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Ion exchange properties and selectivity of PSS in an electrochemically switchable PPy matrix

K.-M. MANGOLD, C. WEIDLICH, J. SCHUSTER and K. JÜTTNER*
Karl-Winnacker-Institut der DECHEMA e.V., Theodor-Heuss-Allee 25, 60486, Frankfurt am Main, Germany
*(*author for correspondence e-mail: juettner@dechema.de)*

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Abstract

A composite of polypyrrole (PPy) and polystyrenesulfonate (PSS) exchanges cations and is a promising material for the technical application of water softening. The ion exchange properties of electrochemically prepared PPy(PSS) are studied by investigating the polymer using an electrochemical quartz crystal microbalance (EQCM) and by analysing the solution surrounding the polymer by atomic absorption spectroscopy (AAS). The exchange of cations by PPy(PSS) is found to be caused by three driving forces: electrochemical oxidation/reduction of PPy; chemical oxidation of PPy by dissolved oxygen; gradients of cation concentration between polymer and solution. The ion selectivity of PPy(PSS) is investigated and ion exchange isotherms for the binary systems Ca^{2+}/Na^{+} and Ca^{2+}/Mg^{2+} are determined.

1. Introduction

Cation exchanger resins based on polystyrenesulfonate (PSS) cross-linked by divinylbenzene are well established in water treatment, e.g. water softening [1]. These resins have to be regenerated with acid, saline solutions or by water electrolysis. From an economic and ecological point of view this regeneration process is disadvantageous. Therefore an electrochemically switchable ion exchanger is an innovation. The discovery of conducting polymers opened up the possibility to design switchable cation exchangers. The composite of PPy with PSS is a promising material [2–8]. It exhibits cation exchange properties and can be electrochemically controlled. Based on PPy(PSS), we developed a new type of electrochemically switchable cation exchanger for water softening [9–11]. The composite is formed by electrochemical or chemical oxidation of pyrrole in the presence of NaPSS, yielding a PPy(PSS) film on electrodes or PPy(PSS) nanoparticles [12, 13].

The absorption (water softening) and desorption (regeneration) of cations by this PPy(PSS) composite occurs according to the scheme shown in Figure 1: in its totally reduced (neutral) state PPy is not involved in cation exchange processes and the sulfonic acid groups of PSS absorb cations to maintain electroneutrality. This situation is comparable to pure PSS, i.e. PPy only acts as a matrix for PSS. When the ion exchange process is completed, PPy(PSS) is regenerated electrochemically by applying anodic polarization. This leads to the oxidation of PPy and the formation of cationic chain segments (polarons, bipolarons [14]) which are neutralized by the anionic sulfonic acid groups of PSS. To maintain electroneutrality, previously absorbed cations are released from PPy(PSS) into the solution. Strictly speaking, PPy(PSS) is not a traditional cation exchanger. It absorbs and desorbs cations depending on the applied potential and the degree of oxidation of PPy(PSS).

Knowledge of the ion exchange properties of PPy(PSS) is incomplete. In this paper two main topics are discussed, concerning the possibility of ion exchange occurring parallel to electrochemical polarization and the selectivity of PPy(PSS) for different cations (alkali and alkaline earth metals). The objective of this work is to determine the cation exchange behaviour and selectivity of PPy(PSS) concerning the technical application for softening drinking water.

2. Experimental

2.1. *Polymer preparation*

Electrochemical polymerization of PPy(PSS) was carried out using 0.1 M pyrrole in 0.1 M NaPSS aerated aqueous solution using a three-electrode arrangement with an Ag/AgCl reference electrode (saturated KCl) and a platinum mesh counter-electrode. For electrochemical quartz crystal microbalance (EQCM) experiments (ELCHEMA EQCN-501 nanobalance and

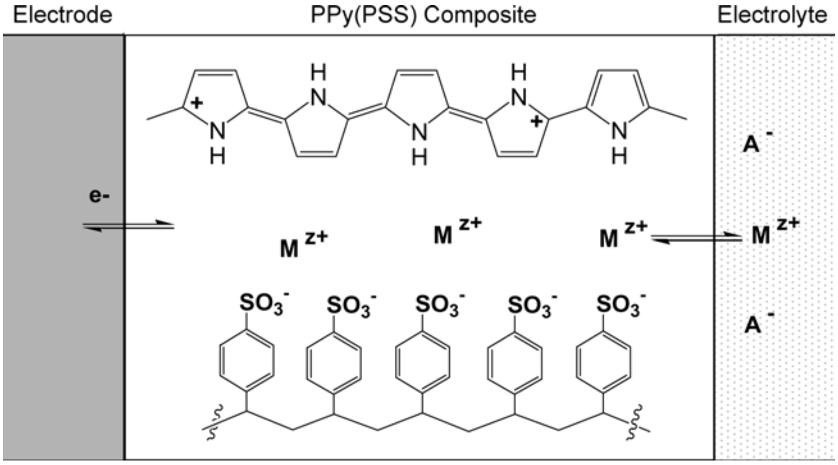

Fig. 1. Scheme of cation exchange at a PPy(PSS) composite.

PS-605 potentiostat) potentiodynamic electropolymerization was performed on a gold-layered (0.2 cm^2) quartz crystal (resonance frequency 10 MHz). In order to minimize viscoelastic effects the thickness of the PPy(PSS) layer was less than 1 μm [15, 16] (calculated from the polymerization charge [17]).

For AAS experiments, PPy(PSS) was prepared by galvanostatic electropolymerization (potentiostat: EG&G 263A) on a glassy carbon cylinder electrode (geometric area: 9 cm^2; Sigradur G; HTW) mounted on a PTFE cylinder. To obtain a PPy(PSS) layer approximately 3 μm thick [17], a current density of 1 mA cm^{-2} was applied for 720 s (electrode potential about 0.6 V).

