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Potentiometric responses of ion-selective electrodes after galvanostatically controlled incorporation of primary ions

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ABSTRACT

A new method of quantitative incorporation of primary cations into ion-selective membrane by means of galvanostatic cathodic polarization/conditioning, before measurement step, was proposed and tested on the example of potassium-selective electrode with ionophore – valinomycin in poly(vinyl chloride) based membrane and with polypyrrole solid contact. Open circuit potential values recorded after polarization can be quantitatively explained by changes of primary cations and ionophore concentration in the surface part of the membrane. The influence of potassium ions concentration in the membrane (in relation to ion exchange sites amount) on the shape of potentiometric calibration plots was also observed. Improved characteristics, with extended linear range, can be obtained for membrane of minor loading with primary cations (around 25%), the responses are relatively stable in course of following calibrations.

1. Introduction

Potentiometric ion-selective electrodes (ISEs) are important tools of modern analytical chemistry, they are useful for various applications: clinical, environmental and industrial. Due to recent achievements related to ISE parameters optimization, e.g. detection limit lowering, selectivity improvement as well as all-solid-state construction, novel polymeric materials, miniaturization and relatively low cost, potentiometry with ISEs can successfully compete with other methods [1–4].

Improvement related to analytical parameters results mainly from more precise adjustment of ion fluxes at all interfaces, as well as membrane and internal solution or solid transducer composition. It is generally accepted that stable responses are obtained for bulk saturated membranes, i.e. for the case where the charge of ion exchanging sites is compensated by that of primary ions. However, studying the actual composition of the membrane and processes occurring inside ion-selective membranes, especially resulting in ions accumulation and composition changes, is not an easy task and often requires compromising membrane composition [5–12]. Therefore, attempts to quantify absolute amount of ions present in the membrane are especially rare in the literature [13]. In our recent paper concerning poly(*n*-butyl acrylate) membranes it was shown that the molar ratio of two different cations intentionally introduced to the membrane in form of two cation exchangers (with primary and interfering cations) highly affects the shape of potentiometric calibration plot: from classical (with detection limit close to 10^{-5} M), through extended linear range with lowered detection limit, to super-Nernstian behaviour, with decreasing amount of the salt with primary cations [14]. In another paper, using mass spectrometry technique to study the membrane composition, the influence of conditioning solution concentration on the concentration of primary silver ions in the membrane and its relation to potentiometric plots has led to similar conclusions [13].

On the other hand, new research areas and application possibilities in the field of ion selective electrodes are open using external polarization. In this case galvanostatic technique becomes especially promising, as it enables simple elimination of ohmic drop and brings results in the form of potential values, readily comparable with results of open circuit potentiometry. A number of papers on this issue has been significantly growing for 10 years, these works concern, e.g. detection limit lowering, both for internal solution [15–18] and all-solid-state sensors [19–21]. Bobacka [22,23], using a simple equivalent circuit model, has shown that chronopotentiometry could bring useful diagnostic information concerning all-solid-state sensors components and interfaces. Bakker and Shvarev have proposed a working mode with short galvanostatic pulses (pulstrodes), which resulted in adjustable selectivity and enhanced sensitivity of sensors [24,25]. This method is especially useful for determination of biologically important multi-charged ions [26], where open circuit potentiometry gives either drifts due to spontaneous extraction of ions or slopes in order of a few mV per decade (under equilibrium conditions). Current based methods are also helpful in obtaining unbiased selectivity coefficients [27,28].

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Moreover, chronopotentiometry can be a basis for non-classical use of ion-selective electrodes: in coulometric titration [29], in “flash titration” in diffusion layer, to determine acidity [30] or total concentration of various forms of a given ion (Ca^{2+} [31]). It can be also used in membrane conditioning as well modification of membrane composition and solid contact composition of all-solid state sensors [20,32].

In the present work, galvanostatic polarization is for the first time applied for controlled incorporation of primary ions into the ion-selective membrane, as a way of precise adjustment of membrane composition. This method is much simpler and faster compared to previously used incorporation of ion exchangers with various cations [14] (now, chemical preparation of lipophilic salts with different cations is avoided) and the polarization/conditioning procedure is much shorter than used previously [20]. A relation between the galvanostatically modified membrane composition and potentiometric characteristics as well as response stability is studied. As a model system poly(vinyl chloride) (PVC) based potassium-selective electrode containing ionophore – valinomycin, with polypyrrole solid contact was used in the study. The membranes were prepared to contain ions originating from ion exchanger: sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, while primary potassium ions were intentionally introduced in course of cathodic galvanostatic polarization. The effect of membrane pretreatment on potentiometric response, recorded in KCl solutions of various concentrations, is evaluated.

