$ for *o*-NPOE. The respective plasticizers' lipophilicity is $\log P_{\mathrm{TLC}}(\mathrm{DOS}) = 10.0$ and $\log P_{\mathrm{TLC}}(o\text{-NPOE}) = 5.4$ and the lipophilicity of NaTPB is $\log P_{\mathrm{TLC}} = 6.28$ [21,22].

The electrodes containing only sodium salt (NaTPB) in the membrane cocktail were characterized by a range of linear responses from (Ia): 10^{-1}–10^{-3} M and (Ib): 10^{-1}–10^{-4} M NaCl. In the case of *o*-NPOE-plasticized NaTPB-based membrane (Ia), only after a very short time of conditioning was the potentiometric response towards sodium ions observed. The recorded potentials of electrode (Ia) during the second and third calibration were practically independent of the logarithm of sodium cation activity (the slope decreased from 47.4 mV/dec. after 1 h through 15.1 mV/dec. after 24 h, to 3.2 mV/dec. after 92 h). For the electrode with the membrane containing DOS (Ib), after applying a short conditioning (1 h), linear responses (slope 51.0 mV/dec.) were obtained for the activity range given above. After 24 h conditioning, the calibration curve slope increased to 54.5 mV/dec. and then started to decrease (35.9 mV/dec. after 94 h).

Introducing ionophore for sodium ions to the membrane composition resulted in an improved, extended linear response range, as expected. All the calibration curves recorded for the electrodes in *series* II were linear within the NaCl activity range from 10^{-1} M to 10^{-5} M with a close-to-Nernstian slope, e.g. after 24 h conditioning:

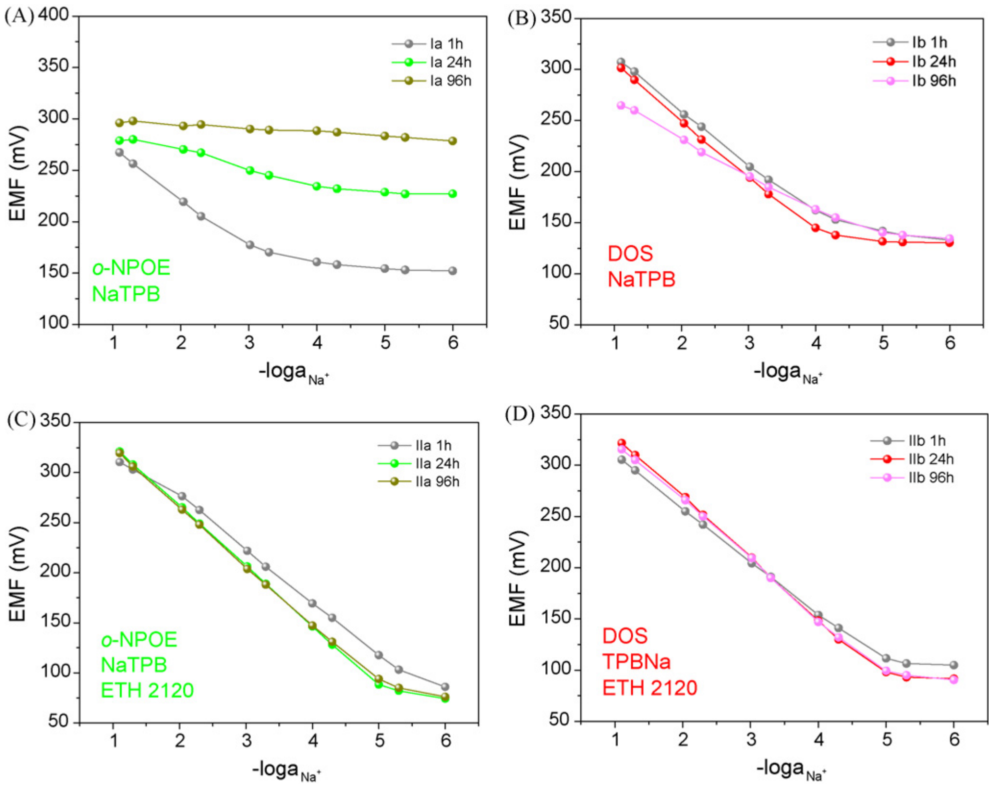

Fig. 1. Open-circuit potentiometric responses of sodium-selective electrodes prepared using two plasticizers: *o*-NPOE (A and C) and DOS (B and D). Electrodes *series* I contained 0 wt% (A and B) and electrodes *series* II contained 2 wt% (C and D) ionophore in the membrane. All membranes contained NaTPB.

59.0 mV/dec. for (IIa) membrane, 58.6 mV/dec. for (IIb) membrane, and after 92 h: 58.4 (IIa) and 56.8 (IIb) mV/dec. After introducing ionophore, the influence of the dielectric constant of the plasticizers on the slope values of the calibration curves was not pronounced, which indicates that the dielectric constants of the plasticizer do not significantly affect the response of the electrodes, contrary to the membranes in *series* I. However, the results obtained indicate that the stability of the slope value of the linear part of the calibration plots for those electrodes contacted with *o*-NPOE as a solvent mediator (*series* IIa) is a little better compared to the electrodes with DOS (electrodes *series* IIb).

3.2. *Impedance responses of PVC membranes*

The EIS measurements were made for all four of the above-mentioned groups of electrodes after a controlled time of soaking in pure 10^{-3} M NaCl. The impedance spectra were recorded in the frequency range of 0.2 MHz to 10^{-2} Hz (*series* a) and 10^{-3} Hz (*series* b) using a sinusoidal excitation signal with an amplitude of 0.01 V or 0.1 V depending on the level of noise in the signal. The measurements were performed at open-circuit potential in a solution of 10^{-3} M NaCl. Every measurement was repeated for 3 samples in every group of electrodes.

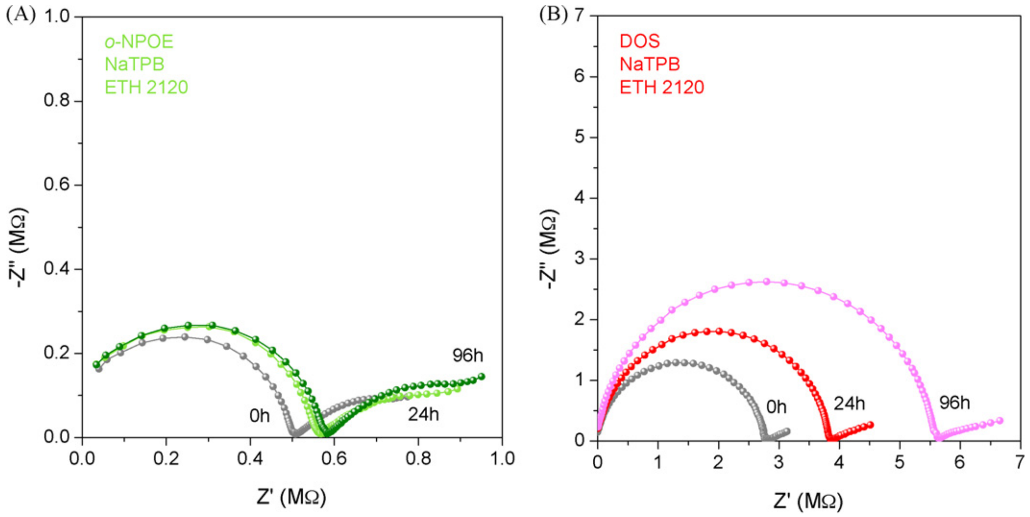

Fig. 2. The exemplary Nyquist plots of the impedance spectra recorded in 10^{-3} M NaCl for (A) IIa and (B) IIb membranes after different soaking times showing the increases in bulk membrane resistance.