All chemicals were of analytical grade (Aldrich, Merck). PSS (sodium salt; $M_w = 70{,}000$; Aldrich) consists of linear chains. Pyrrole (Aldrich) was distilled before use. The polymers were prepared at room temperature.

2.2. *Ion exchange experiments*

Electrochemical quartz crystal microbalance experiments were performed at room temperature (22 ± 2 °C) in aerated 0.1 M $CaCl_2$ solution using a three-electrode arrangement (Au working electrode; Pt counter electrode; Ag/AgCl reference electrode). The proportionality factor used for calculating the mass from the frequency was 0.87 ng Hz^{-1}.

Ion exchange experiments analysed by AAS were performed at room temperature (22 ± 2 °C) using a general procedure: subsequent to electropolymerization the electroactivity of PPy(PSS) was determined by several cyclic voltammograms in 0.1 M $CaCl_2$ solution.

The absorption of cations was achieved by potentiostatic polarization at −0.7 V in stirred 0.005 M $CaCl_2$ solution for 300 s, or binary mixtures of $CaCl_2$/NaCl (total concentration 0.005 or 1 M) and $CaCl_2$/$MgCl_2$ (total concentration 0.005 M), respectively.

The desorption of cations was performed after a washing procedure with distilled water to remove adherent Ca cations. The washing process was controlled by AAS and continued until Ca^{2+} was no longer detectable. Desorption experiments were performed by immersing the PPy(PSS) electrode in a cell filled with 25 ml stirred aerated or deaerated 0.005 M KCl or NaCl solution. Electrochemical oxidation of the composite was achieved by potentiostatic polarization at different potentials (0.1, 0.2, 0.3 or 0.4 V) for 300 s. Samples were taken from the solution before and after the polarization and the concentration of the desorbed cations was measured by AAS (Perkin Elmer 1100 B).

Deaerated solutions were made by bubbling Ar for about 15 min through the solution and keeping it in a weak Ar stream during the polarization.

The potentiostatic polarization was applied to reduce the danger of overoxidation of PPy [18] and to improve the long-term stability of the composite and the reproducibility of the experiments.

3. Results and discussion

While in PSS resins the chains are cross-linked by *p*-divinylbenzene, the composite PPy(PSS) consists of unbranched PSS chains cross-linked by PPy.

The composition of electrochemically formed PPy(PSS) was characterized by elemental analysis. From the amount of N (12.65%) and S (6.52%) the ratio of pyrrole and styrenesulfonate for a pristine polymer is calculated to be about 4.4:1, which means PPy(PSS) is composed of “building blocks” of about 9 pyrrole and 2 styrenesulfonate units, i.e. the degree of oxidation of PPy (doping level) is 0.22. This is in agreement with typical values (0.25) for PPy [3, 19].

The ion exchange of conducting polymers can be tracked by analysing the polymer, e.g. by EQCM [4, 20], impedance spectroscopy combined with EQCM [21], elemental analysis [19, 22] and XPS [23]. Also changes in the ion concentration of the surrounding solution can be conversely detected by optical probe beam deflection [24], radiotracer methods [25] and analysis of the ion concentration in the solution. This study is based on EQCM investigations concerning the cation content in the polymer as well as AAS analysis yielding the cation content in the solution.

3.1. *Ion exchange properties of PPy(PSS) investigated by EQCM*

Electrochemical quartz crystal microbalance experiments were performed in a quasi-steady state. Prior to each measurement PPy(PSS) was cyclically polarized several times. Figure 2 shows mass and current density curves of PPy(PSS) in $CaCl_2$. The current exhibits a typical capacitive-like curve shape [5]. The mass curve shows an increase with decreasing potential, indicating absorption of Ca cations and the corresponding desorption of Ca cations (mass decrease) with increasing potential.

From charge and mass differences the molar mass of exchanged solvated cationic species was calculated, assuming a current yield of 100% at a scan rate of $0.5\ \mathrm{V\ s^{-1}}$. From the mass to charge ratio of $0.67\ \mu\mathrm{g\ mA^{-1}\ s^{-1}}$ ($0.1\ \mathrm{M}\ CaCl_2$) the exchange of the solvated cation $Ca^{2+} \times 5H_2O$ was calculated.

The experiments described in the following section were performed in the potential regions marked in Figure 2 (absorption at -700 mV, desorption from $+100$ to $+400$ mV).

3.2. *Influence of polarization, oxygen and concentration gradients*

Three factors can be identified which promote the absorption and desorption of cations by PPy(PSS):

(i) Electrochemical oxidation of PPy(PSS), leading to the release of cations to maintain electroneutrality within the polymer;

(ii) Chemical oxidation of PPy(PSS) by dissolved oxygen accompanied by a release of cations to maintain electroneutrality;

(iii) Ion exchange driven by gradients of cation concentration between PPy(PSS) and the surrounding solution.

The release of cations by electrochemical oxidation of PPy(PSS) (i) [2–5, 7] and the oxidation (doping) of PPy by dissolved oxygen (ii) have been described [26]. The ion exchange of pure PSS driven by concentration gradients is also well-known [1], but to our knowledge ion exchange processes due to gradients of cation concentration between PPy(PSS) and the solution (iii) have so far not been studied in detail.

