DOI: 10.1002/masy.201050104

Ion-selective Membranes Prepared Upon Layer-by-Layer Assembly of Azamacrocycles and Polyelectrolytes

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Summary: Recent studies on ion transport across multilayered membranes of azamacrocycles and polyelectrolytes are reviewed. Membranes were built up on porous PAN/PET supports using electrostatic layer-by-layer assembly. Two types of separation membranes were prepared, type I consisting of protonated hexaazacyclooctadecane and polyvinylsulfate, and type II of hexaazacyclo-octadecane hexaacetic acid and protonated polyvinylamine. Ion transport was studied under dialysis, nanofiltration and reverse osmosis conditions. Type I membranes were suitable for efficient separation of mono- and divalent anions, whereas type II membranes were suited for separation of mono- from di- and trivalent cations.

Keywords: layer-by-layer assembly; macrocyclic compounds; polyelectrolytes; separation membranes

Introduction

In previous studies[1,2] it was demonstrated that highly efficient ultrathin separation membranes can be prepared upon alternating electrostatic layer-by-layer (lbl) adsorption of cationic and anionic polyelectrolytes[3] on porous supporting membranes. The self-assembled membranes are suitable for alcohol-water separation under pervaporation conditions, ion separation, water softening and desalination under nanofiltration and reverse osmosis conditions.[1,2] In a continuation of our studies we tried to improve the transport selectivity of the membranes by replacing one of the two polyelectrolytes by a macrocyclic compound. Macrocycles such as calix[n]arenes, polyazacrown ethers and cyclodextrins are important building blocks in supramolecular chemistry and able to specifically interact with certain metal ions and molecules. Recent studies have shown that membranes containing p-sulfonato-calixarenes are able to complex distinct metal ions.[4] They show enhanced selectivity in cation transport and can be used for enrichment of rare earth metal ions,[5] for example. First studies on membranes containing polyazamacrocycles complexed with copper (II) ions indicate a high selectivity in anion transport.[6,7] Purpose of the present work is to review recent studies on ion transport across lbl-membranes consisting of polyazamacrocycles and polyelectrolytes. Membranes of protonated 1,4,7,10,13,16-hexaazacyclooctadecane (hexacyclen, **aza6**) and poly-vinylsulfate (PVS) (type I), and protonated polyvinylamine (PVA) and 1,4,7,10,13,16-hexaazacyclooctadecane hexaacetic acid (hexacyclen hexaacetic acid, **az6ac**) (type II) were studied. Figure 1 shows the polyelectrolytes and macrocycles used in this work.

Our study demonstrates that the separation characteristics of the membranes are strongly influenced by the macrocycles. Cu-complexed aza6 is able to improve the selectivity in anion transport, while az6ac provides a high selectivity in cation transport.

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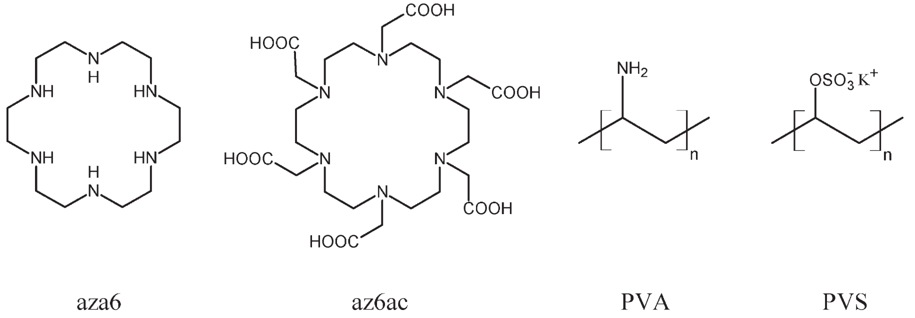


Figure 1.
Schematic presentation of macrocycles, polycations and polyanions used for layer-by-layer assembly.

