

Tailor-made membranes for alcohol/water pervaporation and ion separation prepared upon layer-by-layer adsorption of polyelectrolytes

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ABSTRACT: The paper is concerned with separating membranes prepared upon layer-by-layer adsorption of cationic and anionic polyelectrolytes on a porous substructure. The use of the resulting composite membranes for alcohol/water separation under pervaporation conditions, and for the separation of mono- and divalent ions is described. It is demonstrated that a suitable choice of the polyelectrolytes and the optimisation of the preparation conditions allow to tailor membranes with excellent separation capability.

Introduction

Useful membranes are characterised by a high flux and a high selectivity. Either properties can be combined by preparation of so-called composite membranes consisting of a porous supporting membrane coated with a thin, homogeneous, pore-free separating layer^{1,2)}. The separating layer is usually prepared by casting from solution. Likewise, the separating layer can be prepared by alternating layer-by-layer adsorption of cationic and anionic polyelectrolytes³⁾ on porous or pore-free supporting membranes⁴⁻⁶⁾. The method is schematically represented in Fig. 1. A porous substructure previously hydrophilised in O₂-plasma is dipped into a solution of a cationic polyelectrolyte, so that a thin layer of this compound is adsorbed and the surface charge is reverted. Subsequent dipping of the substrate into a solution of an anionic polyelectrolyte again leads to adsorption of a thin layer, and the surface charge is rendered negative again. Multiple repetition of the adsorption steps leads to a polyelectrolyte multilayer film, which has several advantages over separating layers cast from solution: Each adsorption step adds about 0.5 nm to the total thickness of the separating membrane⁷⁾, which allows to prepare ultrathin, homogeneous coatings of precisely controlled thickness. Moreover, a wide variety of polyionic compounds³⁾ can be adsorbed, which allow to tailor appropriate membranes for various separation problems. First experiments on the separation of gases⁴⁻⁶⁾, ions^{8,9)}

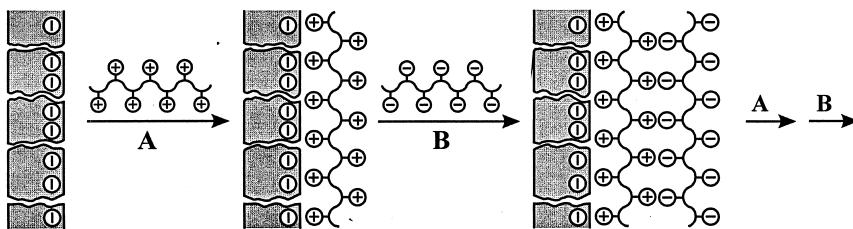


Fig. 1: Scheme of layer-by-layer adsorption of polyelectrolytes on plasma-treated porous supporting membrane. Multiple repetition of steps A and B leads to the ultrathin separating layer.

and liquid mixtures^{6,9-13)} have already been reported. Purpose of the present contribution is to demonstrate that upon a careful choice of the polyelectrolytes and an optimisation of the processing conditions polyelectrolyte multilayer membranes can be tailored, which are especially useful for distinct separation problems. This is demonstrated for the alcohol/water separation under pervaporation¹⁴⁾ conditions, and for the separation of mono- and divalent ions in aqueous solution. The separation behaviour and the influence of the polyelectrolyte structure and the processing parameters on flux and separation will be described.

Pervaporation

Pervaporation¹⁴⁾ of the alcohol/water mixtures was carried out using the apparatus schematically represented in Fig. 2. The alcohol/water mixture ('feed solution') of constant temperature ($T = 58,5\text{ }^{\circ}\text{C}$) was circulated from a 2 l reservoir to the pervaporation cell at a flow rate of 250 ml/min. The cell consists of a feed half cell and a permeate half cell with the membrane mounted in between. The permeate half cell was evacuated to a pressure $\leq 0.2\text{ mbar}$. The permeate was collected in the first condenser cooled with liquid nitrogen. After pervaporation for 2 to 3 hours, the collected mass was weighed, and the flux was calculated from the mass/time data. The water content in the permeate was analysed using gas chromatography or refractive index measurements.