A simplified model can illustrate the effect of the driving forces (Figure 3). Taking a PPy(PSS) composite with incorporated M_1^+ cations in an aerated solution (electrolyte: $M_2^+\ A^-$), three different situations can be identified: (a) PPy(PSS) can be oxidized electrochemically or chemically (by oxygen) to form PPy^+(PSS). These oxidized (doped) segments release M_1^+ cations into the solution. (b) In addition there are PPy(PSS) segments which are electrochemically inactive and not accessible to ion exchange, but can be oxidized by dissolved oxygen which also leads to the release of M_1^+ cations. (c) In contrast to the oxidized segments, the

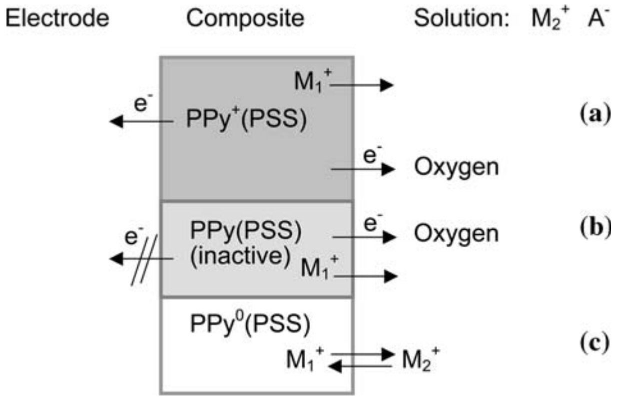

Fig. 3. Scheme illustrating the consistency of a PPy(PSS) composite.

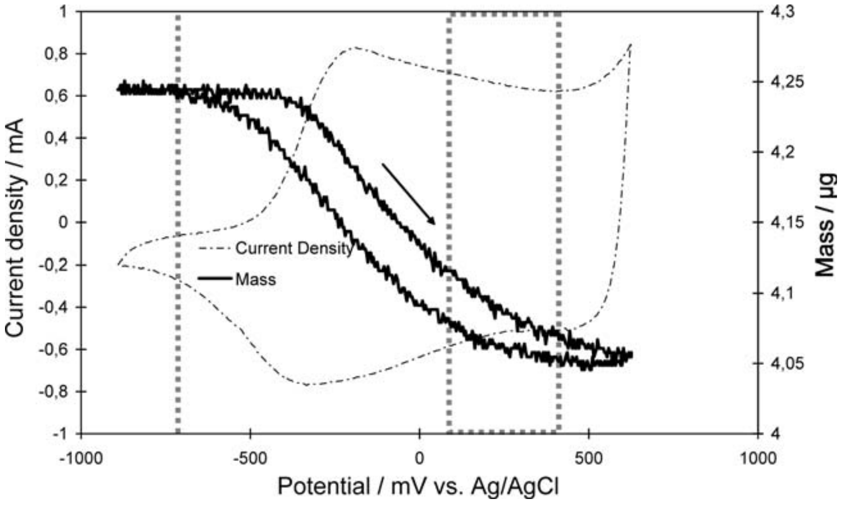

Fig. 2. Cyclic voltammetric (-) and mass (-) response of PPy(PSS) in $0.1\ \mathrm{M}\ CaCl_2$, scan rate $0.5\ \mathrm{V\ s^{-1}}$. The marked potential region indicates experimental parameters for absorption (-700 mV) and desorption ($+100$ to $+400$ mV) experiments (see Chapter 3.2).

reduced ones ($PPy^0(PSS)$) can participate in ion exchange processes (replacement of M_1^+ by M_2^+). The ratio of these segments is potential-dependent.

To study these processes in detail, extensive ion exchange experiments were made and the solutions were analysed by AAS. The absorption/desorption procedure in these studies approaches the conditions in a technical water softening unit and the investigations were restricted to the cations Ca^{2+}, Mg^{2+}, K^+, Na^+ relevant to drinking water. The general procedure for cation absorption/desorption was as follows: prior to the absorption experiments, PPy(PSS) was polarized at 0.1 V for 300 s in order to transform PPy into a defined oxidation state. Subsequently Ca^{2+} was absorbed by polarizing PPy(PSS) at −0.7 V for 300 s in an aerated 0.005 M $CaCl_2$ solution.

On account of the small concentration reduction (typically 50 μM) from the high initial concentration (0.005 M) it is difficult to measure the absorption of Ca^{2+}. Therefore the AAS measurements were restricted to the determination of desorption of cations. After a washing procedure, desorption was performed in a 0.005 M KCl solution.

Figure 4 shows the current yield (Figure 4a) and the concentration of the Ca cations released and the charge (Figure 4b), respectively. The decreasing current yield with increasing desorption potential is due to an increase in side reactions, e.g. overoxidation of PPy. The current yield higher than 100% at low oxidation potential 0.1 V, indicates a side reaction leading to an additional release of Ca^{2+}. This can be explained by an increase in cation desorption caused by the chemical oxidation of PPy by oxygen (ii).

To clarify the effect of electrochemical polarization (i) and dissolved oxygen (ii), desorption experiments at 0.1 V were performed in deaerated and aerated solutions. In deaerated solution an average anodic charge of 282 ± 25 mA s, leading to an average Ca^{2+} desorption of 1.63 ± 0.25 mg l^{-1}, was determined (current yield: 70%). However, in aerated solution an average anodic charge of 182 ± 21 mA s and an average Ca^{2+} desorption of 1.84 ± 0.23 mg l^{-1} were measured (current yield 122%). The anodic charge in deaerated solution was higher than in aerated solution. This suggests that, simultaneous to electrochemical polarization, PPy is also doped by oxygen. Therefore in aerated solution the amount of desorbed Ca^{2+} can be divided into a part due to electrochemical polarization and a part due to oxygen doping (assuming superposition of electrochemical polarization and oxygen doping). Taking the current yield determined in deaerated solution (70%) as a result of solely electrochemical polarization, the amount of electrochemically desorbed Ca^{2+} in the aerated solution can be calculated from the anodic charge to be 1.06 mg l^{-1}. Thus in aerated solution 58% of the total amount of desorbed Ca^{2+} is released by electrochemical polarization, whereas 42% of the desorbed Ca^{2+} is due to doping of the polymer by dissolved oxygen. The apparent current yield of 122% in aerated solution is the result of the two simultaneous Ca^{2+} desorption processes: electrochemical polarization and oxygen doping.

