Monovalent selective membrane for electrodialysis desalination of water for agriculture

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Abstract. Agriculture is the world's largest consumer of water accounting for about 70% of freshwater withdrawals. Faced with scarcity of pure water, it results in need in desalination to produce water for agricultural needs from brackish water, seawater or polluted sources. Widely used technologies reduce total salinity decreasing also the levels of calcium, magnesium, sulphates and phosphates required for normal growth of plants. Recently a layer-by-layer adsorption of charged polymers was proposed for creation of functional materials that would preferentially remove monovalent ions such as Na⁺ and Cl⁻. Our previous studies demonstrated the creation of cation selective membrane basing on affordable heterogeneous cation exchange membrane that specifically separated Na⁺ from Na⁺/Ca²⁺ mixed solution during electrodialysis. Further characterization showed that, in addition to the expected increase in specific selectivity with respect to singly charged counterions, there was an increase in the overall selectivity with respect to counterions. We provide data from measurements of electrical conductivity, diffusion permeability, and the results of calculating the transport numbers of counterions, demonstrating an increase in selectivity.

1. Introduction

A number of membrane technologies are proposed for purification or correction of the composition of the solutions [1–4]. Desalination of brackish, saline or polluted waters to produce irrigation waters is considered as economically worthwhile for intensive production [5] and for dry climates [5,6], but the mainstream membrane technologies, including the reverse osmosis, decrease the total mineralization [7], meaning that the ions necessary for the normal functioning of living organisms, such as Ca²⁺, Mg²⁺, SO₄²⁻ and PO₄³⁻ will be removed along with undesirable monovalent ions such as Na⁺ and Cl⁻, potentially leading to nutrient deficiencies [8]. Therefore, the introduction of the stage of remineralization of solutions is required [9]. It is implemented as addition of fertilizers [10], which adds costs and can result in excessive concentration of monovalent ions in treated water, or as mixing of desalted water with brackish water [5], which may result in excessive level of monovalent ions as well. Hence the selective demineralization with monovalent selective membranes, such as monovalent selective electrodialysis, was proposed for agricultural producers with high requirements to water quality, such as greenhouses [10].

A simple method that makes it possible to significantly increase the monovalent selectivity of membranes with respect to singly charged ions is the layer-by-layer adsorption of charged polymers from solution [11], which forms a system of layers with alternating charge signs of fixed groups. There
are a number of studies confirming an increase in the specific selectivity of membranes after such a modification [12–14].

In addition to the sought after effect of increasing the monovalent selectivity of the membrane with respect to singly charged ions, the application of surface layers can have other advantages. It can be hypothesized that the deposition of polymer layers on porous materials would close the voids on their surface, and for heterogeneous ion exchange membranes intended for electrodialysis the adsorbed layers can fill the so-called macropores [15]—gaps with a diameter of the order of hundreds of microns, formed between the ion exchanger and the reinforcing mesh or inert binder. The presence of gaps in the structure of ion exchange membranes creates cavities inside the membrane filled with electroneutral solution, through which ions same charged to the functional groups of the membrane can move, passing from the concentration chamber back to the desalination chamber [16]. This reduces the apparent transport numbers of ions across the membrane and the current efficiency achieved [17]. Accordingly, blocking large pores with deposited polymer layers may increase the energy efficiency of heterogeneous membranes.

In this communication, we show the change in the selectivity of a heterogeneous cation exchange membrane to counterions as a result of the deposition of layers of polymers—polyallylamine hydrochloride and sodium polystyrene sulfonate. For this end, we calculate the transport numbers of Na\(^{+}\) and Ca\(^{2+}\) ions from the results of measurements of the electrical conductivity and diffusion permeability of membranes in 0.5 mol/L NaCl and 0.25 M CaCl\(_2\) solutions.

2. Materials and Methods

The MK-40 membrane is produced by the Russian company Shchekinoazot [18]. It is used industrially as part of electrodialysis and hybrid installations; in particular, studies are known that consider its long-term operation for correcting the acidity of water and recycling the process solutions [19].