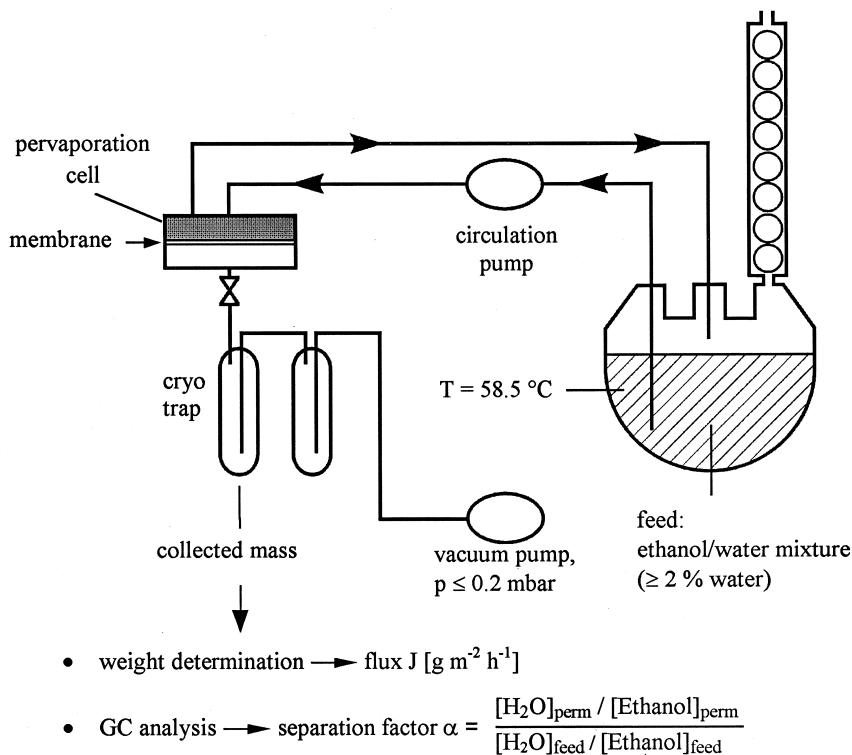


Fig. 2: Schematic diagram of the pervaporation apparatus.

In Fig. 3, flux and water content of the permeate are plotted as a function of the number of adsorbed layer pairs of polyallylamine/polystyrenesulfonate (PAH/PSS)⁹. Three main results were found: Firstly, the water content in the permeate was always higher than in the feed solution, which only contained 6,2 % (w/w). This indicates preferential transport of water across the membrane. Secondly, an increase of the membrane thickness led to a decrease of the flux and an increase of the water content in the permeate. Thirdly, annealing of the membrane prior to pervaporation led to a decrease of the flux and an improvement of the separation capability. Similar effects are known from other membranes and were discussed already previously¹⁵). However, even after annealing the water content in the permeate was not very high and did not exceed 70 %, the separation

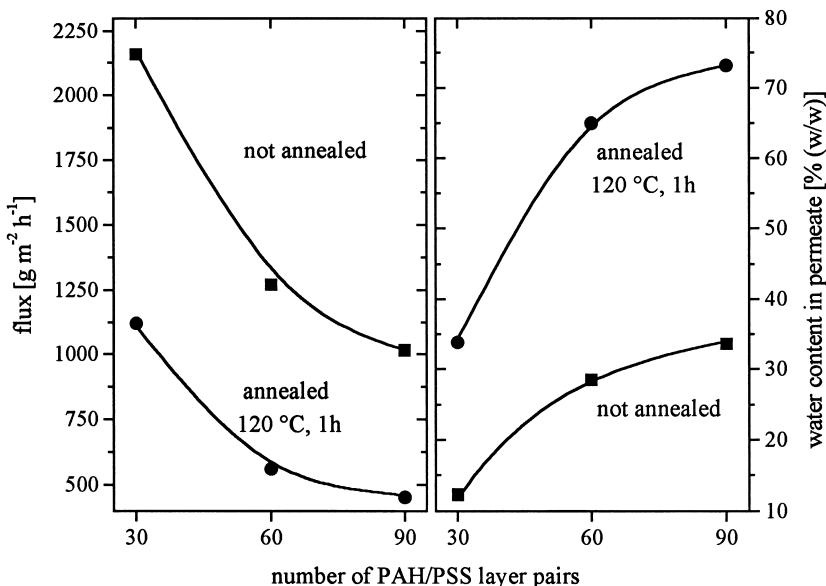


Fig. 3: Effect of the number of adsorbed layer pairs of PAH/PSS on flux and water content in the permeate for samples with and without thermal treatment at 120 °C for 1h. Feed solution: Ethanol/water mixture with 6.2 % (w/w) water⁹.

factor α (for definition of α see Fig. 2) was not higher than 70. Obviously, the water-enrichment of the PAH/PSS membrane was only poor.