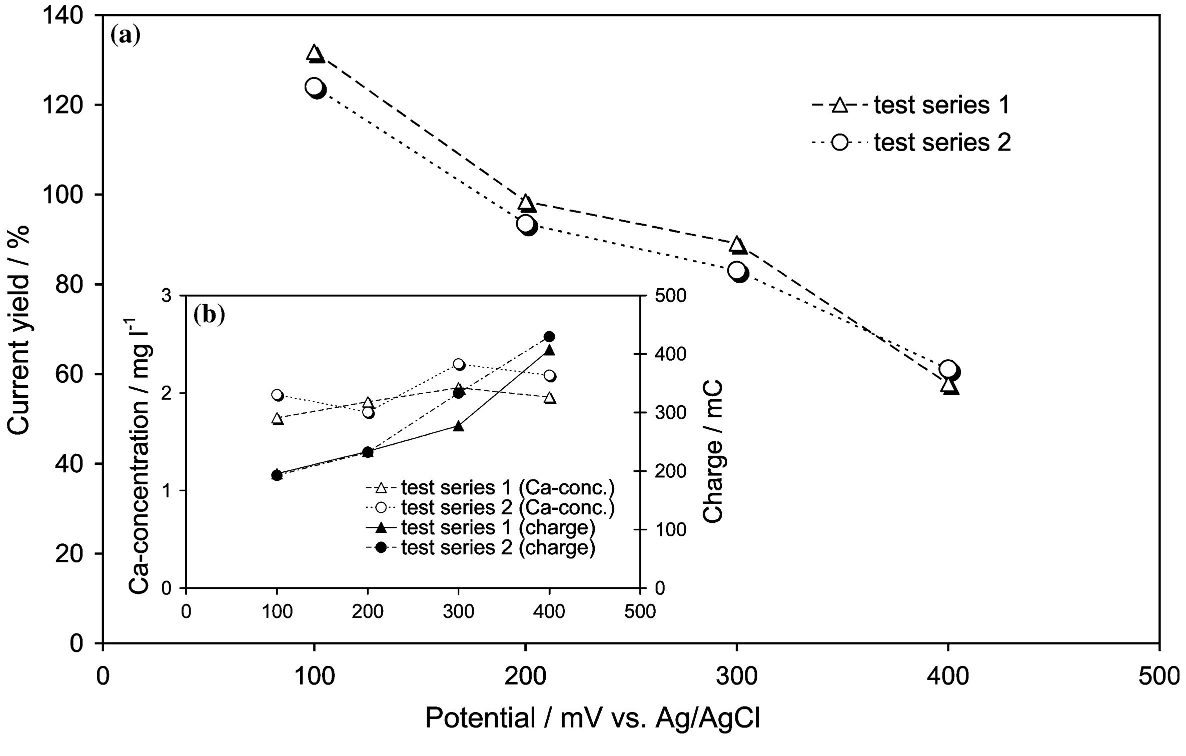

Fig. 4. Current yield (a) calculated from the concentration of exchanged Ca cations and the charge (b) in dependence on desorption potential in aerated 0.005 M KCl solution.

At a higher potential (0.4 V) the situation is different. The anodic charges and the Ca^{2+} concentration in aerated solution is 418 ± 16 mA s and 2.069 ± 0.158 mg l^{-1}, respectively. In deaerated solution these values are 514 ± 20 mA s and 2.131 ± 0.127 mg l^{-1}, respectively. The calculated current yields in aerated (60%) and in deaerated solution (50%) are lower compared to that at 0.1 V. Obviously an anodic side reaction is prominent at 0.4 V. Again the release of Ca^{2+} can be divided into an electrochemical part and an oxygen part, but only 16% of the total amount of desorbed Ca^{2+} is due to oxygen doping which diminishes at higher potentials.

Figure 5 shows the time-dependent release of Ca^{2+} from PPy(PSS) driven by several combinations of electrochemical polarization at 0.1 V (i), oxygen doping (ii) and concentration gradient (iii). Curve A shows a Ca^{2+} transient at constant open circuit potential (OCP) in deaerated solution. Curve A is the result of ion exchange (iii) and exhibits the lowest steady state Ca^{2+} concentration. In the presence of oxygen without electrochemical polarization (curve B) the OCP increases by about 70 mV and the steady state Ca^{2+} concentration is higher due to desorption caused by chemical oxidation (mechanism ii) as well as by ion-exchange (iii). Electrochemical polarization in the absence of oxygen results in a distinctly higher Ca^{2+} concentration compared to the situation discussed above (curve C). Now mechanism (i) and (iii) are responsible for the release of Ca^{2+}. The highest value of steady state Ca^{2+} concentration is established by electrochemical polarization in the presence of oxygen (curve D). In this case the release of Ca^{2+} is driven by all three mechanisms (i–iii). The additional release of Ca^{2+}, compared to curve C, is probably due to the activation of electronically isolated segments by dissolved oxygen. In all cases (curves A–D) the steady state concentration is established after a few minutes.