2. Experimental

2.1. Apparatus and reagents

In the open circuit potentiometric experiments a multichannel data acquisition setup and software (Lawson Labs. Inc., 3217 Phoenixville Pike, Malvern, PA 19355, USA) were used, stable (within ±0.2 mV) potential readings were recorded. In other electrochemical measurements galvanostat–potentiostat CH-Instruments model 660A (Austin, TX, USA) and conventional three-electrode cell, with platinum sheet as counter electrode, was used. The pumps systems 700 Dosino and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solutions.

Tetrahydrofuran (THF), PVC, bis(2-ethylhexyl) sebacate (DOS), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) and ionophore valinomycin were from Fluka AG (Buchs, Switzerland).

Doubly distilled and freshly deionised water (resistance 18.2 MΩ cm, Milli-Qplus, Millipore, Austria) was used throughout this work. All other reagents were of analytical grade and were obtained from POCh (Gliwice, Poland) with the exception of monomer pyrrole, obtained from Aldrich (Steinheim, Germany). Distilled pyrrole was stored in a refrigerator and prior to its use was purified by passing through an alumina gel mini-column.

2.2. Ion-selective membranes

The ion selective membrane contained 1.9% of NaTFPB, 3.0% of valinomycin, 31.1% of poly(vinyl chloride) and 64.0% of plasticizer – DOS. Total 120 mg of membrane components were dissolved in 1.5 mL of THF and applied as described below.

2.3. Working/indicator and reference electrodes

Glassy carbon disc electrodes of area 0.07 cm^2 (Detektor, Poland) were used in experiments with polypyrrole membrane electrodes. The substrate electrodes were polished with Al_2O_3, 0.3 μm. A mirror smooth polishing was avoided to prevent peeling off the relatively thick polymer film. The double junction silver/silver chloride reference electrode with 1 M lithium acetate in outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used. The recorded potential values were corrected for the liquid junction potential calculated according to Henderson approximation.

2.4. Polypyrrole films

Polypyrrole films were obtained in course of potentiostatic electrodeposition at 0.9 V, passing charge 3.6 C/cm^2, from aqueous solution containing 0.05 M pyrrole and 0.1 M NaCl to yield polypyrrole doped with chloride anions. Thus obtained conducting polymer films were thoroughly rinsed with deionised water and directly covered by the cocktail of membrane components to obtain all-solid-state potassium selective electrodes.

2.5. All-solid-state potassium selective electrodes with polypyrrole contact

Polypyrrole films obtained as described above were placed in a position with the polymer film facing up. The top of the electrode was covered with pipetted 50 μL THF solution of membrane components, resulting in c.a. 200 μm thick membrane.

The obtained electrodes were conditioned for overnight in 10^{-3} M NaCl and then (after rinsing) were polarized galvanostatically (if not stated otherwise). Galvanostatic polarization was carried out in 0.01 M KCl solution, using different currents and times (see Section 3), afterwards the electrodes were conditioned again in 10^{-3} M NaCl solution or in water for overnight; alternatively they were studied directly after polarization.

Each experiment with galvanostatic polarization was carried out for a new contact/membrane.

Mean ion activities were calculated according to Debye–Hückel theory [33]. All experiments were performed at ambient temperature (23 °C).

3. Results and discussion

3.1. Open circuit conditioning

The as-prepared ion-selective membranes used in these experiments contained ion exchanger with sodium counter-ions and potassium ionophore – valinomycin, i.e. potassium ions were initially absent in the membrane. After preparation the electrodes with membranes were overnight conditioned in 1 mM NaCl solution, this conditioning was aimed to equilibrate the membrane with aqueous solution, however, in the absence of primary, potassium, ions.

The next step was open circuit conditioning in 0.01 M KCl solution to analyze the rate of spontaneous ion exchange of Na^+ by K^+ ions in the membrane. Fig. 1 shows calibration plots recorded after different conditioning times in 0.01 M KCl. Directly after conditioning in NaCl solution the recorded plots show a significant super-Nernstian effect for concentrations close to $10^{-4.5}$ M, suggesting transient behaviour related to spontaneous K^+ ions extraction. For the following calibrations the super-Nernstian effect gradually diminishes.