Multilayer Assembly and Membrane Preparation

The separating layer was built up on a porous polyacrylonitrile/ polyethylene terephtalate (PAN/PET) supporting membrane using electrostatic layer-by-layer assembly. The substrate with pore size of 20–200 nm was activated with oxygen plasma before use. The preparation of type II separating membranes is schematically shown in Figure 2.

In the first step the activated substrate is dipped into the solution of PVA resulting in adsorption of the positively charged compound and reversion of the surface charge. After careful washing with MilliQ-water the substrate is dipped into the solution of az6ac, again resulting in adsorption and reversion of the surface charge. Depending on the number of adsorbed layers the thickness of the separating membrane can be precisely controlled in the nanometer range. Further details on the preparation conditions are described in the literature.[6,8]

The lbl-assembly of aza6/PSS was confirmed by UV measurements on a quartz substrate (Figure 3a). Since PVA and az6ac do not contain UV-absorbing chromophors, the lbl-assembly of the compounds was confirmed by ATR-FTIR measurements on a ZnSe crystal (Figure 3b). A linear increase of the adsorption with number of dipping cycles is shown in the insets of Figure 3.

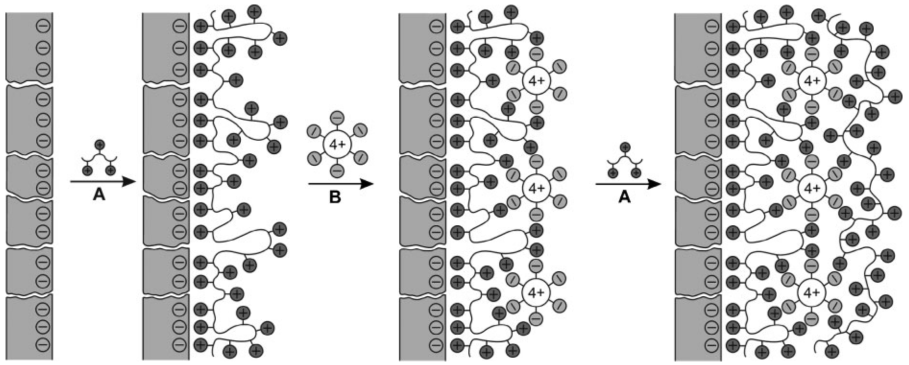


Figure 2.
Scheme of membrane preparation upon alternating layer-by-layer assembly of PVA and az6ac. Az6ac is four-fold protonated at pH 6 of the dipping solution. The actual orientation of the macrocycles is unknown.