Ion exchange driven by the gradient of cation concentration between composite and solution (iii) is studied separately by working at OCP in deaerated solution (see curve A in Figure 5). In this experiment a PPy(PSS) composite loaded with Ca^{2+} is transferred to a 0.005 M KCl solution leading to the cation exchange process which is comparable to ion exchange of pure PSS:

$$Ca^{2+}_{PPy(PSS)} + 2K^{+}_{solution} \rightleftarrows Ca^{2+}_{solution} + 2K^{+}_{PPy(PSS)} \quad (1)$$

The question arises, does ion exchange (mechanism iii) occur parallel to electrochemical polarization of PPy(PSS) (i) and, if so, to what extent? To answer this question the following two-step experiment was made: in the first step a PPy(PSS) composite loaded with Ca^{2+} was polarized at different potentials (0.1; 0.2; 0.3; 0.4 V) for 300 s in a deaerated 0.005 M KCl solution and the Ca^{2+} concentration of this solution was determined (first regeneration). Subsequently, after a washing process in a second step the composite was polarized at 0.4 V for 300 s in a 0.005 M NaCl solution and the concentrations of K^{+} were determined (second regeneration).

The Ca^{2+} concentration found after the first regeneration $[Ca^{2+}]_{1.regeneration}$ is the result of electrochemical polarization (i) and also of ion exchange (iii). The K^{+} concentration found after the second regeneration $([K^{+}]_{2.regeneration})$ is exclusively the result of ion exchange (iii) which occurred during the first regeneration. In order to determine the amount of Ca^{2+} released by electrochemical polarization $([Ca^{2+}]_{corr})$ the Ca^{2+} concentration after the first regeneration solution $[Ca^{2+}]_{1.regeneration}$ has to be corrected according to:

$$[Ca^{2+}]_{corr} = [Ca^{2+}]_{1.regeneration} - 0.5[K^{+}]_{2.regeneration} \quad (2)$$

Figure 6 shows that with increasing potential the concentration of electrochemically released Ca ions

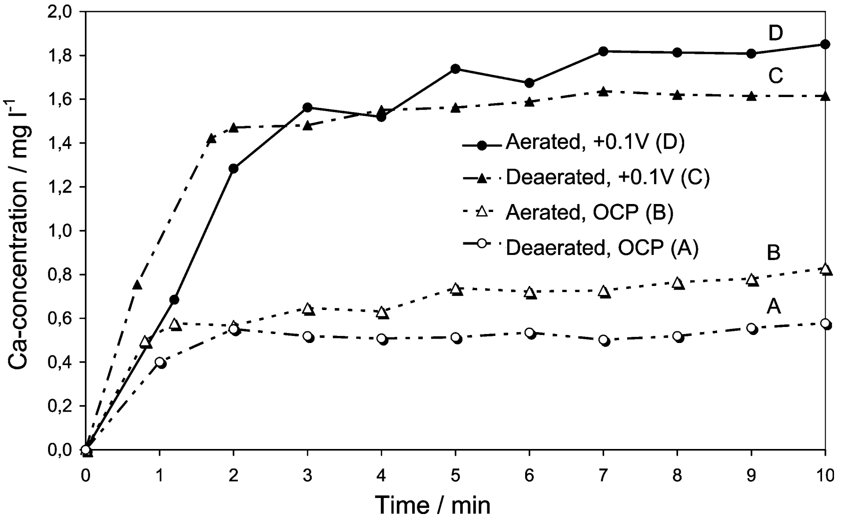

Fig. 5. Concentration of desorbed Ca cations in dependence on different desorption conditions in 0.005 M KCl solution.

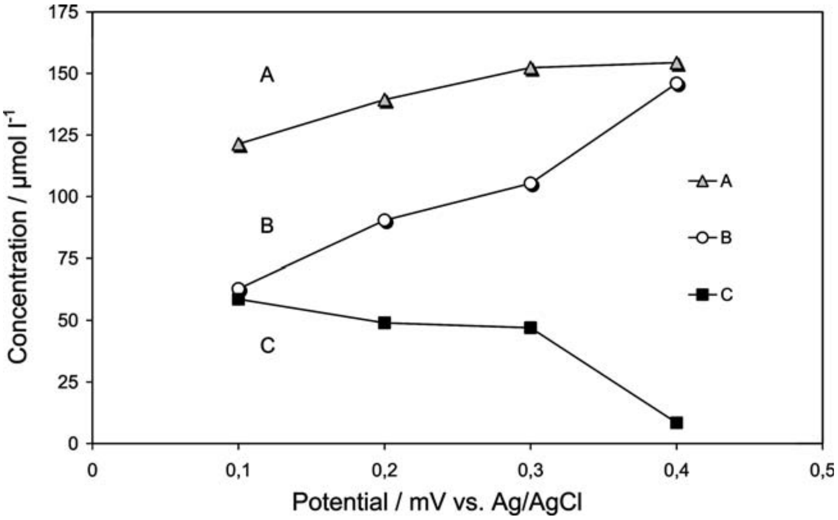

Fig. 6. Cation concentrations determined in a two-step experiment (after Ca^{2+} absorption at −0.7 V in 0.005 M $CaCl_2$): 1.regeneration 300 s in 0.005 M KCl at the given potentials, 2.regeneration 300 s in 0.005 M NaCl at 0.4 V. (A) sum of 2 $[Ca^{2+}]_{corr} + [K^+]_{2.regeneration}$; (B) electrochemically desorbed 2 $[Ca^{2+}]_{corr}$ calculated from Equation 2; (C) concentration of K^+ found at the second regeneration $[K^+]_{2.regeneration}$.

$[Ca^{2+}]_{corr}$ increases (curve B). On the other hand the concentration of K ions $[K^+]_{2.regeneration}$ decreases with increasing potential (curve C). This can be explained by assuming that the reduced segments of PPy(PSS) participate solely in the ion exchange process (Equation 1). This assumption can be proved by applying the Nernst equation.