The super-Nernstian potential drop, resulting from decreased K^+ ions concentration close to the membrane surface, recorded for the first calibration, can be used to estimate the flux of ions being incorporated to the membrane. The deviation from the linear Nernstian dependence for concentration lower than $10^{-4.5}$ M is above 100 mV, suggesting that the surface concentration of K^+ ions is two orders of magnitude lower than in bulk, thus it can be assumed as

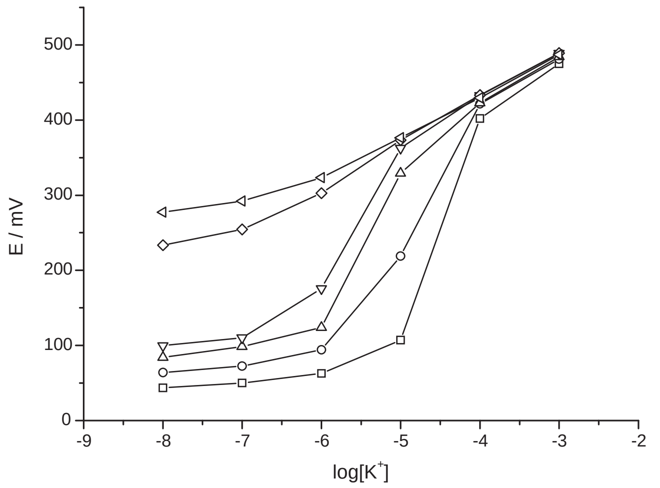

Fig. 1. Potentiometric plots recorded for the electrodes recorded following overnight conditioning in 1 mM NaCl: directly after conditioning (squares) and after additional 1 h, 2 h, 3 h, 4 h, 5 h conditioning in 0.01 M KCl (plots with increasing potentials for KCl concentration below 10^{-6} M).

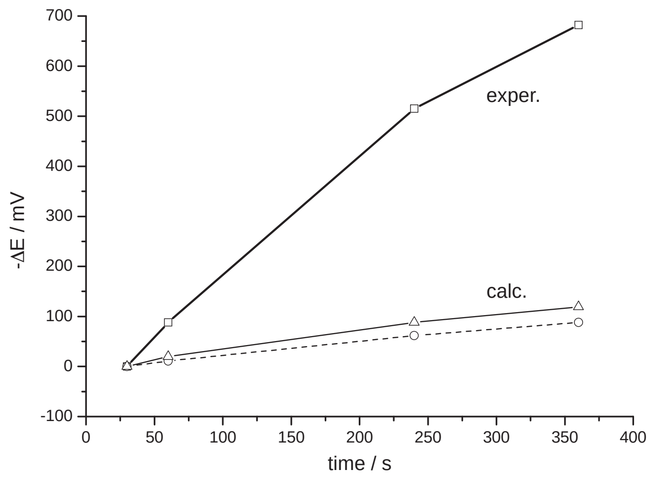

Fig. 2. Dependence of potential measured directly after galvanostatic polarization (2 μA) on polarization duration time (presented as difference of potential for a given time and potential recorded after 30 s electrolysis): experimental data (squares), calculated data using Eq. (4) (dashed line) and calculated data using Eq. (4) and including change of polypyrrole layer potential, see text (solid line, triangles).

close to 0. The observed concentration polarization can be related to the flux of extracted cations, *J*, using equation [34]:

$$c(0,t) = c^0 \pm 2J\sqrt{\frac{t}{D\pi}} \tag{1}$$

where $c(0,t)$ and c^0 are the surface and bulk (solution phase) concentration of K$^+$ ions, *D* is diffusion coefficient of K$^+$ ions in the solution, *t* is time of contact of the electrode with solution before potential reading. The sign "+" or "–" points to increase or decrease of the surface concentration as a result of diffusional transport (in the present case the sign "–" is applicable). Assuming then K$^+$ ions bulk concentration $c^0 = 10^{-4.5}$ M, $c(0,t) = 0$ M and using Eq. (1) for $t = 10$ s, $D = 2 \times 10^{-5}$ cm^2 s^{-1} [35], the estimated flux is $\sim 10^{-11}$ mol cm^{-2} s^{-1} for K$^+$ ions free membrane, then, as expected, it decreases as the membrane becomes saturated.

3.2. Galvanostatic polarization, no post-conditioning

In a next experiment, the rinsed electrodes with membranes containing NaTFPB (absence of K$^+$ ions) were overnight conditioned in 1 mM NaCl solution. Then they were transferred to 0.01 M KCl solution and immediately cathodic galvanostatic polarization was applied. This step was intended to introduce different and controllable amounts of potassium ions to the membrane. The occurring electrode reaction is reduction of the solid contact – semi-oxidized polypyrrole, the charge used and the amount of polypyrrole were adjusted to avoid complete reduction of the polymer. This process is connected with ion transfer – due to cation exchanging properties of the membrane – can be assured by incorporation of potassium ions from solution to the membrane where they interact with the ionophore. In the same time, charge changes of the polymer can be compensated either by incorporation of sodium ions from the ion-selective membrane or by release of chloride ions from the conducting polymer to the membrane. The possibility of chloride ions release to the membrane phase was confirmed by mass spectrometry with laser ablation of the membrane material [32]. Typical chronopotentiometric plots with gradually decreasing potential were recorded (cf., e.g. Fig. 1 in Ref. [32]).