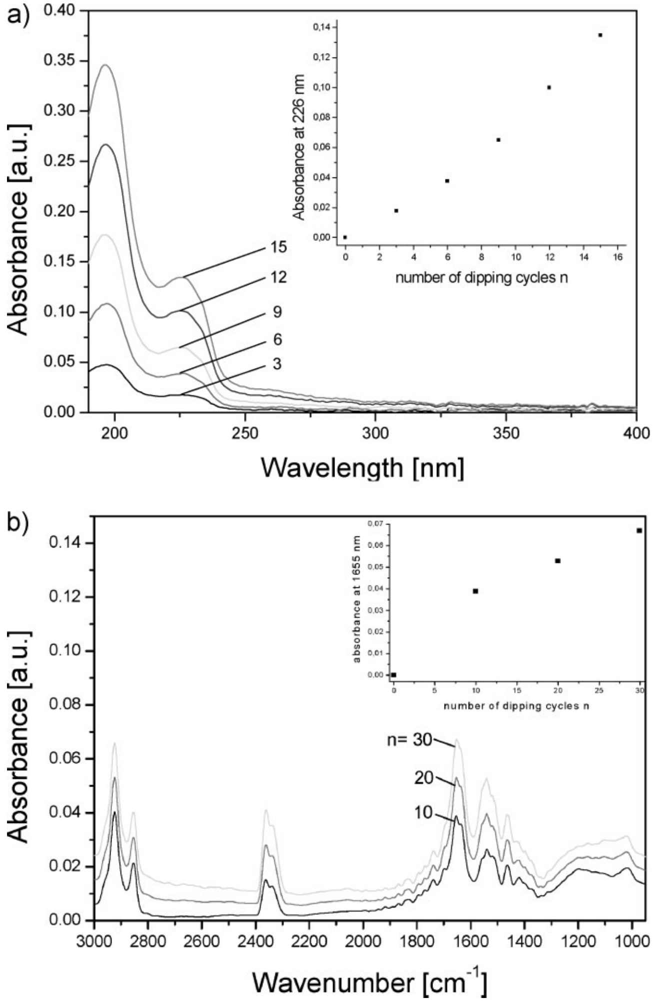


Figure 3.
Layer-by-layer assembly of **aza6**/PSS on a pretreated quartz substrate (adapted with permission from ref. [6]. Copyright 2007 American Chemical Soc.) (a) and of PVA/**az6ac** on a ZnSe crystal (b).

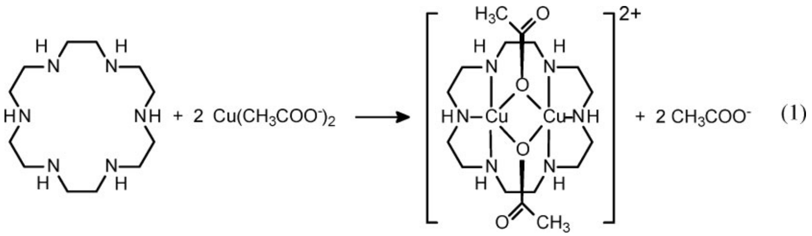
Complexation of aza6/PVS Multilayers with Copper(II) Acetate

The protonation of aza6 is highly pH-dependent. At pH values above 10.2, aza6 is almost completely non-protonated, whereas at pH below 1.0 it is completely (6-fold) protonated, the protonation equilibria.[9] being

$$\mathrm{aza6} \xrightleftharpoons[\mathrm{p}K_a\ 10{,}2]{H^+} \mathrm{aza6\cdot H^+} \xrightleftharpoons[\mathrm{p}K_a\ 9{,}2]{H^+} \mathrm{aza6\cdot 2H^+} \xrightleftharpoons[\mathrm{p}K_a\ 8{,}7]{H^+} \mathrm{aza6\cdot 3H^+} \xrightleftharpoons[\mathrm{p}K_a\ 4{,}1]{H^+} \mathrm{aza6\cdot 4H^+} \xrightleftharpoons[\mathrm{p}K_a\ 2{,}0]{H^+} \mathrm{aza6\cdot 5H^+} \xrightleftharpoons[\mathrm{p}K_a\ 1{,}0]{H^+} \mathrm{aza6\cdot 6H^+}$$

Previous studies[6,7] have demonstrated that the best conditions for multilayer built-up are at pH 6, i.e., where aza6 is mainly present in the triply protonated state. Therefore membranes were always built up from dipping solutions of pH 6.

Unfortunately, aza6/PVS membranes are highly permeable for electrolyte solutions, but the selectivity in ion transport is poor. In order to improve the selectivity, the membranes were treated with a 0.1 M aqueous copper acetate solution resulting in strongly enhanced selectivity. The reaction of aza6 with copper acetate proceeds under formation of a binuclear complex as indicated in eq. 1:[10]



The complexation was confirmed by UV measurements on a quartz substrate and ATR-FTIR measurements on a ZnSe crystal. UV measurements indicate the formation of a copper complex with absorption maximum at 650 nm, also visible to the eye by the blue coloration of the film. ATR-FTIR measurements indicate an additional absorption band at 1540 cm^{-1} originating from the carboxylate stretching mode of the acetate counterion (Figure 4).

Figure 5 shows a model of the complexation of aza6 with copper acetate in aza6/PVS membranes. Treatment with copper acetate proceeds under complex formation with triply protonated aza6. The protons are released from the macrocycle and the positively charged, divalent complex is formed. The surplus sulphate groups of PVS continue to be fixed in the membrane and induce a negative surplus charge, which is responsible for a strong rejection of divalent anions as demonstrated in the following chapter.