This affordable membrane contains not only an ion conducting cation exchanger, but also a reinforcing polyamide mesh and a polyethylene as an inert binder. This results both in its advantage, which is stability during storage and operation, and in its disadvantages that include lower, in comparison with competing homogeneous membranes, limiting current of counterions [20], lower electrical conductivity and higher diffusion permeability of salt.

Shchekinoazot supplies the membranes in a dry form, therefore, before use, they must be equilibrated with the treated solution. For gradual and gentle equilibration, the membranes were placed in a 30% solutions of NaCl or CaCl\(_2\), were kept under constant stirring for 8 hours, then the solutions were diluted with the same volume of distilled water and kept for another 8 hours, after which the solution was replaced with a working solution (NaCl with a concentration of 0.5 mol/L or CaCl\(_2\) with a concentration of 0.25 mol/L) and left under periodical replacement of the solution until a constant electrical conductivity of the equilibrating solution was achieved.

After equilibration, the surface of the membrane was first homogenized by applying a layer of LF-4SC perfluorinated cation-exchange polymer (sold as a 7% dispersion in the mixture of water and low molecular weight aliphatic alcohols by Plastpolymer, Russia), which is known to be able to adhere to polyethylene and form a continuous layer. For this, the membrane samples were removed from the solution, wiped with filter paper to remove surface moisture, and glued with tape to the bottom of the Petri dish, leaving in the centre an area not smaller than the working window of the cell for measuring diffusion permeability. Then, 0.5 mL of the LF-4SC dispersion was distributed over the formed window and left for half an hour to evaporate the solvent and to harden the film.

Note that this stage includes the presence of the swollen membrane outside the solutions, which can lead to partial dehydration of the ion exchanger grains in its composition at a constant size of polyethylene, which can lead to an irreversible increase in macropores [15] and a decrease in selectivity.

After that the adsorption of the polymer layers was started.

The first polymer was polyallylamine hydrochloride (purchased from Sigma-Aldrich, USA), 100 mL of a 1 g/L solution (in distilled water produced on site) of which was poured into a Petri dish and left in contact for 30 min.
After that, the solution was poured off, the membrane was rinsed with distilled water, and 100 mL of a 1 g/L polystyrene sulfonate solution in distilled water (purchased from Sigma-Aldrich, USA) was poured into a Petri dish. The contact time was also 30 minutes.

Then, in the same way, another layer of polyallylamine hydrochloride and another layer of sodium polystyrene sulfonate were applied. Then the membranes were detached from the Petri dish and placed in working solutions for a day.

To study the properties of the modified samples and compare them with the initial values, the electrical conductivity and diffusion permeability of three types of membranes were measured, namely: the initial MK-40; membrane, on which only a homogenizing layer of LF-4SC was applied (in our previous works it was designated as MK-40+1 [21]) and a membrane on which a homogenizing layer of LF-4SC and four adsorbed layers were applied (polyallylamine hydrochloride - sodium polystyrene sulfonate - polyallylamine hydrochloride - sodium polystyrene sulfonate), in our previous works such a membrane was designated as MK-40+5 [22].

The electrical conductivity was calculated by the difference method by measuring the resistance of the membrane with a surrounding solution of 0.5 mol/L NaCl or 0.25 mol/L CaCl$_2$ and a solution without a membrane using a tweezer cell connected to an immitance meter, the electrode area of which is known and is equal to 1 cm$^2$. The measurements were repeated ten times for each membrane sample. The thickness of the membrane was determined from ten points within the modified area using a micrometer.

The formula for calculating conductivity is as follows:

$$\kappa_m = \frac{d_m}{R_{\text{tot}} - R_s}$$

where $\kappa_m$ is the conductivity of the membrane, $R_{\text{tot}}$ is the resistance of the membrane in solution, $R_s$ is the resistance of the solution, $d_m$ is the thickness of the membrane.