For the electrochemical oxidation of PPy(PSS) the following reaction equation holds:

$$\left(\mathrm{Py}^0(\mathrm{SS}^-)_\alpha(\mathrm{Ca}^{2+})_{0.5\alpha}\right)_n \rightleftarrows (\mathrm{Py}^{\alpha+}(\mathrm{SS}^-)_\alpha)_n + 0.5\alpha n\mathrm{Ca}^{2+} + \alpha n e^- \quad (3)$$

with pyrrole monomer unit (Py), styrenesulfonate monomer unit (SS^-), apparent number of transferred electrons per pyrrole monomer unit α and degree of polymerization *n*.

The redox process of conducting polymers can be described by the Nernst equation [27, 28] according to (assumed activity coefficients are unity):

$$E = E_0 + \frac{\mathrm{RT}}{\alpha n\mathrm{F}} \ln\left(\frac{[\mathrm{Py}^{\alpha+}(\mathrm{SS}^-)_\alpha]^n[\mathrm{Ca}^{2+}]^{0.5\alpha n}}{\left[\mathrm{Py}^0(\mathrm{SS}^-)_\alpha(\mathrm{Ca}^{2+})_{0.5\alpha}\right]^n}\right) \quad (4)$$

Assuming that the reduced segments of PPy(PSS) are exclusively accessible to ion-exchange, the number of these segments should be proportional to $[K^+]_{2.regeneration}$:

$$\left[\mathrm{Py}^0(\mathrm{SS}^-)_\alpha(\mathrm{Ca}^{2+})_{0.5\alpha}\right]^n \leftrightarrow [\mathrm{K}^+]_{2.\mathrm{regeneration}}$$

And the number of oxidized segments as well as $[Ca^{2+}]^{0.5\alpha n}$ should be proportional to the square root of $[Ca^{2+}]_{corr}$ (Equation 2):

$$[\mathrm{Py}^{\alpha+}(\mathrm{SS}^-)_\alpha]^n \leftrightarrow [\mathrm{Ca}^{2+}]^{0.5}_{\mathrm{corr}} \leftrightarrow [\mathrm{Ca}^{2+}]^{0.5\alpha n}$$

Then Equation 4 is rewritten as:

$$E = E_0 + \frac{RT}{\alpha F} \ln \frac{[\mathrm{Ca}^{2+}]_{\mathrm{corr.}}}{[\mathrm{K}^+]_{2.\mathrm{regeneration}}} \quad (5)$$

From the slope of E vs. $\ln([Ca^{2+}]_{corr}/[K^+]_{2.regeneration})$ α was calculated as 0.27. The apparent number of transferred electrons per pyrrole monomer unit α is also the doping level, which was determined separately from elemental analysis as 0.22 (see above). This substantiates the assumption that the reduced segments of PPy(PSS) exclusively take part in the ion-exchange process (Equation 1).

A further interesting point is the sum $2[Ca^{2+}]_{corr} + [K^+]_{2.regeneration}$ as a measure of the total share of active segments in PPy(PSS) (Figure 3a and c). Active segments mean oxidized or reduced segments which are accessible to ion exchange. This sum is not constant for all polarization potentials (curve A in Figure 6). Therefore there must be some inactive PPy(PSS) which is neither accessible to electrochemical polarization nor to ion exchange (Figure 3b). The share of this part is potential-dependent, i.e. the higher the potential, the lower it is. The potential-dependent formation of inactive segments can be explained by slow structural and conformational changes [29, 30] combined with slow desorption of ions and solvent molecules during the insulating-to-conducting conversion of the composite [31]. On the other hand the inactive segments are accessible to doping by dissolved oxygen, as has been demonstrated by the higher amount of release of Ca^{2+} from polarized PPy(PSS) in aerated solutions (curve D in Figure 5) compared to deaerated ones (curve C in Figure 5).

3.3. *Selectivity of PPy(PSS)*

The selectivity of the cation exchanger PPy(PSS) is not only of theoretical interest but also of practical importance for technical applications, such as water softening or separation processes. The major task in water softening is the removal of Ca^{2+} and Mg^{2+} from solutions containing comparable amounts of Na^+ and K^+. Therefore the selectivity measurements carried out in the binary solutions of $CaCl_2/NaCl$ and $CaCl_2/MgCl_2$ provide useful information.

The equilibrium of the ion exchange process is described by the ion-exchange isotherm, which is based on the law of mass action [1]. The typical ion exchange reaction for water softening with Ca^{2+} and Na^+ in solution is

$$2 \cdot R^- - Na^+ + Ca^{2+} = (R^-)_2Ca^{2+} + 2Na^+ \tag{6}$$

which leads to the equation

$$\frac{[Ca^{2+}]^* \gamma_{Ca}{}^*}{[Na^+]^{*2} \gamma_{Na}^{*2}} = K \frac{[Ca^{2+}] \gamma_{Ca}}{[Na^+]^2 \gamma_{Na}^2} \tag{7}$$

where $[Ca^{2+}]^*$, $[Na^+]^*$ and $[Ca^{2+}]$, $[Na^+]$ are the concentrations in the solid polymer phase and in the liquid phase, respectively. In Equation 6, R^- represents the uncompensated SO_3^- groups of the PPy(PSS) composite. If the concentrations are substituted by the corresponding molar fractions X_i of the involved species (Ca^{2+}, Na^+) and the activity coefficients γ_i are constant, the "ion-exchange isotherm" is converted into:

$$\frac{X_{Ca}^*}{(1 - X_{Ca}^*)^2} = K_{Na}^{Ca} \frac{C^*}{C} \frac{X_{Ca}}{(1 - X_{Ca})^2} \tag{8}$$