Ion Permeation

First studies on ion permeation across aza6/PVS membranes were carried out under

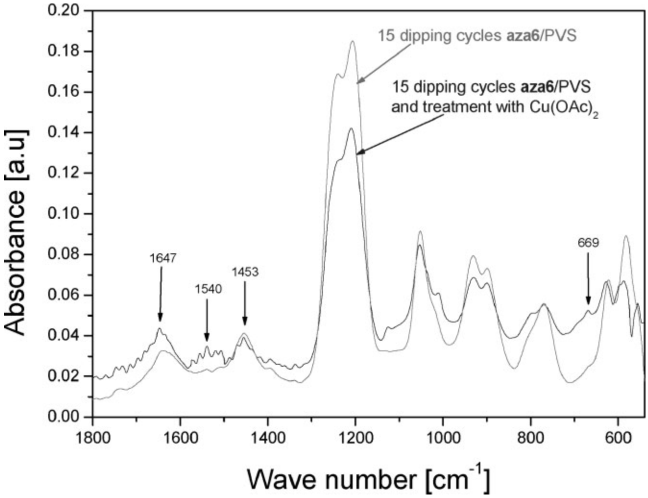
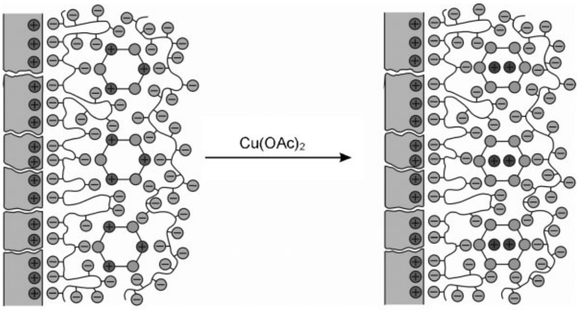


Figure 4.
ATR-FTIR spectrum of aza6/PVS multilayers built up on a ZnSe crystal after treatment with 0.1 M aqueous copper acetate solution (adapted with permission from ref. [6]. Copyright 2007 American Chemical Soc.).



$$[\mathbf{aza6}\cdot 3\,H]^{3+}\cdot 3\,PVS^{-} + 2\,Cu(OAc)_2 \rightarrow [\mathbf{aza6}\cdot 2\,CuOAc]^{2+}\cdot 2\,PVS^{-} + 2\,HOAc + H^{+} + PVS^{-}$$

Figure 5.
Scheme and chemical equation of complex formation between triply protonated aza6 and copper acetate in aza6/PVS membrane (from ref. [6]).

dialysis conditions. For the permeation experiments a U-shaped two-chamber apparatus was used (Figure 6, left). Details are described in the literature.[6]

Permeation rates P_R were determined by measuring the increase in conductivity per unit time, $(\Delta\Lambda/\Delta t)$, in the permeate (Figure 6, right) and calculating P_R from eq. 2:

$$P_R = (\Delta\Lambda/\Delta t)(V_o - \Delta V)/\Lambda_m Ac \qquad (2)$$

with $(V_0–\Delta V)$ being the volume of the permeate side after correction of the osmotic flow. Λ_m is the molar conductivity, and A and c are the membrane area and the feed concentration, respectively. Separation factors α represent the ratio of P_R values of the corresponding salt solutions.

Ion Permeation Across aza6/PVS Membranes

In Figure 7 the permeation rates of various solutions of sodium salts and metal chlorides through aza6/PVS membranes (60 layer pairs) are plotted. It is apparent that the permeation rates of divalent anions are much lower than those for the monovalent anions (Figure 7, left). This is due to the strong electrostatic repulsion of the anions by the negative surplus charge of the membrane already discussed above.