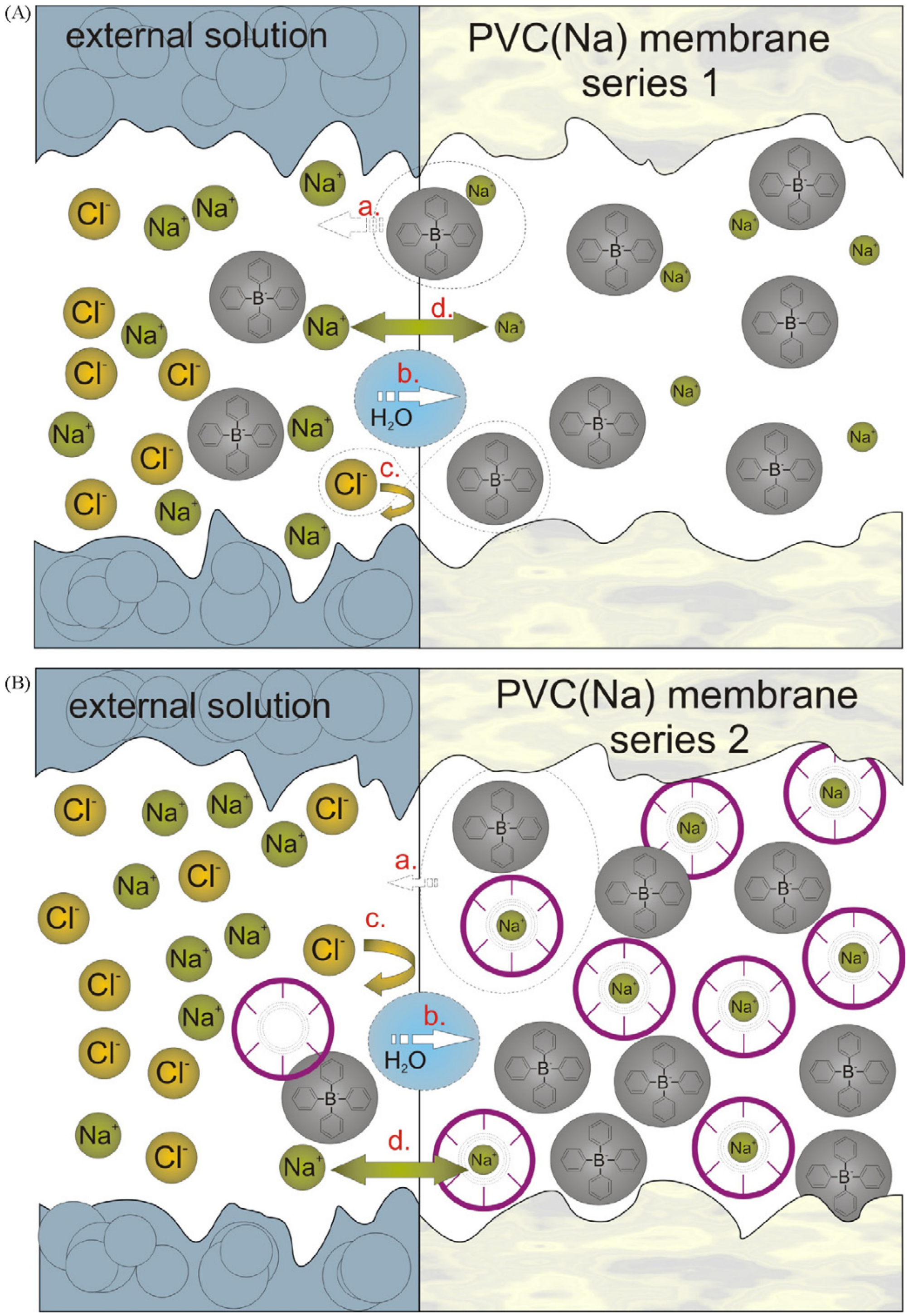

Fig. 3. Scheme of the ion-exchange processes which can occur at the interfaces of PVC-Na electrode (A, *series* I; B, *series* II) during the conditioning process.

