Brackish water desalination using electrodialysis with monovalent selective membranes

V Titorova¹, E Kirichenko² and K Kirichenko¹

¹Kuban State University, 149, Stavropol'skaya st., Krasnodar, 350040, Russia
²Kuban State Agrarian University named after I T Trubilin, 13, Kalinina st., Krasnodar, 350044, Russia

E-mail: K.a.nebav@gmail.com

Abstract. Electrodialysis with selective membranes is used to desalinate surface waters while preserving the polycharged ions. Layer-by-layer adsorption of alternating positively charged and negatively charged polyelectrolytes at the surface of the substrate membrane is known as a simple and cheap method for the production of selective membranes. In this article we investigate model membranes surficially coated from one side with two types of anion exchange modifiers and conclude that for both types of created samples a high limiting current of salt ions is observed but the intensity of a side process, a shift in the pH of the treated solution, increases after the modification. We propose that it is more reasonable to modify membranes by this method with polymeric quaternary ammonium substances, which are less catalytically active in water dissociation reaction. This will reduce the energy demand of the process and will improve the quality of treated waters.

1. Introduction
For the successful and sustainable implementation of agricultural activities, water is needed for irrigation [1]. The water available in a given area may not be applicable for irrigation; it may have an unsuitable qualitative or quantitative composition of dissolved salts [2], as well as be polluted by industrial, municipal or agricultural wastewater and therefore require pretreatment [3]. To reduce mineralization, traditional sorption methods, such as the introduction and sedimentation of bentonite or other materials [1], and reverse osmosis [4], where a pressure gradient separates the solvent from the incoming solution by a filtration through a semi-permeable membrane, are typically used. The shortcomings of these approaches include, among other things, the problem that salt ions are eliminated nonselectively, and in addition to monovalent ions (Na⁺, Cl⁻, NO₃⁻), which can cause soil salinization if their concentration is excessive, polyvalent ions (Ca²⁺, SO₄²⁻, Mg²⁺) that are required for the normal growth of animals and plants [4] are also removed.

There are methods that make it possible to selectively separate the monovalent ions, and electrodialysis, which is based on the transport of ions through selectively permeable membranes under the action of an electric force, is one of them [5]. To create the monovalent selectivity in electrodialysis it was proposed to use special pulsed electric fields, hydrodynamic modes and the special grade membranes [6]. Some major ion exchange membrane companies even have selective membranes as a special grade product [7], but such materials are less widespread and more expensive as regular ones. It was suggested that the monovalent selectivity of membranes may be boosted in a magnitude unattainable by any other method through a layer-by-layer adsorption of polyelectrolytes.
with alternating signs of the charge of functional groups from their solutions [8]. This approach has shown the emergence of monovalent selectivity even in noncharged porous substances [9], which means that it can be used to improve the properties of not only expensive special grade, but also cheap standard grade membranes.

In the published articles reporting on the performance of laboratory and pilot scale setups with membranes modified according to this method, polystyrene sulfonate [9-12] is used as a polyelectrolyte carrying the negatively charged groups and polyallylamine [9,10] or polyethyleneimine [11,12] are used as a polyelectrolyte carrying the positively charged groups. Use of polyallylamine and polyethyleneimine for creation of selective membranes for pretreatment of water for agricultural purposes is problematic since polyethyleneimine can have a negative effect on the development of the cardiovascular system of fish [13], and polyallylamine is irritating for eyes and skin [14]. Both modifiers can get into the treated water, and then into the reservoirs, if the coating layer is damaged.

In present article we characterized the membranes layer-by-layer coated with polymers used in published sources and proposed a way to improve this approach. For this end we studied the transport characteristics of cheap MK-40 membrane coated with polyethyleneimine or polyallylamine, which in later will serve as basis for development of membranes with high monovalent selectivity. To evaluate the energy efficiency of future electrodialyzers with such membranes we found the experimental limiting current densities (LCDs) and assessed the rate of the side process - the water dissociation, which, depending on the value of potential drop, leads to acidification or alkalinization of the desalted solution.

2. Materials and methods

At this stage of modeling the natural brackish water was imitated with a NaCl solution, since these ions do not undergo transformation during the measurement of transport properties, and because with a growing number of participating ions and ionic forms the interpretation of i-V curves gets more complicated and at some point it becomes ambiguous. The working concentration was 0.02 M (1.17 g/L) NaCl, which corresponds to brackish water.