Since the permeation rate of sodium chloride is quite high ($8.54^{*}10^{-6}$ cm s^{-1})

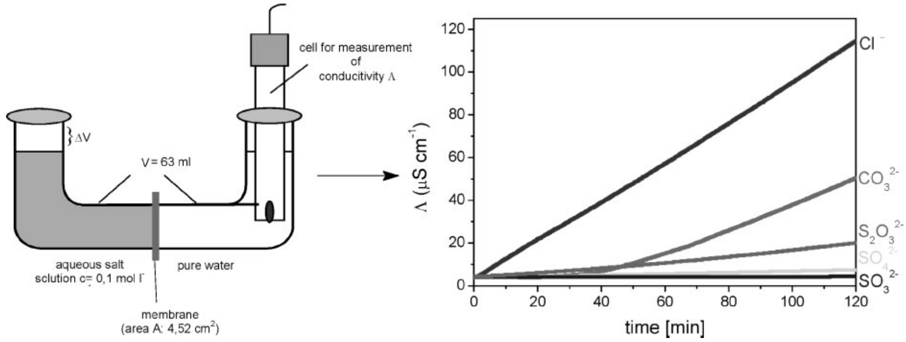


Figure 6.
Apparatus for measuring ion permeation (left) and plot of conductivity against time for determination of $(\Delta\Lambda/\Delta t)$ (right).

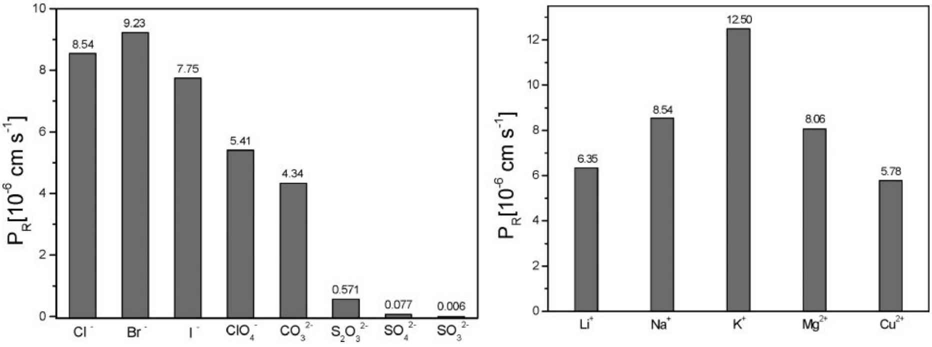
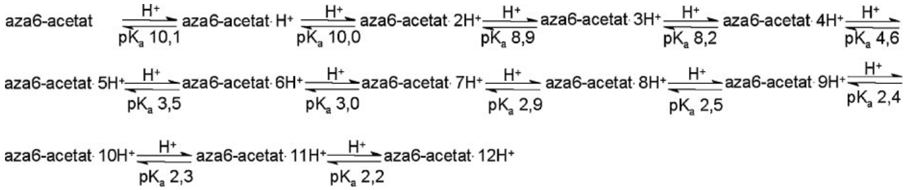


Figure 7.
Permeation rates of 0.1 M aqueous solutions of various sodium salts (left) and metal chlorides (right) across aza6/PVS membranes made from dipping solutions of pH 6 and 60 dipping cycles (adapted with permission from ref. [6]. Copyright 2007 American Chemical Soc.).

and the P_R values of sodium sulfate and sulfite are very low (0.077^*10^{-6} cm s^{-1} and 0.0006^*10^{-6} cm s^{-1}, respectively), high separation factors α (Cl^-/SO_4^{2-}) of 110 and α (Cl^-/SO_3^{2-}) of 1420 can be calculated. Electrostatic repulsive forces on the cations are much weaker than on the anions, and no real discrimination is found for the transport of mono- and divalent cations although the charge density is very different (Figure 7, right).

Ion permeation across PVA/az6ac membranes

Due to the pH-dependent protonation of az6ac, the formation of PVA/ac6ac membranes is highly pH-dependent. Because of the six COOH groups and the six nitrogen atoms, twelve protonation states are possible:[11]



In order to study the effect of pH on ion permeation, membranes were prepared at four different pH-values pH the dipping solution, and ion permeation across the membranes was studied. In Figure 8, it can be seen that membranes prepared at pH 2 or 8 exhibit a high flux for all cations and the separation factor is poor. The best selectivity is found at pH 6, where α (Na^+/Mg^{2+}) is 28.