Directly after cathodic polarization using current 2 μA the electrode was rinsed with water, immersed in 1 mM KCl solution and immediately open circuit potentials were measured. The obtained data were presented in Fig. 2. These results show significant influence of applied polarization time, with longer polarization duration, for the same current, the potentials recorded became lower. It should be stressed that the membrane just after polarization represents a transient behaviour related to concentration profiles and possible ion exchange in bathing solution.

The applied current can be recalculated to K$^+$ ions flux, *J*, by equation:

$$J = \frac{I}{nFA} \tag{2}$$

where *A* is electrode surface area, *n* is number of electrons (equal to 1). The galvanostatically forced flux can be now compared with that related to spontaneous ions incorporation resulting from the presence of ion exchange sites in the membrane. For the applied current 2 μA the flux is around 3×10^{-10} mol cm^{-2} s^{-1}, i.e. considerably higher than that related to spontaneous K$^+$ ions extraction to K$^+$ ions free membrane (around 10^{-11} mol cm^{-2} s^{-1} or lower for longer times, see previous section).

In the previous works [32,36], it was shown that surface concentration of galvanostatically incorporated primary cations can be described by equation taking into account concentration polarization under conditions of constant ion flux and diffusional transport [Eq. (1)], where now $c(0,t)$ and c^0 are the surface and bulk concentration of K$^+$ ions in the membrane, *D* is diffusion coefficient of K$^+$ ions in the membrane. Under applied conditions (solution resistance around 1 kΩ, current around 2 μA) the ohmic drop in the solution is small – in the range of 2 mV, thus the assumption on diffusional transport in the solution is reasonable. On the other hand, the membrane contains lipophilic salt – ion exchanger which can play a role of supporting electrolyte – lowering the migration effects.

Therefore, neglecting spontaneous K$^+$ ions extraction (see comment to Eq. (2)) and assuming now that initial bulk membrane concentration of K$^+$ ions, $c^0 = 0$, Eq. (1) suggests a linear dependence of surface concentration of primary ions on square root of time or on applied current. This was verified experimentally, basing on results of LA ICP MS experiments [32,36].

The surface concentration $c(0,t)$ determined from Eq. (1) can be then inserted into Nernst equation:

$$E = E^0 + 0.059 \log \frac{a\mathrm{K}^+}{fc(0,t)} \tag{3}$$

where E^0 is a constant, aK$^+$ is activity of potassium ions in solution, *f* is activity coefficient of K$^+$ ions in the membrane. Joining Eqs. (1)

and (3), the change of potential in time period from t_1 to t_2, for bulk concentration in the membrane, $c^0 = 0$, can be expressed as:

$$E(t_2) - E(t_1) = -\frac{0.059}{2} \log \frac{t_2}{t_1} \tag{4}$$

Additional effect which can be responsible for recorded potential decrease with reduction time increase can be reduction of the solid contact – polypyrrole. A dependence of potential on reduction time for the electrode coated only by polypyrrole layer (of the same polymerization charge as used for electrodes with ion-selective membranes) using current 2 μA was recorded in a separate experiment (data not shown).

Fig. 2 presents comparison of experimental results with calculated potential changes. The calculated data represent a sum of potential difference obtained from Eq. (4) (for $t_1 = 30$ s, $t_2 = 60$, 240 or 360 s) and potential change resulting from polypyrrole reduction (taken from chronopotentiometric curve of reduction at electrode coated by polypyrrole layer). It can be noticed that the experimentally recorded potential decrease is more significant than calculated one. This difference can be explained by concentration polarization of ionophore, with rapidly decreasing concentration in the surface layer of the membrane, in the presence of cathodic current. In this case the valinomycin transport in the membrane is also governed by Eq. (1), where concentrations and diffusion coefficient relate to the ionophore in the membrane. From the considerable potential lowering (observed in Fig. 2) it can be predicted that for the applied current and longer time, the ionophore concentration decreases significantly at the surface (this effect is visible also on chronopotentiometric curve of cathodic polarization showing transition time under these conditions, not shown). Taking into account the diffusion coefficient of ionophore in the plasticized PVC based membrane: 2×10^{-8} cm^2 s^{-1} [37] and the applied current value, the change of ionophore concentration in the surface layer of the membrane: $c^0 - c(0,t)$ for the applied current and the longest time (360 s) is close to 0.05 M, i.e. comparable with bulk concentration of valinomycin in the membrane. This denotes virtual absence of ionophore in the surface part of the membrane and thus the electrode is expected to lose its selectivity.

Fig. 2 shows also potential changes calculated only from Eq. (4), representing changes of potassium ions concentration in the surface part of the membrane. These changes are negligibly small when compared with experimental data, confirming that K$^+$ ions concentration increase in the membrane has minor influence on the potential changes accompanying cathodic polarization.