The "selectivity coefficient" K_{Na}^{Ca} is the characteristic parameter of the particular exchanger resin and the ions involved in the repartition process. The molar fraction X_{Ca}^* of Ca^{2+} in the polymer is a function of the molar fraction X_{Ca} in the solution and depends on the concentration ratio of the ionic groups C^* in the polymer matrix and the salt concentration $C = [Na^+] + [Ca^{2+}]$ in the solution. At constant C^* the selectivity for Ca increases with decreasing C. In common ion exchanger resins C^* is constant, e.g. for PSS the ion exchanger capacity for Ca ions is typically 24 kg m^{-3} [1]. However, for the composite PPy(PSS) the concentration C^* is variable and depends on the degree of oxidation of PPy, which can be controlled by electrochemical polarization at different electrode potentials E (see Figures 1 and 2). As a point in case, for potentials $E \leq -0.4$ V the PPy matrix is in the reduced state and the positive charges on the PPy chains disappear almost completely. As a consequence most of the SO_3^- groups of the PSS can participate in the ion exchange process (see Figure 1). At potentials $E \geq -0.4$ V the degree of oxidation increases and the major part of the SO_3^- groups is compensated by PPy^+, leading to a decrease in the ion exchanger capacity C^* and a reduction of the selectivity.

Selectivity measurements of the PPy(PSS) composite were carried out in the reduced state of PPy. In these experiments, an equilibrium state is reached under

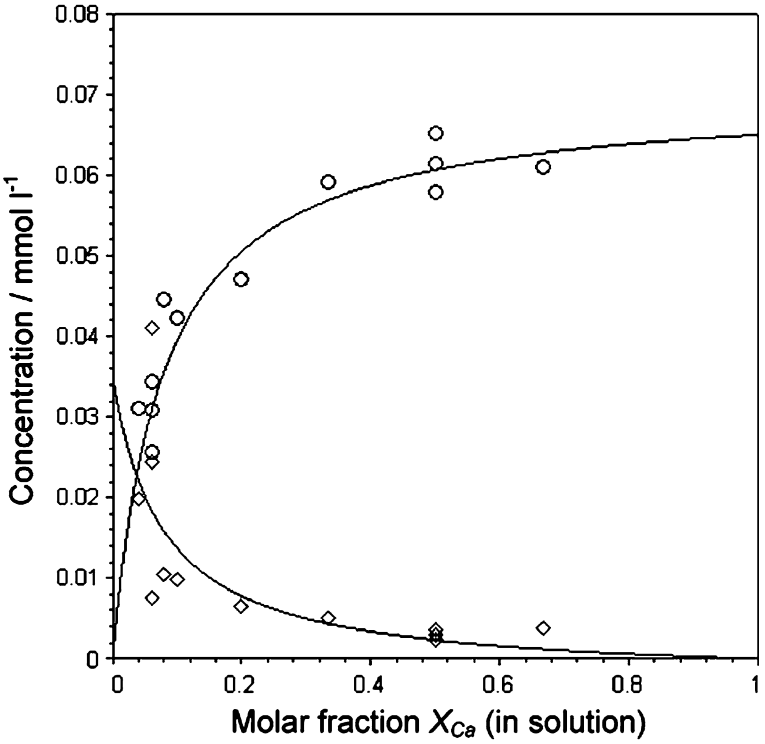

Fig. 7. System PPy(PSS)/x M $CaCl_2 + y$ M NaCl with $C = (x+y) = 0.005$ M; equilibration at $E = -0.7$ V for $t = 300$ s. Concentrations of $[Ca^{2+}]$ (○) and $[Na^+]$ (◇) were determined by AAS after anodic polarization at $E = +0.4$ V in 0.005 M KCl solution (300 s) as a function of the molar fraction $X_{Ca} = x/(x+y)$.

potentiostatic conditions at $E = -0.7$ V for 300 s in deaerated solutions with different molar ratios of Ca^{2+}/Na^{+} or Ca^{2+}/Mg^{2+}. As described in the experimental part, the amounts of the cations $[Ca^{2+}]^*$, $[Na^{+}]^*$, and $[Mg^{2+}]^*$ in the polymer were determined by solution analysis (AAS) after anodic polarization at $E = +0.4$ V in 0.005 M KCl solution, where the cations in the polymer are desorbed almost completely. For example, Figure 7 shows the increase of Ca^{2+} and decrease of Na^{+} in the regeneration solution with increasing molar fraction X_{Ca}.

From these data, the molar fractions X^*_{Ca} in the polymer were calculated and plotted vs. the molar fraction X_{Ca} in the absorption solution. The corresponding ion-exchange isotherms for the Ca/Na system are shown in Figure 8 for $C = 0.005$ M and $C = 1$ M.

As expected, the selectivity of Ca^{2+} is considerably higher in 0.005 M than in 1 M solution. The dashed line indicates absence of selectivity, which means that the molar fractions of the constituents in the polymer equal those in the solution. In addition to the experimental points, simulated curves with $K^{Ca}_{Na} = 9$ and $C^* \approx 1$ M are shown in Figure 8 (solid lines) for different concentrations. The experimental points are close to the simulated curves; however, the concentration dependence deviates slightly from the theoretical prediction. This may be due to changes in the activity coefficients because of the very high concentration differences in both experiments, namely $C = 1$ M and 0.005 M. However, the results exhibit strong selectivity for bivalent cations, which is caused by the stronger Coulombic interactions with the fixed SO_3^- anions in the polymer.