At pH 6, az6ac is four-fold protonated at the nitrogen atoms, the COOH groups being fully ionized. In the multilayered film, it can be assumed that the carboxylate groups interact with the positively charged amino groups of protonated PVA, while the protons within the macrocycles create a positive surplus charge, resulting in electrostatic repulsion of cations. A schematic representation of the four-fold protonated structure of az6ac and the structure of a PVA/az6ac membrane at pH 6 is shown in Figure 9.

Because of the positive surplus charge, the PVA/az6ac membrane exhibits a high permeation rate for monovalent sodium ions (NaCl: 8.5^*10^{-6} cm s^{-1}), and low permeation rates for $CaCl_2$: 0.6^*10^{-6} cm s^{-1}, and $MgCl_2$: 0.3^*10^{-6} cm s^{-1} (Figure 10, left). Consequenly, the separation factors α (Na^+/Ca^{2+}) = 14 and α (Na^+/Mg^{2+}) = 28 are high. Electrostatic repulsive forces on

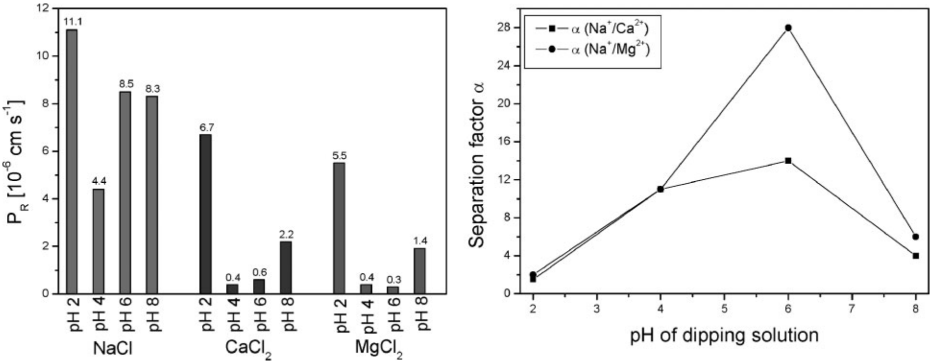


Figure 8.
Permeation rates of 0.1 M aqueous metal chloride solutions across PVA/az6ac membranes prepared at different pH of the dipping solutions (left), and plot of the separations factors α as a function of the pH of the dipping solutions (right).

the anions are generally poor and therefore the separation factors α (Cl^-/SO_4^{2-}) and α (Cl^-/SO_3^{2-}) are also poor, i.e., 2.9 and 5, respectively (Figure 10, right).

Nanofiltration and Reverse Osmosis Measurements

The ion separation was also studied under nanofiltration (NF) and reverse osmosis (RO) conditions. NF and RO are pressure-driven processes. The pressure applied across the membrane is 5–30 bar for NF and up to 100 bar for RO. For all experiments a home made apparatus working under dead-end conditions was used. Further details are described in the literature.[12]

After measuring the volume V of the permeate per unit time Δt, the total flux J through the membrane was calculated by using eq. (3):

$$J = V/A\,\Delta t\,[\mathrm{lm^{-2}h^{-1}}] \qquad (3)$$

A represents the membrane area ($36.8\,cm^2$). The salt rejection R was calculated using eq. (4):

$$R = (1 - c_p/c_f) \times 100[\%] \qquad (4)$$

with c_p and c_f being the salt concentration in feed and permeate. c_p and c_f were determined by using HPLC.