We therefore tried to improve the separation capability by varying the polyelectrolyte structure and by optimising the processing parameters. Let us first concentrate on the effect of the polyelectrolyte structure. In Fig. 4, a very idealised model of the polyelectrolyte multilayer membrane is shown. According to this model, the membrane exhibits a physical network structure, the ion pairs representing the cross-linking units. From this model one can derive that cross-linking density and mesh size are controlled by the charge density ρ_c of the polyelectrolyte complex. ρ_c can be expressed as the number ratio of ion pairs (= 1) and carbon atoms per repeat unit of the polyelectrolyte complex.

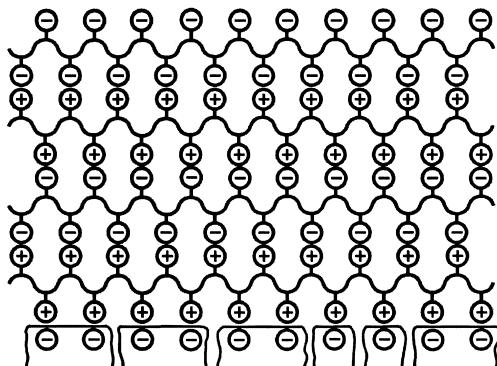


Fig. 4: Idealised structure of the polyelectrolyte complex membrane with the polyelectrolytes being completely ionised.

In Fig. 5, flux and separation behaviour of various polyelectrolyte multilayer membranes are plotted versus the ρ_c parameter. The flux was found to be inversely proportional to ρ_c . The water content in the permeate increased with ρ_c . Obviously a high separation is obtained at the easiest, if the charge density of the network is high. The clarity of this correlation is surprising, especially because in the definition of ρ_c any contribution from specific structural elements such as the flexibility of the main chain and the side groups, presence of aromatic or aliphatic units, and different polar groups in the polyelectrolytes has been neglected. The origin must be that at a high ρ_c value of the polyelectrolytes only small, highly polar meshes are formed, which are well permeable for the highly polar water molecules, but less permeable for the ethanol molecules because of their lower hydrophilicity.

Besides the chemical structure of the polyelectrolyte, the degree of ionisation of the polar groups is another parameter affecting the charge density of the network. The degree of ionisation is determined by the pH of the polyelectrolyte solution used for membrane preparation. For primary amino groups, for example, a complete protonation is only observed at low pH values. At moderate pH, only partial protonation occurs so that considerably more polyelectrolyte material has to be adsorbed to neutralise the surface charges of the membrane. As a consequence, the thickness of the polyelectrolyte multi-

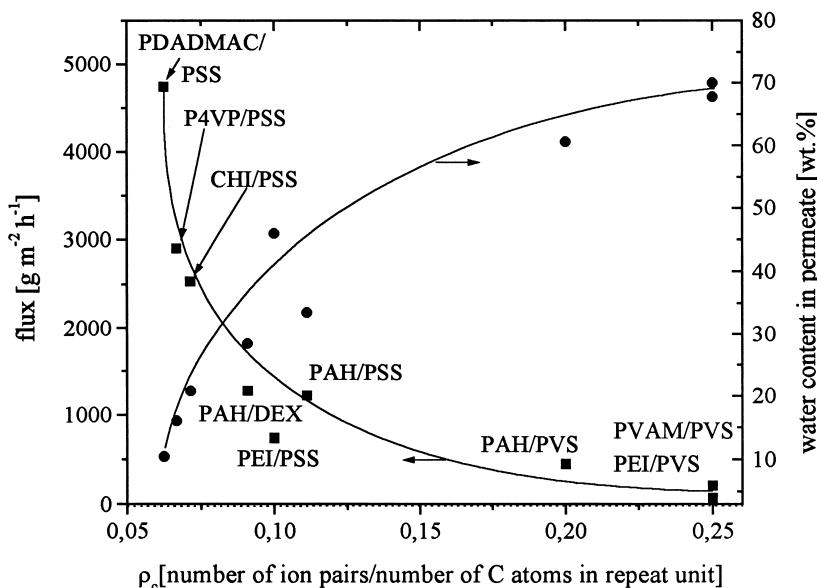


Fig. 5: Dependence of flux and water content in permeate on the charge density ρ_c of the polyelectrolyte complex. Feed solution: 6.2 % (w/w) water; separating membranes always consist of 60 layer pairs of polyelectrolyte complex¹². PAH: poly(allylamine); P4VP: poly(4-vinylpyridine); CHI: chitosan; PVAM: poly(vinylamine); PDADMAC: poly(diallyldimethylammonium bromide); PEI: branched poly(ethyleneimine); PSS: poly(styrenesulfonate); DEX: dextrane; PVS: poly(vinylsulfate).