All the spectra show a high-frequency semicircle, which is due to the bulk resistance of the ion-selective PVC membrane, and the diameter of this semicircle is equal to the bulk resistance of the membrane. Examples of the observed spectra for the electrodes in *series* II (plasticized with *o*-NPOE or DOS) are presented in Fig. 2.

Generally, in the case of the membranes in *series* a (plasticized with *o*-NPOE), the bulk resistance is lower because the tendency of dissociation of ion-pairs is larger, which results in a higher concentration of the charges in the PVC membrane [21,23]. The magnitude of the specific bulk resistance is mainly governed by the dielectric properties of the plasticizer and the physicochemical parameters of the ions that participate in the ion-exchange processes and which are complexed by ionophore. Of the two membrane types (a and b), the one with the more polar plasticizer *o*-NPOE creates a polymer matrix in which mass/ion transport processes are more promoted than in the less polar DOS [24–29]. Therefore, in the latter case the possible leakages of lipophilic membrane components in contact with the aqueous bathing solution should be less pronounced.

The long soaking time leads to an increase in the bulk resistance value. In view of data published so far, this time-dependent increase in the membrane resistance can be sought in the leaching of the electroactive species from the membrane, including the impurities

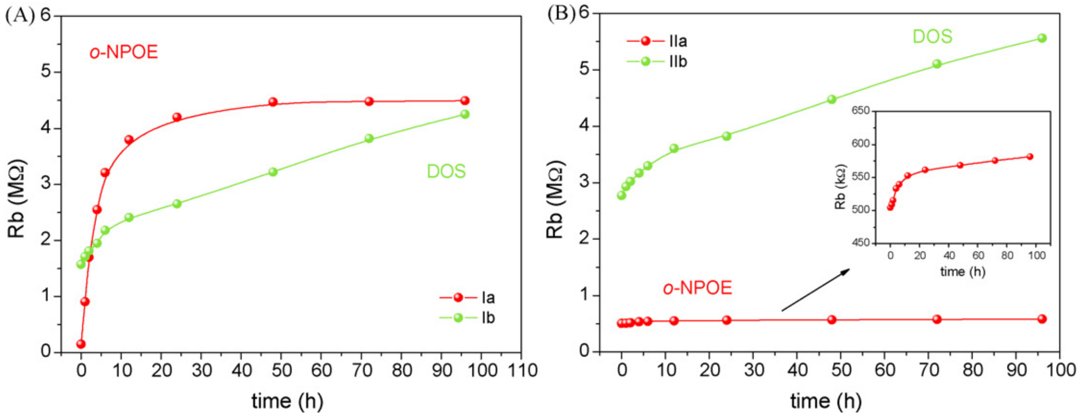

Fig. 4. Plots of bulk resistance (Rb) against time for membranes (A) *series* I and (B) *series* II contacted by 0.001 M NaCl after different conditioning times.

present in the PVC matrix, the membrane anisotropies, the exudation of solvent, and/or the time-dependent water uptake [30–32]. The possible processes of losing or gaining ions to/from the contacting aqueous solutions are shown in Fig. 3. These effects are interdependent and could be interpreted by coupling the potentiometric response to the EIS characteristics, as suggested recently [33].

The bulk resistance of the *o*-NPOE-plasticized NaTPB-based membrane without ETH 2120 (type Ia) rapidly increases at the beginning of the soaking process (about 5 times per hour during soaking in 10^{-3} M NaCl) and then stabilizes. For the di(2-ethylhexyl)sebacate (DOS) membranes with NaTPB (type Ib), the bulk resistance gradually increases from 1.57 MΩ to 3.92 MΩ after 96 h of soaking, and the initial increase is only about 9%. The change of membrane resistance of the *o*-NPOE(DOS)-plasticized NaTPB-based membrane with ETH 2120, shows an increase in the specific bulk resistance of 0.9% and 5.7% for IIa and IIb, respectively, during 1 h of soaking. The evolution of the bulk resistance is governed by the properties of the plasticizer and significantly depends on the soaking time, as shown in Fig. 4.