Nanofiltration Through aza6/PVS Membranes

The pressure-driven transport of a mixed aqueous electrolyte solution across aza6/PVS membranes (20 and 60 bilayers) treated with copper(II) acetate was studied. The feed solution contained sodium chloride and sodium sulfate in 1:1 molar ratio

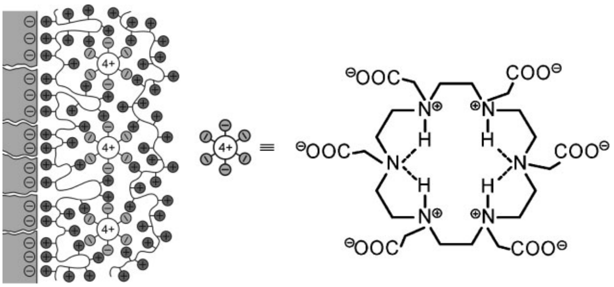


Figure 9.
Scheme of the structures of az6ac and the PVA/az6ac membrane prepared at pH 6.

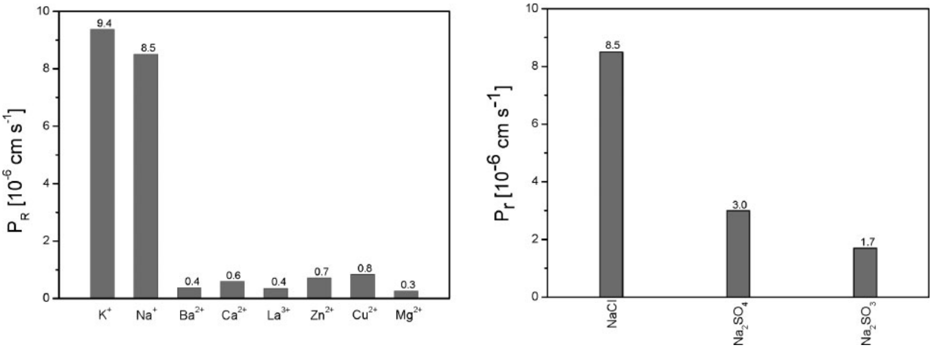


Figure 10.

Permeation rates of 0.1 M aqueous solutions of various metal chlorides (left) and sodium salts (right) across PVA/az6ac membranes prepared from dipping solutions of pH 6 containing 0.5 M sodium chloride.

(conc: 10 mM each) The total flux increased with the applied pressure and decreased strongly with the number of layer pairs deposited. For 20 layer pairs and 14 bar, the total flux was 17.61 $\text{l m}^{-2}\,\text{h}^{-1}$, and for 60 layer pairs and 25 bar, the flux was 0.85 $\text{l m}^{-2}\,\text{h}^{-1}$. Ion rejection was best for membranes with 60 layer pairs. The applied pressure was 15 bar (Figure 11).

At this pressure, rejections of sulfate and chloride ions were 98.6 and 56.5%, respectively. The selectivity $\text{Cl}^-/\text{SO}_4^{2-}$ was 31.07. At higher pressure, rejection decreased. Since the feed solution was constantly stirred at 700 rpm, the concentration polarization cannot be strong. We believe that the decrease mainly originates from a structural change of the separation layer induced by the higher applied pressure.

Reverse Osmosis Through PVA/az6ac Membranes

The pressure driven transport of aqueous sodium and calcium chloride (0.01 M) across PVA/az6ac membrane (60 bilayers) was studied as a function of the applied pressure. Figure 12 shows that the salt rejection is optimum at the highest applied pressure of 40 bar. The rejections of calcium chloride and sodium chloride are 94 and

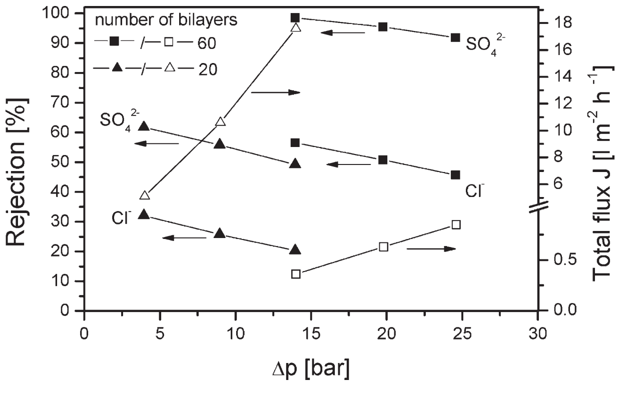


Figure 11.