layer is increased^{7,16}, while the charge density is decreased. In Tab. 1, flux and water content in the permeate are listed for PAH/PSS membranes prepared at different pH values. As shown in Tab. 1, a maximum water content in the permeate and a minimum in the flux occurs at pH 2,1. At that pH, most of the polar groups of PAH and PSS are present in an ionised state so that upon the salt formation a dense network structure is formed. At higher pH, the amino groups are increasingly deprotonated and the charge density of the membrane is decreased. As a consequence, the flux is increased, and the separation gets worse. As recently shown, the most suitable pH for preparation of a dense network exhibiting maximum separation corresponds with the mean of the pK_a values of the two oppositely charged polyelectrolytes¹⁴.

Tab.1: Flux and water content in the permeate for PAH/PSS membranes (thickness: 60 layer pairs) prepared from polyelectrolyte solutions of different pH. Feed solution: 6.2% water (w/w).

pH	H ⁺ -conc. [mol l ⁻¹]	Flux [g m ⁻² h ⁻¹]	Water content in permeate [%]
2.44	0.00362	3860	13.0
2.10	0.00794	822	38.2
1.79	0.0162	1270	28.5

Our study indicates that the ethanol/water separation can be substantially improved, if polyelectrolytes of high charge density are used and if the separating membrane is processed at an optimum pH value of the polyelectrolyte solution. In fact, the plots of Fig. 6a and b indicate that the separation capability of poly(vinylamine)/poly(vinylsulfate) (PVAM/PVS) and poly(ethyleneimine)/PVS (PEI/PVS) separating membranes is superior to the previously described PAH/PSS membrane¹⁰). The PVAM/PVS and PEI/PVS membranes are considerably more stable than the PAH/PSS membrane, which is already decomposed at a water concentration in the feed solution above 20 %. The PVAM/PVS membrane is able to enrich water at any composition of the feed solution. For example, at 20 % water in the feed, a separation factor of 700 is reached, while the flux is about 500 g m⁻² h⁻¹, a fairly good value. At higher water content in the feed, still higher flux values are found. A similar behaviour is found for the PEI/PVS membrane except that this membrane is only suited for ethanol/water separation, if the water content in the feed is lower than 50 %.

In Fig. 7a and b, pervaporation of various alcohol/water mixtures through the PVAM/-PVS membrane is characterised. It is shown that mixtures of 1-propanol/water or 2-propanol/water are more efficiently separated than the ethanol/water mixtures, because the transport of the more hydrophobic propanol is less favoured by the highly polar membrane. Except for very small water concentration in the feed, i.e. less than 5 %, the permeate always contains more than 95 % water. For example, the separation factor of the 80/20 mixture of 2-propanol/water is about 7000. Simultaneously, the flux of propanol/water mixtures is much higher than of ethanol/water mixtures, probably because