All the above observations may indicate a role of the leaching of NaTPB in to the contacting solution, which therefore calls for inspection of the leaching process by an independent method, e.g. DP CSV, as proposed in this paper.

3.3. Determination of NaTPB concentration in storage solution

After conditioning, the solutions used during this process were examined by differential pulse cathodic stripping voltammetry in order to determine the concentration of NaTPB.

Examples of the DP CSV voltammograms recorded for the storage solution of the electrodes in *series* I and additions of standard NaTPB solution are presented in Fig. 5. The recovery (based on three repetitions of analysis and using the standard additions method) was determined using three different samples spiked by 0.15 μM, 0.3 μM and 0.8 μM of NaTPB. Acceptable recovery (98–105%) shows that the proposed method can be used to determine NaTPB and assess the leaching of this compound during the conditioning of polymer electrodes.

The determined values of NaTPB concentration in the 2 mL solutions used for conditioning (10^{-3} M NaCl) after different soaking times are presented in Fig. 6.

According to the results obtained, if the membranes do not contain ionophore the outflow of NaTPB is governed solely by the properties of the plasticizers. The tendency of NaTPB to leach from the membrane is greater in the case of more hydrophilic *o*-NPOE than DOS (Fig. 3).

The *o*-NPOE-plasticized membrane without ETH 2120 rapidly loses both Na^+ and TPB^- ions to a contacting solution of NaCl during the first 12 h of conditioning. In the case of the DOS-plasticized membrane without ionophore, this process runs more slowly, but nevertheless does take place as well.

In the presence of ionophore in the membrane (*series* II), the rate of loss of both (Na^+ and TPB^-) ions is much less since Na^+ is effectively retained in the membrane by the ETH 2120 ionophore and the TPB^- ions are confined in the membrane by the electroneutrality condition (Fig. 3A and B; process a). The loss of NaTPB from the membrane is coupled with the inability of Cl^- to transfer from the solution to the membrane phase (Fig. 3A; process c.) [25].

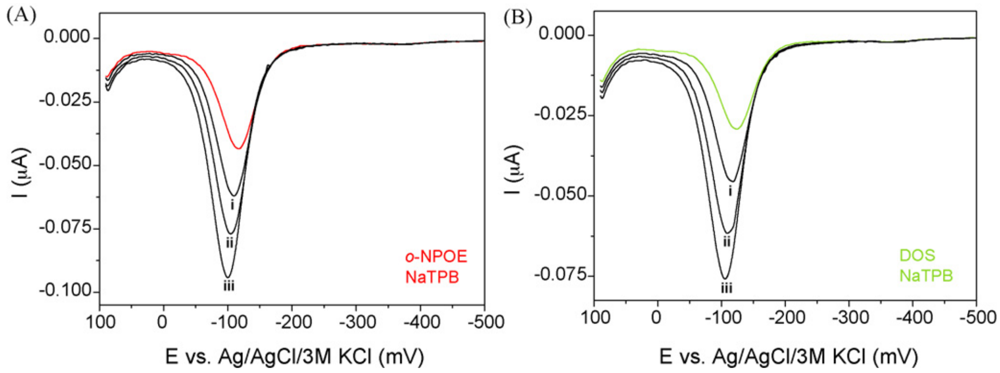

Fig. 5. Voltammograms obtained for 50 μl conditioning solution of (A) electrodes *series* Ia and (B) electrodes *series* Ib in 0.02 M NaCl after 48 h of membranes storage (red and green line, respectively) and standard additions: (i) 0.25 μM, (ii) 0.5 μM, and (iii) 0.75 μM NaTPB. Instrumental parameters: $\Delta E = -20$ mV, $E_s = 3$ mV. Pre-concentration potential $E_{acc} = 90$ mV and time $t_{acc} = 15$ s. Stirring rate, 500 rpm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