A heterogeneous MK-40 cationite membrane manufactured by Shchekinoazot was selected as a substrate since it is cheap, has good mechanic properties, resistant to chemical agents and high temperatures. Compared to homogeneous analogues, such as cationic membranes produced by DuPont under Nafion trademark, it has inferior but still acceptable electrochemical characteristics. To increase the LCD and electrical conductivity of this heterogeneous membrane we used the previously proposed coating with the cation exchange polymer to create homogenizing layer[15]. After creation of the homogenizing layer of MF-4SC we submerged a substrate in solution to adsorb a layer of polymeric amine, fixed groups of which are charged oppositely to the sulfonic groups of the previous layer. Polyallylamine or branched polyethyleneimine was adsorbed from 1 g/L aqueous solution during 1 hour.

The mass transport properties of the commercial and laboratory-made membranes were estimated on the basis of i-V curves. The cell for these measurements is described in detail in [16], here we give only the parameters being important for this work: the laboratory scale electrodialyzer was flow-through with laminar liquid flow in chambers. Polarizing Pt electrodes were inert. The potential drop at the membrane is recorded using Luggin electrodes. The products of electrode reactions were separated from the studied membrane by buffer chambers formed by Pt electrode from one side and auxiliary cation exchange membrane (CEM) and anion exchange membrane (AEM) from the other. The glass electrodes were mounted in tanks framing the desalination channel to record the pH difference and thereby judge the rates of the water dissociation on the studied membrane in comparison with paired auxiliary membrane. The curves were recorded under current density sweeping from zero to approximately two theoretical LCDs calculated for monolayer CEM.

The i-V profile of a monopolar membrane ideal for desalination has the following characteristics: its general slope, the V/i ratio which is areal electrical conductivity, the magnitude of the Ohmic losses at the membrane will inversely depend on, must be high; the experimental LCD (found as intersection
of tangents drawn to curve at its first bend), which determines the operating current of commercial electrodialyzer, should be equal to the theoretical LCD or exceed it to give the maximum productivity of the plant; and the length of the inclined plateau which is formed after the limiting state is reached should be small, since the shape of this particular section is determined by the processes forming the main non-Ohmic losses in intensive regimes.

To demonstrate a difference between of the i-V curves of a CEM with adsorbed layer of polyamine and the i-V curve of a membrane that promotes the water dissociation we will show a characteristics of a MA-41 commercial AEM manufactured by Shchekinoazot by a technology analogous to that for MK-40 except for ion exchange resin will be presented. Hot rolling of MK-40 involves a strongly acidic KU-2 sulfonic cationite and for MA-41 it is a strongly basic AV-17 quaternary ammonium anionite. The hastening of water dissociation at this membrane occurred after it was coated with a layer of MF-4SC homogeneous cation exchange material by casting from a 20% dispersion [16].

3. Results

Figure 1 gives the i-V curves of the commercial MK-40 membrane, its two aforementioned modifications and i-V curve of modified MA-41 that possesses a high rate of water dissociation, which was recorded in previous experiments and presented here for comparison.

![i-V curves of a MK-40 with a homogenized surface (solid line), with a homogenizing layer and polyallylamine layer (MK-40+MF-4SC+PAA, dashed line) or with a homogenizing layer and polyethyleneimine layer (MK-40+MF-4SC+PEI, dash-dot line). The dotted line shows the properties of a membrane that promoted water dissociation and the gray line indicates the theoretical LCD.](image-url)
Figure 1 shows that the curve of the MK-40 with a homogenized surface possesses a LCD close to the theoretical one, that the slope of its initial region is greater and the plateau region is shorter than that of a sample with active water dissociation.

Figure 2 shows the pH difference at the ends of desalination chamber registered when recording the i-V curves.

![Figure 2](image)

**Figure 2.** The pH difference at desalination channel recorded during registration of i-V curves of a MK-40 with a homogenized surface (solid line), with a homogenizing layer and polyallylamine layer (MK-40+MF-4SC+PAA, dashed line) or with a homogenizing layer and polyethyleneimine layer (MK-40+MF-4SC+PEI, dash-dot line). The dotted line shows the properties of a membrane that promoted water dissociation.