To determine the diffusion permeability, the samples were placed in a two-chamber cell. The outflow tract, operating in the solution circulation mode, and the outflow chamber entering it are initially filled with working solutions - 0.5 mol/L NaCl or 0.25 mol/L CaCl$_2$. The receiving path, also operating in the circulation mode, and the chamber included in it are initially filled with distilled water. The receiving chamber is equipped with a conductometric cell connected to a conductometer and a glass electrode connected to a pH meter. The recorded conductivity values were used to calculate the concentrations according to the calibration dependence. Knowing the change in concentration over time and the size of the working window of the membrane $S$ (4.0 cm$^2$) and the volume of the solution in the desalination tract $V$ (400 mL), it is possible to calculate the salt flux using the equation:

$$J = \frac{V \frac{dC}{dt}}{S}$$

where $J$ is the flux of the equivalents of a salt (NaCl or ½ of CaCl$_2$), $C$ is the equivalent concentration of the salt, $t$ is the time.

Knowing the flux of the salt, it is possible to calculate the integral coefficient of the diffusion permeability through the Peers equation:

$$P_{\text{integral}} = \frac{Jd_m}{C}$$

knowing the integral coefficient of the diffusion permeability, it is possible to calculate the local coefficient of the diffusion permeability:

$$P = P_{\text{integral}} \left( \frac{d \ln P_{\text{integral}}}{d \ln C} + 1 \right)$$
which was then used with electrical conductivity of the membrane to calculate the counterion transport number:

\[
t_+ = \frac{1}{2} + \left(1 - \frac{PF^2C}{2RT\kappa_m}\right)^{1/2}
\]

where \(t_+\) is the counterion transport number, \(F\) is the Faraday constant, \(R\) is the gas constant, \(T\) is the absolute temperature.

3. Results and Discussion
The measured thicknesses, calculated electrical conductivities, diffusion permeability values and transport numbers of sodium and calcium are given in Table 1.

| Property                        | MK-40          | MK-40+1         | MK-40+5         |
|---------------------------------|----------------|-----------------|-----------------|
| Thickness, \(d\), \(\mu m\)     | 525±3          | 528±2           | 571±2           |
| Electrical conductivity, \(\kappa_m\), mS-cm\(^2\) | 9.57           | 9.68            | 7.47            |
| Integral diffusion permeability, \(P_{\text{integral}}\), \(\mu m^2/s\) | 9.45           | 10.35           | 6.35            |
| Counterion transport number     | 0.98           | 0.98            | 0.99            |

Table 1. Selected properties of the commercial MK-40 membrane and of the two experimental samples: the MK-40 with applied homogenizing polymer and the MK-40 with applied homogenizing layer and four layers of polymers with alternating charges of functional groups.

The application of a layer of LF-4SC slightly rises the electrical conductivity, increases the diffusion permeability and reduces the counterions transport number through the membrane. This can be explained by the addition of the stages of drying and re-swelling of the membrane, which, given the ability of the ion exchanger included in the membrane to approximately double in dimensions when swelling, the weaker and slower swelling of polyamide fibre and the inability of polyethylene to swell, leads to deformation of the membrane matrix and to an increase in the macropore size.

The adsorption of polymer layers occurs without drying the samples and leads to the formation of polymer layers capable of blocking large pores on the membrane surface through which nonselective solution transfer occurs; therefore, this stage is accompanied not by an increase, but by a decrease in electrical conductivity and diffusion permeability. Note that a stronger increase in the calculated transport numbers of counterions was found for the CaCl\(_2\) solution as compared to the NaCl solution, which can be explained by the large hydrated radius of the calcium ion [23] and the more effective blocking of the nonselective transfer of the salt that contains a larger hydrated ion.

4. Conclusion
Layer-by-layer deposition of polymers was previously used to increase the monovalent selectivity of membranes intended for electrodialysis desalination of water for agriculture, such as salinity reduction of brackish water for irrigation in greenhouses. In the present part of our continuing characterization of modified heterogeneous membranes in artificial mixed Na\(^+\)/Ca\(^{2+}\) solutions with total salinities lying in the range of brackish water, we have shown that a side effect of this modification of the membrane surface can be an increase in the selectivity with respect to counterions as compared to coions, which is expressed in an increase in the transport numbers. Since the ion transport numbers directly affect the
current efficiency of the electrodialysis process, layer-by-layer modification in this way can increase the energy efficiency of the technique.

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