Figure 9 exhibits the ion exchange isotherm of PPy(PSS) for the Ca/Mg system in 0.005 M solution. Even for a mixture with two bivalent cations in the solution, the composite PPy(PSS) shows slightly higher selectivity for Ca^{2+}. This may be explained by the different radii of the solvated cations [32]. In this case, the ion exchange isotherm must be rewritten as follows:

$$\frac{X^*_{Ca}}{(1 - X^*_{Ca})} = K^{Ca}_{Mg} \frac{C^*}{C} \frac{X_{Ca}}{(1 - X_{Ca})} \tag{9}$$

4. Conclusion

The ion exchange properties of PPy(PSS), especially the influence of electrochemical polarization, dissolved oxygen and concentration gradients on the desorption of cations, were studied. Experiments demonstrate that each of these driving forces can induce cation desorption in the same order of magnitude. The results are interpreted by a simplified model of PPy(PSS) composed of oxidized, reduced and inactive segments.

For uni- and bivalent cations the selectivity of PPy(PSS) is comparable to that of pure PSS. Therefore PPy does not significantly influence the ion exchange properties of PSS but enables electrochemical regeneration control and the absorption and desorption of cations. Regarding the ion exchange properties, the composite PPy(PSS) is a promising candidate for an electrochemically switchable ion exchanger for water softening.

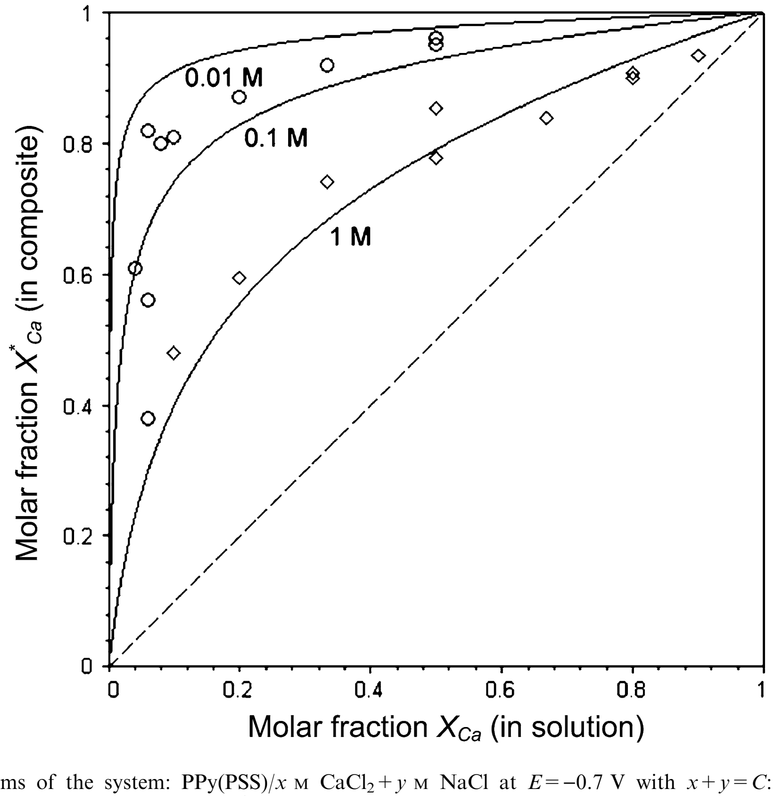

Fig. 8. Ion-exchange isotherms of the system: PPy(PSS)/x M $CaCl_2 + y$ M NaCl at $E = -0.7$ V with $x + y = C$: 1 M (◇) and 0.005 M (○); curves (——) calculated by Equation 8 with $K^{Ca}_{Na} = 9$, $C^* = 1$ M; and $C = 1$, 0.1, 0.01 M.

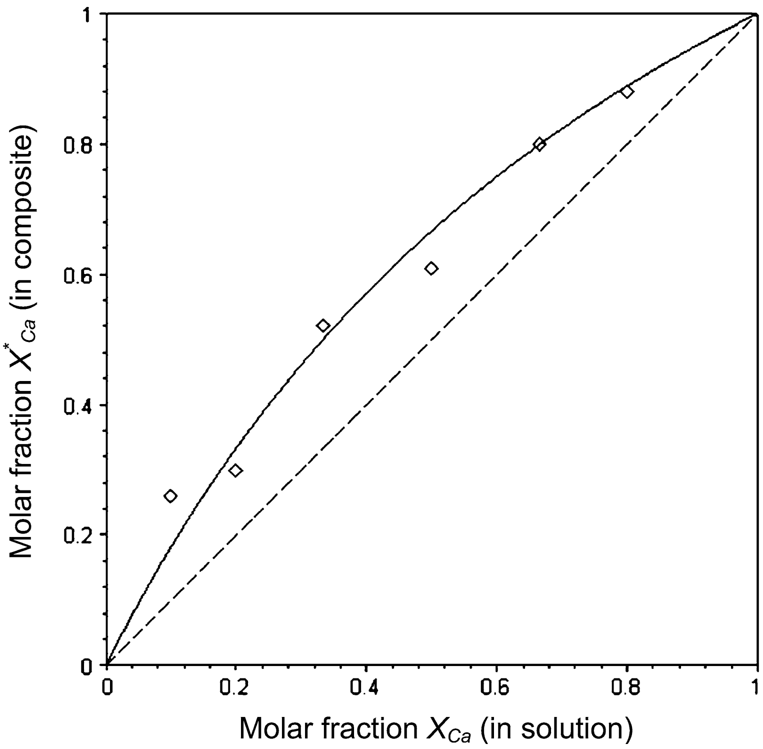

Fig. 9. Ion-exchange isotherm of the system: PPy(PSS)/x M $CaCl_2 + y$ M $MgCl_2$ at $E = -0.7$ V and $(x+y) = 0.005$ M (◇); curves (——) calculated by Equation 9 with $K_{Mg}^{Ca} = 0.01$, $C^* = 1$ M and $C = 0.005$ M.

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