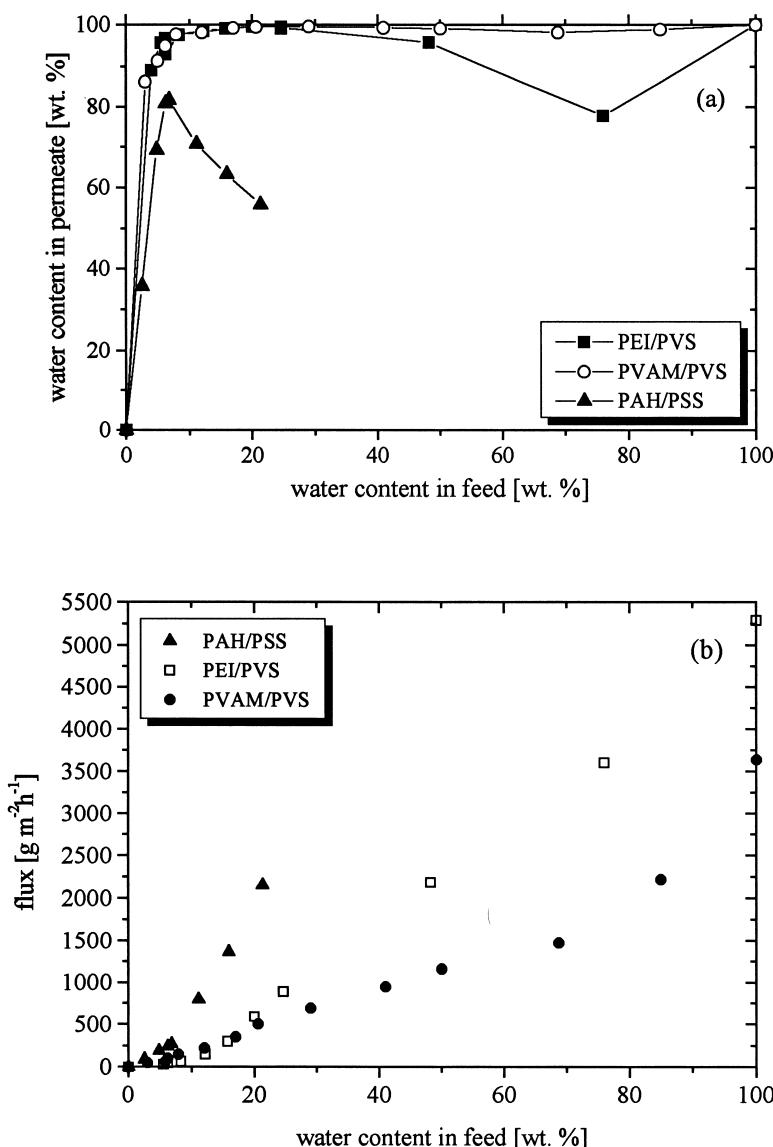


Fig. 6: Dependence of water content in permeate (a) and flux (b) on water content in feed solution for PVAM/PVS, PEI/PVS and PAH/PSS membranes. All samples consist of 60 layer pairs. PAH/PSS and PEI/PVS membranes were annealed at 90 °C for 1h prior to pervaporation¹².

of the weaker hydrogen bonding between propanol and water molecules. For example, the 80/20 mixture of 2-propanol/water exhibits a high flux of $1,5 \text{ kg m}^{-2} \text{ h}^{-1}$, while for an ethanol/water mixture of the same composition the flux is only $0,5 \text{ kg m}^{-2} \text{ h}^{-1}$.