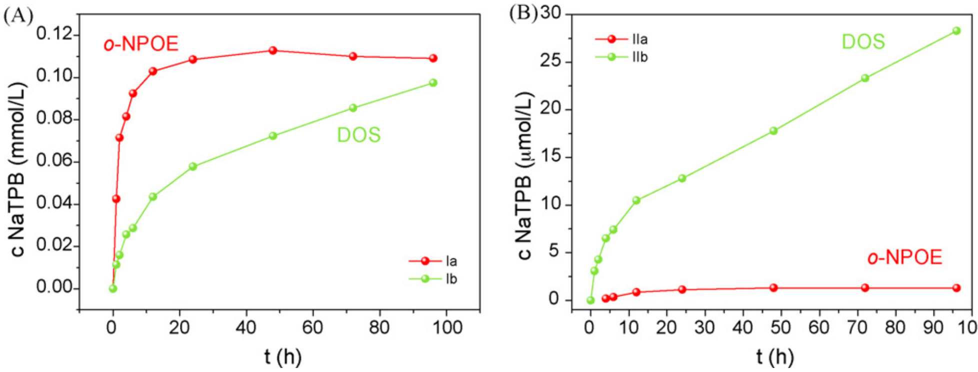

Fig. 6. The concentration of NaTPB leached out from membranes *series* I (A) and *series* II (B) into 2 mL of conditioning solution after different times of storage.

In the case of the *o*-NPOE or DOS-plasticized membranes with ETH 2120, a different interrelation between the loss of NaTPB during the conditioning process and the properties of the plasticizer was found. The leaching of NaTPB during conditioning was more significant for the membranes plasticized with DOS than with *o*-NPOE. This remains in agreement with the observations of other authors [25,34], who attributed this fact to a possible difference in viscosity of the plasticizers. Nevertheless, our study confirms the recent conclusion by Zook et al. [35] that the mechanistic role of anionic additives for ISEs with plastic membranes calls for further elucidation.

The results obtained with DP CSV are in a very good agreement with those of the potentiometric and impedance measurements. The leaching of NaTPB confirmed by DP CSV is manifested in the lowered calibration curve slopes and in the increased membrane resistance. The correlation between potentiometric and EIS behaviour observed can be theoretically interpreted by the Nernst–Planck–Poisson model [1,36–39]. This model, in particular, allows interpreting the influence of membrane components' concentrations, membrane permittivity, transport parameters (diffusion coefficients) as well as solution–membrane ion-partition processes and charge-transfer rates.

Accordingly, a new avenue for ISE signal formation and quality self-diagnostics is opened. We suggest that the voltammetry coupled with impedance spectroscopy method can be successfully used to study the potentiometric behavior of ISEs with the membranes based on poly(vinyl chloride).

4. Conclusions

The DP CSV method presented in this paper for the electrochemical determination of sodium tetraphenylborate using the hanging mercury drop electrode (HMDE) allows for quantitative determination of the NaTPB loss from polymeric membranes during conditioning in aqueous solutions with acceptable accuracy. The reproducibility of the method, measured as RSD equal to 2.3% (with each measurement performed on a fresh surface of the working electrode) and the acceptable recovery (97–104%) shows that the proposed method can be successfully used to determine the NaTPB outflow from PVC membranes into the conditioning/storage solution.

In all the studied membranes, a loss of NaTPB during the conditioning process was observed. When the membrane does not contain the ionophore, the NaTPB outflow occurs more rapidly when the membranes are plasticized with the more hydrophilic *o*-NPOE. During 24 h conditioning, the electrodes lose their potentiometric sensitivity and the membrane resistance increases significantly. In the case of membranes with DOS, this process occurs more slowly, which may also be attributed to some association between the cations and anions in the membrane. It is also clearly shown that, if the membranes contain ionophore, the loss of anionic membrane additives depends on the plasticizer.

By increasing the concentration of the carrier in the membrane, the response towards sodium ions becomes more ideal, and in the case of membranes with *o*-NPOE more stable over time.

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