3.3. Galvanostatic polarization with post-conditioning

After cathodic polarization concentration profiles in the membrane are highly unstable and the following open circuit relaxation significantly affects recorded open circuit potentials. Therefore, to obtain stable and thus analytically useful potentiometric data post-conditioning of the membrane is required leading to achieve uniform distribution of potassium ions in the membrane. The conditioning was carried out in K$^+$ ions free solution to avoid additional and uncontrollable incorporation of K$^+$ ions, compared to those introduced to the membrane in course of galvanostatic polarization. Taking into account the membrane thickness, $d \sim 200$ μm and diffusion coefficient value for mobile species in the membrane, D around 10^{-8} cm^2/s a typical time necessary to obtain such uniform distribution (estimated as d^2/D) is around 10 h, thus overnight conditioning was sufficient. After this conditioning potentiometric plots were recorded.

Therefore, after galvanostatic polarization the electrodes with membranes were overnight conditioned in 1 mM NaCl solution and then calibration plots in KCl solution of variable concentrations were recorded (Fig. 3). In course of polarization variable reduction charges were used, these charge values can be easily recalculated to the amount of incorporated potassium ions. Then, a ratio of moles number of potassium ions to that of ion exchange site in the membrane, i.e. saturation ratio can be calculated (Table 1), it covers the range from below 1 mol.% to slightly above 200 mol.%.

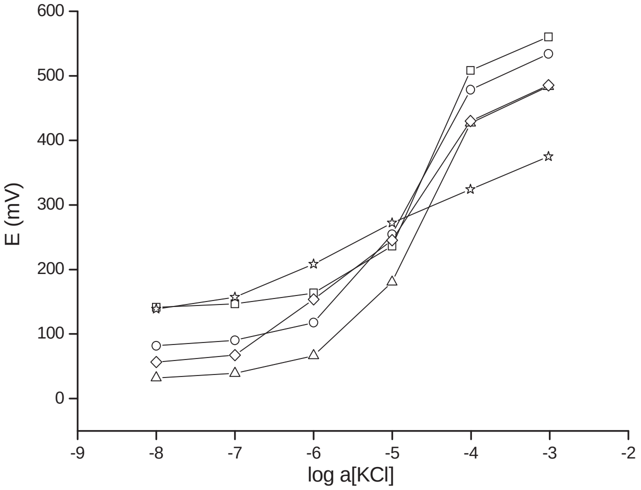

Fig. 3. Potentiometric plots for electrodes after polarization with charges: 0.002 mC (squares), 0.02 mC (circles), 0.2 mC (triangles), 2 mC (diamonds); 20 mC (stars), and following overnight conditioning in 10^{-3} M NaCl.

For polarization charges up to 2 mC (saturation ratio – number of primary ions related to number of ion exchanging sites: 20%) the plots are very similar to that for electrodes not contacting KCl solution before measurement (Fig. 1). All curves exhibit a significant super-Nernstian effect for concentrations lower than 10^{-4} M, suggesting very low concentration of potassium ions in the membrane compared to sodium. For the reduction charge 20 mC the super-Nernstian effect is smaller and it appears at K$^+$ ions concentration around 10^{-5} M. These results suggest exchange of incorporated K$^+$ ions by Na$^+$ in course of post-conditioning in NaCl solution, in spite of high selectivity of valinomycin containing membrane (selectivity coefficient close to 10^{-4} [38]). However, under experiment's conditions extraction of Na$^+$ ions can be highly preferred not only due to absence of potassium ions in the bathing solution, but also due to lower or close to zero concentration of ionophore in the surface part of the membrane, just after cathodic polarization. In such a case Na$^+$ cations would be preferred over K$^+$ owing to higher concentration.

Therefore, due to low selectivity of the polarized membrane, post-conditioning should not be carried out in the presence of higher concentrations of any intentionally added cations able to participate in ion exchange. As a consequence, in the following experiment deionised water was chosen as conditioning medium (hydrogen cations concentration 10^{-7} M is sufficiently low to avoid

Table 1
Parameters of galvanostatic polarization and amount of incorporated potassium ions.

Current (A)	Charge (mC)	Mol.% of K$^+$ (related to ion exchanger[a])
10^{-8}	2×10^{-3}	Below 1[b]
10^{-7}	0.02	Below 1[b]
10^{-6}	0.2	2.4
10^{-6}	2	24
10^{-6}	20	240

[a] Number of moles of ion exchanger in the membrane: 9×10^{-8}.

[b] Uncertainty results from possible influence of spontaneous K$^+$ ions extraction.