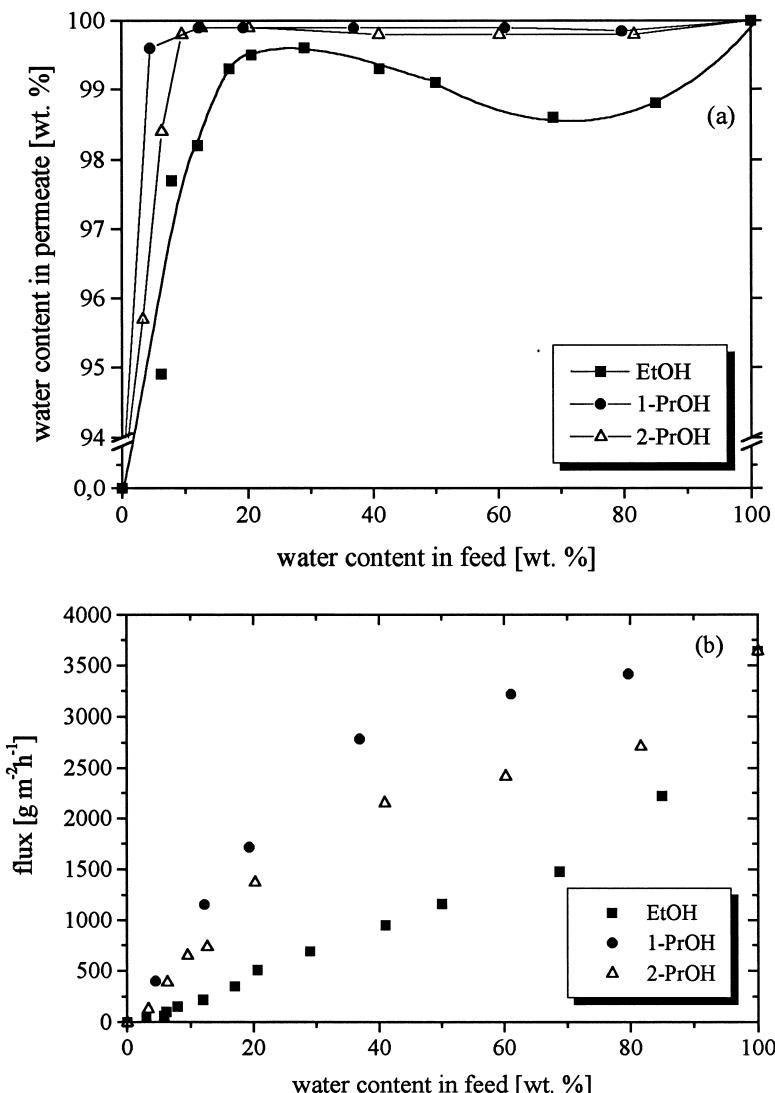


Fig. 7: Dependence of water content in permeate (a) and flux (b) on water content in feed solution for various alcohol/water mixtures. Separating membrane: 60 layer pairs of PVAM/PVS.

Ion separation

The ion permeation through solution-cast bipolar membranes consisting of both negatively and positively charged polyelectrolyte layers was already investigated several years ago^{17,18)}. It was found that divalent cations receive a much stronger repulsive force from positively charged layers than monovalent ones, and that the same holds for the divalent anions, which are rejected by the negatively charged layers. Consequently, the bipolar membranes represent barriers for divalent ions in general and can be used for ion separation^{7,18)}. The self-assembled polyelectrolyte multilayers consist of cationic and anionic polyelectrolytes in alternating fashion and therefore can be described as a multi-bipolar membrane on a molecular level, which likewise should be able to separate mono- and divalent ions. In Fig. 8, a model of the ion rejection by the self-assembled multilayer membrane is represented. The model implies that the ion separation becomes progressively more effective, if the number of adsorbed polyelectrolyte layers is increased.

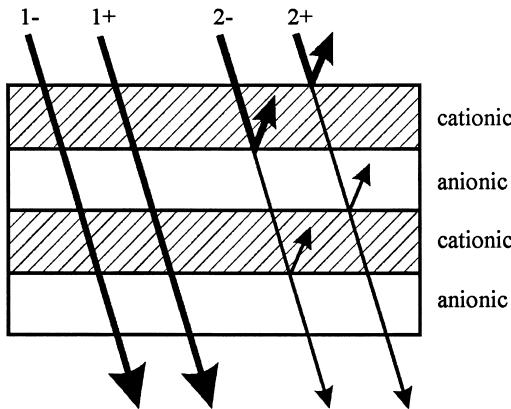


Fig. 8: Rejection model of a multi-bipolar membrane⁹⁾.

In order to study the ion permeation, the cell shown in Fig. 9 was used. The cell consists of two chambers separated by the membrane. One of the chambers contains the aqueous salt solution (concentration: 0.1 mol l^{-1}) and the other one pure water. From the measurement of the initial increase in conductivity ($\Delta\Lambda/\Delta t$) in the water chamber, the permeation rate P_R was calculated using the equation shown in Fig. 9. A possible contri-

bution to $(\Delta\Lambda/\Delta t)$ originating from the osmotic flow of water in the opposite direction was not corrected.

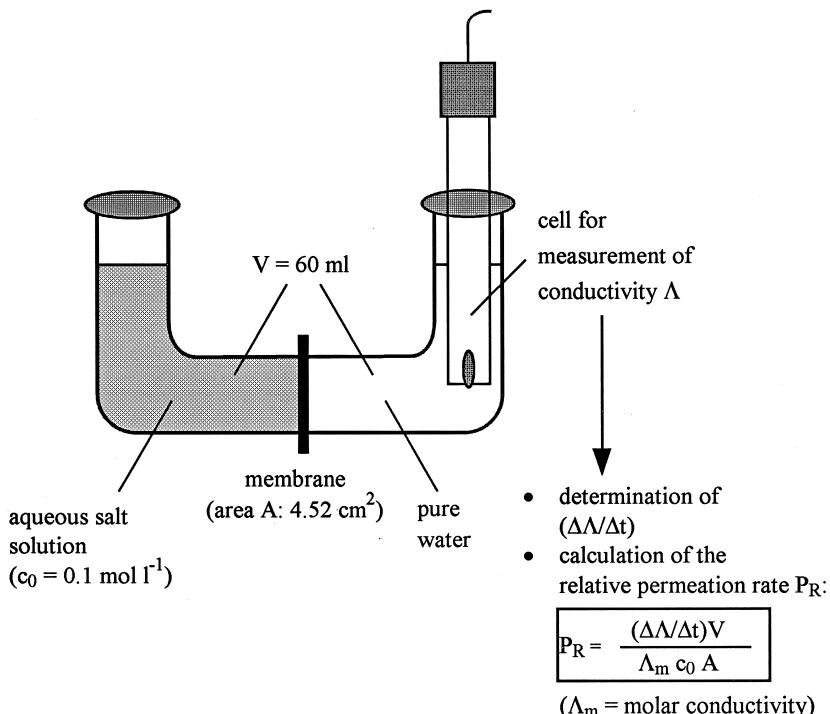


Fig. 9: Schematic representation of the cell used for measurement of ion permeation.