### 4. Discussion

The i-V curves of the two membranes coated with polyamines are different. The curve of the sample which adsorbed polyallylamine is similar to the curve of MK-40 with homogenizing layer. The i-V curve of the sample which adsorbed polyethyleneimine contains an additional region at low currents, the course of which is similar to that of membranes with high rate of water dissociation; when this region is over, the curve becomes normal for a membrane with a lower rate of water dissociation. We link the formation of this site with the existence of a potential barrier to transport of cations in positively charged polyethyleneimine under the action of an external electric field. The lack of this site for sample with adsorbed polyallylamine may be caused by its lesser charge density related to the chemical nature of the modifiers - polyallylamine carries only primary amino groups and is a weaker base than branched polyethyleneimine, which carries primary, secondary and tertiary amino groups.

A unifying feature of the i-V curves of membranes coated with polyamines is that they preserve the LCD, which would make it possible to realize high performance technological processes with these membranes.
The second important issue is a possible pH shift of the purified product. For the purposes of irrigation, it is desirable that the pH of the water would not change. In real membrane systems at high currents there always is some change, since salt ions get depleted at membrane/solution interface due to the difference in transport number of counterions in membrane and in solution, and the products of water dissociation start to make up a significant number of charge carrier. This reaction is also catalyzed by the functional groups, and Zabolotskii et al. composed the row of catalytic activity [17].

Figure 2 demonstrates that in respect to the water dissociation, investigated samples form three groups.

The first group includes the homogenized MK-40 which, paired with the MA-41, performs weak alkalinization of the diluate at low currents and growing acidification at high ones. This pattern is explained by the Cl\(^-\) being more mobile in aqueous solution than Na\(^+\) at the same concentration [18], which means that the depletion of salt counterions and the catalytic water dissociation sets in faster in the water near the CEM surface. When this state arises, the protons produced by water dissociation pass through the CEM, and the retained OH\(^-\) raise the pH. With growing potential drop the salt ions are depleted near the AEM as well, starting a process opposite to that near the CEM and decreasing the pH. When the catalytic water dissociation occurs near both membranes, the overall pH shift is formed by the biggest rate between these reactions. Since the amino groups that make up most AEM are more catalytically active for water dissociation than the sulfonic groups of most CEM, the result usually is decrease of pH.

Specially coated MA-41 forms the second group. Here the pH of treated water decreases at the entire range of potential drops. For it the intensive water dissociation is further promoted due to a bipolar boundary, a zone where fixed ions of opposite charge contact, resulting in very large electric field strength. Due to oppositely charged neighboring areas, under applied external field no salt ions can traverse to bipolar boundary, and as a result, here the limiting state is reached almost from the zero voltages, starting catalytic water dissociation even before the limiting stage is reached at paired membrane. Hence there are no longer such potential drops through the system at which the water dissociation near the (modified) AEM would be weaker than on a paired CEM, hence no alkalinification region is observed in this pH difference curve.

Finally, membranes with adsorbed polyamines form the third group. With them the alkalinization proceeds more intensively than with a commercial MK-40 because of existence of a bipolar boundary. In this regard, both polyallylamine and polyethyleneimine are unsuccessful modifiers, since their fixed groups are very catalytically active in the water dissociation reaction.

We suggest that the rate of water dissociation in systems with membranes layer-by-layer coated with polyelectrolytes with alternating charges of fixed groups may be lowered when the currently used polyethyleneimine or polyallylamine would be replaced with a polymeric quaternary ammonium substances, that, by to the series of catalytic activity [17], is far less active in the water dissociation reaction. Additional benefits that would be achieved by this replacement are increased antimicrobial resistance [19] and better biocompatibility [20].

5. Conclusion

The state-of-the-art method of manufacturing the monovalent selective ion exchange membranes allows creating samples competitive in aspect of transport of salt ions, but it is challenged with high rate of water dissociation which, coupled with membrane transfer of one product, results in alkalinification or acidification of product. To reduce this drawback, we propose to use polymeric quaternary ammonium substances that are less catalytically active in water dissociation reaction as anion exchange modifier. These substances are also thought to be more resistant to biofouling, less toxic to aquaculture than polyethyleneimine or polyallylamine which are currently proposed for such modification.

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