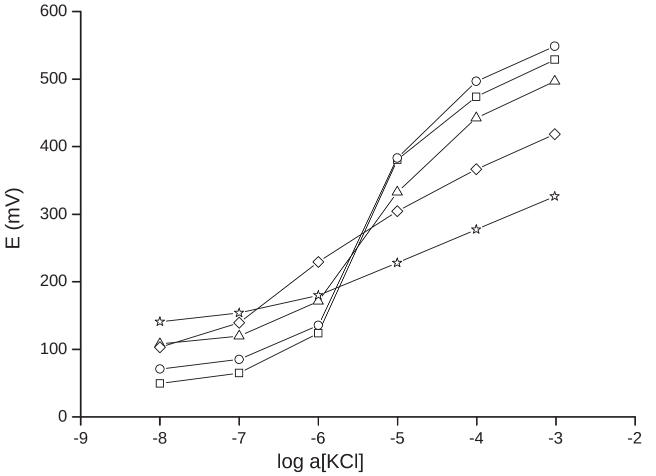

Fig. 4. Potentiometric plots for electrodes after polarization with charges: 0.002 mC (squares), 0,02 mC (circles), 0.2 mC (triangles), 2 mC (diamonds), 20 mC (stars), and following overnight conditioning in water.

undesirable ion exchange effects) to obtain stable potentiometric responses.

For this conditioning protocol, with overnight post-conditioning in water, the shape of calibration plots recorded was highly dependent on the applied reduction charge (Fig. 4). In the case of the lowest charges, leading to potassium cations amount below 3% (in relation to ion-exchanging sites), a characteristic with super-Nernstian effect was recorded, typical for a non-saturated membrane. A similar effect was described previously for Ag^+ selective electrodes, where the amount of primary ions in the membrane was determined by mass spectrometry [13].

With increasing polarization charge (higher amount of incorporated K^+ ions) the super-Nernstian effects were less pronounced and for the highest applied charge (20 mC), corresponding to full membrane saturation, a typical ("classical") plot with linear Nernstian slope and detection limit around 5×10^{-7} M was recorded. Therefore, due to remarkable difference in the shape related to charge passed and thus incorporated potassium ions amount, such plots can serve as a kind of diagnostic tool to estimate the amount of primary ions in the membrane.

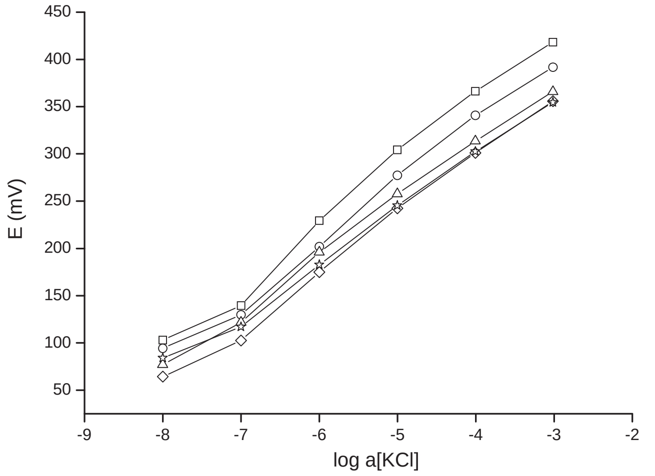

Fig. 5. Potentiometric responses for electrodes after polarization with charge 2 mC and overnight conditioning in water: 1st calibration, 1st day (squares), 10th calibration of the same day (circles), 2nd day (triangles), 3rd day (diamonds), 4th day (stars).

For the reduction charges not lower than 0.2 mC (saturation ratio above 2%) the applied current was 10^{-6} A. This corresponds [Eq. (2)] to the flux J close to 2×10^{-10} mol cm^{-2} s^{-1}, i.e. considerably higher than that resulting from spontaneous ion exchange for K^+ free membrane (see comment to Eq. (2)). Therefore, the amount of incorporated potassium ions is in this case well controlled by applied cathodic charge. Then the potential values recorded for the first point of the calibration plot (i.e. for KCl concentration 10^{-3} M) should be strictly related to the amount of potassium ions incorporated during polarization. In contrast to the case discussed in the previous section, now the distribution of K^+ ions and ionophore in the membrane should be uniform, due to overnight equilibration. In this case, the amount (bulk and surface concentration) of K^+ ions in the membrane is linearly dependent on applied charge, thus for increasing polarization charge a decrease of electrode potential (recorded in 1 mM KCl solution) is expected. Such behaviour was observed experimentally, the lowest potential was recorded for the highest polarization charge: 20 mC. Comparing now potentials recorded in 1 mM KCl solution after polarization with charges 0.2 mC, 2 mC and 20 mC (and following conditioning in water), one can expect 10-fold change in K^+ ions concentration in the membrane for the consecutive plots. Thus, since K^+ ions concentration in the solution is the same (1 mM), the difference in potentials for consecutive plots should be around 60 mV. For instance, the experimentally obtained difference for plots with polarization charges 0.2 and 2 mC is 78 mV, i.e. higher than Nernstian. The additional, over-Nernstian potential decrease (almost 20 mV over theoretical Nernstian slope) can result from more advanced reduction of the solid contact – polypyrrole for longer electrolysis time. To check this effect more quantitatively, a parallel analogous experiment was carried out, where galvanostatic polarization in 0.01 M KCl was replaced by polarization in 0.01 M NaCl. The conditioning procedure was the same as for electrodes polarized in KCl solutions. The potential after 2 mC reduction, recorded in 1 mM NaCl after overnight conditioning was 25 mV lower than after 0.2 mC reduction. Therefore, this difference can well explain the additional decrease resulting in over-Nernstian change in KCl solution.