In Fig. 10, the permeation rates of NaCl and MgCl_2 are plotted versus the thickness of the membrane. With increasing thickness, the permeation rates of the two salts are decreased, but for MgCl_2 the decrease is much stronger than for NaCl . Therefore, the separation factor α (for definition of α see Fig. 9) strongly increases with the membrane thickness. For example, a sample containing 60 layer pairs of PAH/PSS exhibits separation factors α of 15,1 for $\text{NaCl}/\text{MgCl}_2$, and of 9,9 for $\text{NaCl}/\text{Na}_2\text{SO}_4$.

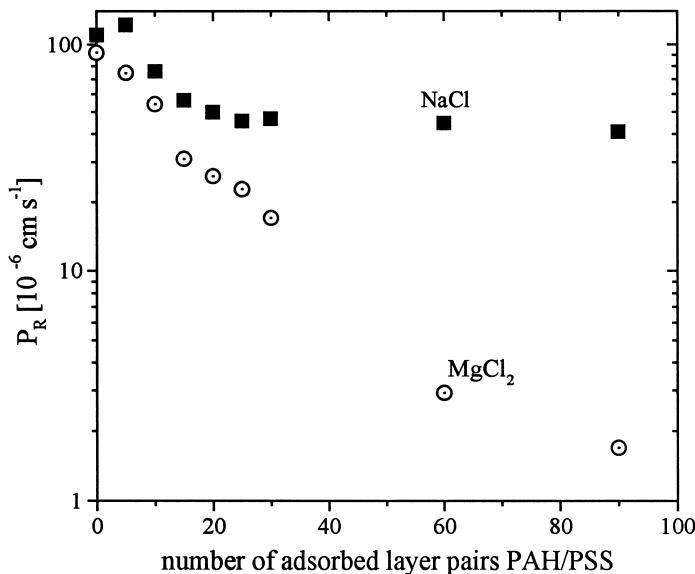


Fig. 10: Effect of the thickness of the separating membrane (PAH/PSS) on permeation rates P_R of NaCl and MgCl_2 ⁸⁾.

The ion permeation is strongly affected by the structure of the polyelectrolytes used for membrane preparation. In Fig. 11, the permeation rates of NaCl and MgCl_2 are plotted as a function of the charge density ρ_c of the polyelectrolyte membrane. The higher the charge density, the lower is the permeation rate, and the difference between the salts with mono- and divalent ions becomes progressively larger with increasing ρ_c . The plots also indicate that membranes with PAH as the cationic polyelectrolyte always exhibit lower permeation rates than membranes containing other polycations. The origin for the especial behaviour of PAH is not yet clear.

Besides the polyelectrolyte structure, the processing parameters such as salt content and pH of the polyelectrolyte solution have a strong influence on the ion permeation, too. The pH controls the ionisation of the polyelectrolytes, which in its turn influences the charge density of the membrane, as discussed above. As recently shown, a low pH value