Plot of rejection R (closed symbols) and total flux (open symbols) of a 10 mM aqueous solution of NaCl/Na_2SO_4 against the applied pressure. Sample: aza6/PVS membrane (60 layer pairs) treated with copper acetate (adapted from ref. [12]).

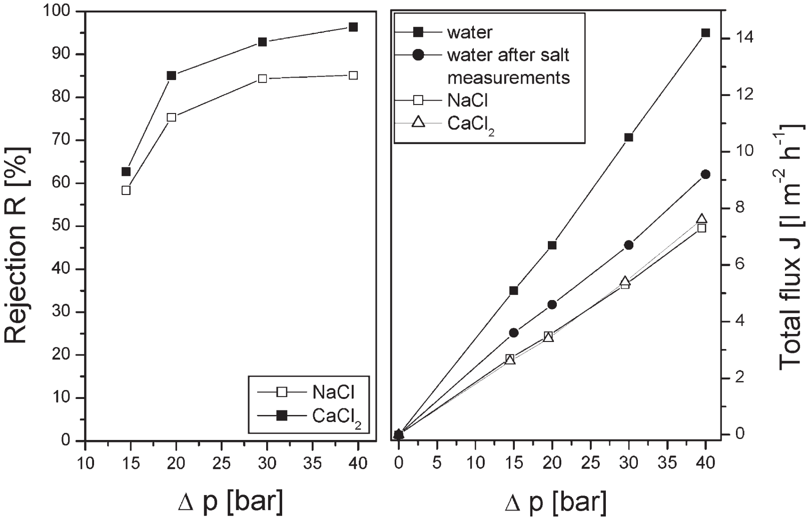


Figure 12.

Rejection R and total flux of 0.01 M aqueous solutions of NaCl and $CaCl_2$ as a function of the applied pressure. Sample: PVA/az6ac membrane, 60 dipping cycles, pH 6.

85%, respectively. The total flux increases linearly with Δp, the water flux reaching a value of $14.3 l m^{-2} h^{-1}$ at 40 bar.

Summary and Conclusions

Our studies show that aza6/PVS and PVA/az6ac membranes can be successfully built up on a supporting membrane using electrostatic layer-by-layer assembly. Protonation of aza6 and az6ac is strongly dependent on the pH of the dipping solutions, and therefore the membrane formation is also pH-dependent. Best conditions for the membrane built-up are at pH 6.

Aza6 is able to form stable complexes with copper acetate, which strongly enhances the selectivity of the membrane. The reason is that negative charges are created, which cause an efficient Donnan-rejection of divalent anions, while divalent cations can pass the membrane. Under nanofiltration conditions, high salt rejections up to 98.6% for sodium sulfate, and 57% for sodium chloride can be reached.

PVA/az6ac membranes exhibit a cationic excess charge resulting in preferential rejection of divalent cations. Under dialysis conditions, high separation factors with α (Na^+/Ca^{2+}) being 14 and α (Na^+/Mg^{2+}) being 28 were found, while under reverse osmosis conditions high salt rejections up to 96.4% for calcium chloride, and 85% for sodium chloride were reached.

Our study shows that the layer-by-layer assembly of membranes containing aza macrocycles can be used in order to modify and improve separation characteristics of the membranes. High selectivities in anion transport could be reached, which were not reported before from polyelectrolyte multilayer membranes.

Acknowledgements: The authors are grateful to Dr. A. Hübner (Sulzer Chemtech, Neuenkirchen) for providing the PAN/PET supporting membranes and to Drs. H. Ellinghorst and Ch. Dölle (IFAM, Bremen) for plasma treatment. The Deutsche Forschungsgesellschaft (project TI219/7-3) is thanked for financial support.

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