The potential difference (for membranes polarized with charge 20 mC and 2 mC), recorded in 1 mM KCl, is preserved also for lower KCl concentrations in solution (10^{-4} and 10^{-5} M). This points to minor contribution of spontaneous incorporation of potassium ions from the solution to the surface concentrations (both in the membrane and in the solution). Only for KCl concentration below 10^{-5} M and polarization charge 2 mC a slight super-Nernstian effect was recorded indicating concentration polarization in solution. For low charges (below 0.2 mC) the amount of potassium ions incorporated during polarization is too low to enable reasonable quantitative comparison. Moreover, for low charges or polarizing current below 10^{-6} A the role of spontaneous K^+ ions extraction can be significant, increasing the actual amount of potassium ions in the membrane.

The most promising results, from analytical point of view, were obtained for polarization charge around 2 mC, corresponding to membrane saturation (with K^+ ions) 24%. The super-Nernstian potential change for K^+ ions concentration in solution below 10^{-5} M is low and the electrode is sensitive to potassium ion changes in solution in the entire studied concentration range from 10^{-3} M to 10^{-8} M. This result is consistent with our earlier report on Ca-selective polyacrylate membrane showing that membrane saturation ratio close to 25% is necessary to obtain linear dependence for extended concentration range [14]. The novelty of this approach concerns easier and precise control of primary ions amount in the membrane optimal for this effect.

The slight super-Nernstian effect observed at KCl concentration 10^{-6} M can be used to estimate the flux of K^+ ions incorporated to the membrane in course of spontaneous extraction. The deviation from the linear dependence for this concentration (10^{-6} M, Fig. 4) is ~20 mV, i.e. corresponds to the ratio surface/bulk concentration of K^+ ions around 0.5. Assuming then K^+ ions bulk concentration $c = 10^{-6}$ M, surface concentration $c(0,t) = 5 \times 10^{-7}$ M, and using Eq. (1) (assuming diffusion coefficient of K^+ ions in solution, $D = 2 \times 10^{-5}$ cm^2 s^{-1} [35] with time $t = 10$ s), the flux of potassium ions can be estimated as $J = 6 \times 10^{-13}$ mol cm^{-2} s^{-1}. Comparing this value with the amount of K^+ ions needed to fully saturate the membrane (change from 24% to 100%), equal to 6×10^{-8} mol, time necessary to completely saturate the membrane is a few days, assuming that the flux is constant in time. Therefore, the obtained almost linear characteristics should be relatively stable in consecutive calibrations (one following another). This was confirmed experimentally by recording consecutive potentiometric plots. The shape of the plots was stable in course of calibrations carried out the same day (Fig. 5), but the potentials shift slightly to lower values, due to incorporation of K^+ ions to the membrane. However, in course of further calibration days (with overnight conditioning in water) stabilization of potential values and linear plot with practically Nernstian slope (59.3 mV dec^{-1}, $R^2 = 0.998$) in the activity range 10^{-7}–10^{-3} M was obtained (Fig. 5). These results clearly show potential application benefits of herein proposed method.

4. Conclusions

This paper describes a method of quantitative incorporation of primary cations (K^+) into ion-selective membrane, by means of galvanostatic polarization and shows a correlation of the shape of resulting potentiometric characteristics and primary ion contents in the membrane. Just after galvanostatic polarization step, differences in potentials for various polarization times were very high owing not only to gradual polypyrrole reduction but predominantly to ionophore depletion in the surface part of the membrane in course of polarization, the latter effect results also in decreased selectivity. The increase of primary cations concentration in the surface part of the membrane, accompanying polarization, is of minor significance for the potential value in this case. However, after polarization and following open circuit conditioning in water (absence of primary ions) different shapes of potentiometric plots were obtained, depending on amount of incorporated primary cations: from plots with super-Nernstian potential change to classical plots with elevated detection limit. It was shown that optimal characteristics with extended linear range and lowered detection limit could be obtained for moderate loading of the membrane with primary cations (close to 25% in relation to ion exchange sites amount).