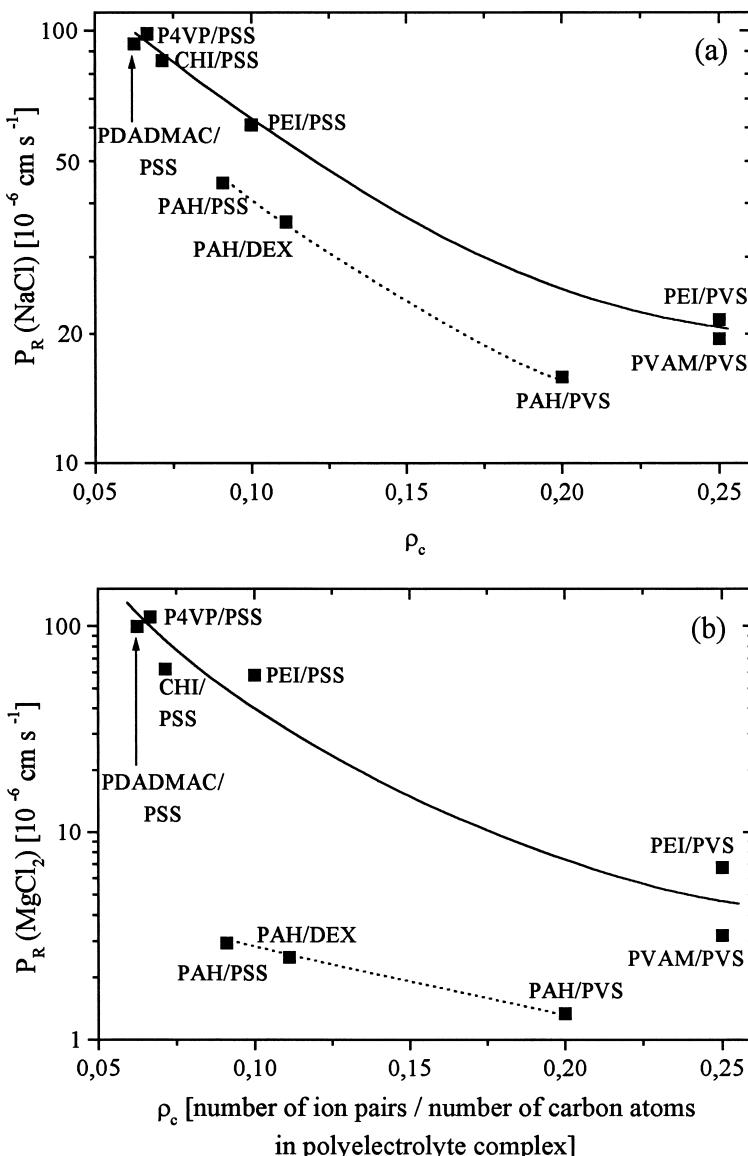


Fig. 11: Effect of charge density ρ_c of polyelectrolyte multilayer on permeation rate P_R of (a) NaCl and (b) MgCl_2 . Separating membranes always consist of 60 layer pairs of polycation polyanion.

favours the formation of a dense, less permeable membrane of high charge density, which exhibits an improved rejection of divalent ions. Upon salt addition to the polyelectrolyte solution, the coil dimensions of the polyelectrolytes are reduced. As a consequence, the polyelectrolytes are no longer adsorbed in a flat conformation, but as coils, so that the individual layers are much thicker⁷ and the permeation rates are decreased. Since especially the P_R values of the salts with divalent ions are decreased, considerably higher separation factors are obtained (Tab. 2).

Tab. 2: Permeation rates P_R of NaCl, MgCl₂ and Na₂SO₄ and selectivities α for PAH/PSS and PVAM/PVS membranes prepared from salt-free and salt-containing polyelectrolyte solution (thickness: 60 layer pairs).

Mem- brane	addition of salt	P_R (NaCl) [10^{-6} cm s ⁻¹]	P_R (MgCl ₂) [10^{-6} cm s ⁻¹]	P_R (Na ₂ SO ₄) [10^{-6} cm s ⁻¹]	α (NaCl/ MgCl ₂)	α (NaCl/ Na ₂ SO ₄)
PAH/ PSS	+	22.5	0.2	0.5	112.5	45.0
PAH/ PSS	-	44.4	2.9	4.5	15.1	9.9
PVAM/ PVS	+	3.1	0.06	0.3	51.7	10.3
PVAM/ PVS	-	19.5	2.4	11.5	8.1	1.7

Summary and Conclusions

Our study indicates that alternating electrostatic adsorption of cationic and anionic polyelectrolytes on porous substrates is a versatile method to prepare composite membranes with ultrathin, pore-free separation layer. By careful choice of the polyelectrolytes and by optimisation of the processing conditions, membranes with excellent separation capability for alcohol/water mixtures or mono- and divalent ions can be tailored. It is also shown that the transport of small molecules and ions through the membrane is strongly a function of the density of the network formed upon the complex formation between the oppositely charged polyelectrolytes. For the separation processes

discussed above, polyelectrolytes with high charge density are especially suited. They are able to form a close, highly polar network structure, which favours the transport of highly polar liquids such as water, and retards the transport of more hydrophobic alcohols, and which rejects the divalent ions of high charge density more strongly than the monovalent ions. In further experiments, the separation of organic liquids of different hydrophilicity will be studied, as well as the ion permeation under reverse osmosis conditions.

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