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References

[1] T. Sokalski, T. Zwickl, E. Bakker, E. Pretsch, Anal. Chem. 71 (1999) 1204–1209.
[2] E. Lindner, R.P. Buck, Anal. Chem. 72 (2000) 336A–345A.
[3] E. Bakker, E. Pretsch, Trends Anal. Chem. 24 (2005) 199–207.
[4] J. Bobacka, A. Ivaska, A. Lewenstam, Chem. Rev. 108 (2008) 329–351.
[5] K. Tohda, Y. Umezawa, S. Yoshiyagawa, S. Hashimoto, M. Kawasaki, Anal. Chem. 67 (1995) 570–577.
[6] B. Schneider, T. Zwickl, B. Federer, E. Pretsch, E. Lindner, Anal. Chem. 68 (1996) 4342–4350.
[7] E. Lindner, T. Zwickl, E. Bakker, B. Thi Thu Lan, K. Tóth, E. Pretsch, Anal. Chem. 70 (1998) 1176–1181.
[8] R. Gyurcsányi, E. Lindner, Anal. Chem. 74 (2002) 4060–4068.
[9] R. Gyurcsányi, E. Lindner, Anal. Chem. 77 (2005) 2132–2139.
[10] L. Yook Heng, K. Tóth, E.A.H. Hall, Talanta 63 (2004) 73–87.
[11] R. Long, E. Bakker, Anal. Chim. Acta 511 (2004) 91–95.
[12] M. Püntener, M. Fibbioli, E. Bakker, E. Pretsch, Electroanalysis 14 (2002) 1329–1338.
[13] A. Michalska, M. Wojciechowski, E. Bulska, K. Maksymiuk, Electroanalysis 21 (2009) 1931–1938.
[14] A. Michalska, K. Pyrzyńska, K. Maksymiuk, Anal. Chem. 80 (2008) 3921–3924.
[15] E. Lindner, R.E. Gyurcsányi, R.P. Buck, Electroanalysis 11 (1999) 695–702.
[16] E. Pergel, R.E. Gyurcsányi, K. Tóth, E. Lindner, Anal. Chem. 73 (2001) 4249–4253.
[17] W.E. Morf, M. Badertscher, T. Zwickl, N.F. de Rooij, E. Pretsch, J. Electroanal. Chem. 526 (2002) 19–28.
[18] I. Bedlechowicz, T. Sokalski, A. Lewenstam, M. Maj-Żurawska, Sens. Actuators B 108 (2005) 836–839.
[19] A. Michalska, J. Dumańska, K. Maksymiuk, Anal. Chem. 75 (2003) 4964–4974.
[20] A. Michalska, Electroanalysis 17 (2005) 400–407.
[21] P. Pawłowski, A. Michalska, K. Maksymiuk, Electroanalysis 18 (2006) 1339–1346.
[22] J. Bobacka, Anal. Chem. 71 (1999) 4932–4937.
[23] J. Bobacka, A. Lewenstam, A. Ivaska, J. Electroanal. Chem. 509 (2001) 27–30.
[24] A. Shvarev, E. Bakker, Anal. Chem. 75 (2003) 4541–4550.
[25] S. Makarychev-Mikhailov, A. Shvarev, E. Bakker, Anal. Chem. 78 (2006) 2744–2752.
[26] A. Shvarev, E. Bakker, Anal. Chem. 77 (2005) 5221–5228.
[27] K.L. Gemene, A. Shvarev, E. Bakker, Anal. Chim. Acta 583 (2007) 190–196.
[28] H. Perera, A. Shvarev, J. Am. Chem. Soc. 129 (2007) 15754–15755.
[29] V. Bhakthavatsalam, A. Shvarev, E. Bakker, Analyst 131 (2006) 895–900.
[30] K.L. Gemene, E. Bakker, Anal. Chem. 80 (2008) 3743–3750.
[31] K.L. Gemene, E. Bakker, Anal. Chim. Acta 648 (2009) 240–245.
[32] P. Pawłowski, A. Michalska, M. Wojciechowski, J. Golimowski, E. Bulska, K. Maksymiuk, J. Solid State Electrochem. 13 (2009) 107–113.
[33] P.C. Meier, Anal. Chim. Acta 136 (1982) 363–368.
[34] Z. Galus, Fundamental of Electrochemical Analysis, Ellis Horwood, PWN, 1994.
[35] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, Butterworth, London, 1959.
[36] A. Michalska, M. Wojciechowski, E. Bulska, K. Maksymiuk, Electrochem. Commun. 10 (2008) 61–65.
[37] J.M. Zook, R.P. Buck, R.E. Gyurcsanyi, E. Lindner, Electroanalysis 20 (2008) 259–269.
[38] E. Bakker, P. Bühlmann, E. Pretsch, Electroanalysis 11 (1999) 915–933.