Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.980970

56 (2015) 3160–3166
December

Taylor & Francis
Taylor & Francis Group

Increasing selectivity of a heterogeneous ion-exchange membrane

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Received 28 July 2014; Accepted 7 October 2014

ABSTRACT

Selectivity, permselectivity, and conductivity are the main ion-exchange membrane parameters. While permselectivity determines how well the membrane separates cations from anions, the selectivity determines how well the membrane transports uni- and multivalent ions. On the other hand, conductivity determines how fast the ions are transported through the membrane. All these parameters depend on many other factors, especially on the membrane structure. It is difficult to develop highly selective (permselective) and highly conductive heterogeneous ion-exchange membranes. Reason for this is porosity: while the conductivity increases with increasing porosity, the selectivity and permselectivity decreases. This work was focused on increasing the selectivity and, at the same time, the conductivity of heterogeneous ion-exchange membranes. It was found that most of the techniques of modification of homogeneous membranes cannot be used with modification heterogeneous ion-exchange membranes. It appears that the choice of a polymer matrix is a key factor in the preparation of heterogeneous ion-exchange membranes with high selectivity to monovalent ions and also high permselectivity while maintaining the same, even a higher conductivity.

Keywords: Ion-exchange membrane; Selectivity; Permselectivity; Conductivity

1. Introduction

Electrodialysis is a separation process which allows a selective removal of ions from solution. One advantage of electrodialysis is that no chemicals are used for resin regeneration and another advantage consists in the division of one stream (feed) into two streams (diluate and concentrate). The ion-exchange membranes with high conductivities and only moderate permselectivities are required for most of the desalination processes. Special applications, however, require ion-exchange membranes with unique characteristics such as a higher selectivity to monovalent ions than bivalent ones, low permeabilities to protons or hydroxyl ions, and a high resistance to fouling and

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Presented at the MELPRO 2014 Conference Membrane and Electromembrane Processes, 18–21 May 2014, Prague, Czech Republic

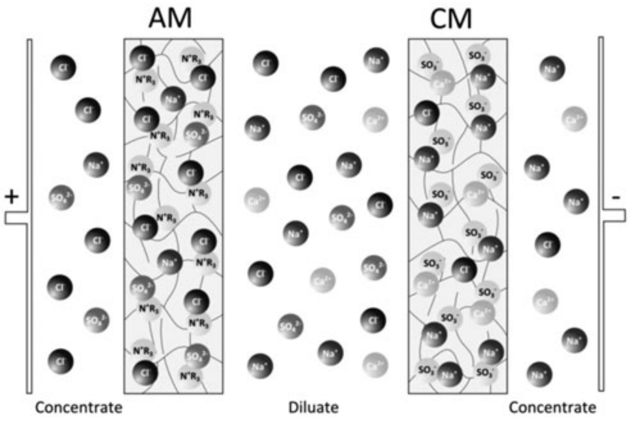


Fig. 1. Scheme of electrodialysis.

elevated temperature resistance. A basic scheme of electrodialysis is shown in Fig. 1.

The permselectivity is sometimes erroneously confused with the selectivity. While the permselectivity determines how well the membrane separates cations from anions, the selectivity determines how well the membrane transports uni- and multivalent ions.

Different ions are transported through the membrane with different kinetics due to different ion mobilities and sizes. Small and univalent ions are transported preferentially while large and multivalent ions are transported extremely slowly. Some co-ions may be transported with corresponding counter ions through the membrane which is caused by structure inhomogeneity, accidental porosity, or other similar factors. Some organic compounds such as surfactants block functional groups in the membrane, and thus, act as membrane poisons.

The permselectivity is connected with current efficiency. In some application such as bipolar electrodialysis or metathesis the limited permselectivity is a key factor for maximum solution purity. In other applications such as desalination of whey, desalination of ground water or bipolar electrodialysis, a high selectivity to monovalent ions is a key factor.

The aim of this work was to find conditions for increasing ion selectivity of heterogeneous ion-exchange membranes, in particular conditions for removing of monovalent ions. In the literature, a large number of articles on increasing membrane selectivity to monovalent ions can be found [1–11]. These modifications deal with both surface modifications and whole structure transformations and they refer to both homogeneous and heterogeneous membranes. However, it can be concluded that there is no general way of preparation of membrane for the separation of monovalent ions.

2. Experimental

2.1. Membranes

2.1.1. Commercial membranes

Heterogeneous anion-exchange membranes Ralex AM(H)-PES (Mega a.s., Czech Republic), homogeneous anion-exchange membrane AR 103 QDP (GE—Ionics), and homogeneous anion-exchange membranes AEM I and AEM II (FUJI) were used.

The surface of Ralex AM(H)-PES membranes was modified by plasma or by sulfonation. Membrane sulfonation was carried out by immersing Ralex AM(H)-PES samples 4 × 30 cm in fuming sulfuric acid (Oleum 105%) for 30 s. Then, the samples were washed in demineralized water for 24 h and dried in air at room temperature (see Table 1).

2.1.2. Preparation of laboratory heterogeneous anion-exchange membranes

The heterogeneous anion-exchange membranes were prepared by a standard procedure [12] by washing, drying, and milling a gel strong-base anion exchangers, based on styrene–divinylbenzene copolymer (Table 2), followed by kneading with low density polyethylene (LDPE) or high modulus polymer (HMP) (Table 3) in weight ratio of 60/40 (resin/PE) (Table 4). The membrane was prepared from the obtained blend by extrusion and lamination with PES fabric on both sides.

2.2. Determination of the relative water content in the membranes

The original sample of size 10 × 10 cm was dried at 75˚C to constant weight. The initial size (length, width, thickness) and weight were recorded. Then, the sample was swelled in demineralized water for minimally 24 h at 25˚C. After full swelling, the sample was quickly dried by filter paper, and the size and weight were recorded. The total water content Δwt was calculated as relative parameter by following Eq. (1).

$$\Delta wt = \frac{wt_w - wt_d}{wt_d} \times 100\% \tag{1}$$

where wt_w is the weight of a wet membrane sample and wt_d is the weight of a dried membrane sample.

The total water content comprises to components: water content in a swollen resin and water content in hydrophobic pores of membrane.

Table 1
Commercial anion-exchange membranes investigated in this work

Membrane code	Characterization	Producer	Treatment
AM(H)-PES	Heterogeneous	Mega a.s.	Unmodified
AM(H)-PES plasma	Heterogeneous	Mega a.s.	Modified by plasma
AM(H)-PES oleum	Heterogeneous	Mega a.s.	Modified with fuming H_2SO_4
AEM I	Homogeneous	FUJI	Unmodified
AEM II	Homogeneous	FUJI	Unmodified
AR 103 QDP	Homogeneous	General electric (Ionics)	Unmodified

Table 2
Strong base styrenic gel anion resin used for heterogeneous membrane preparation

Resin	Functional group	IEC (eq/l)	Moisture retention (wt.%)
Mega standard	Trimethylamine	1.3	50–55
Purolite A420S	Trimethylamine	0.8	60–65
Purolite A600	Trimethylamine	1.4	43–48
Purolite A532E	Bifunctional quaternary amine	0.85	36–45

Table 3
Polymers used for heterogeneous membrane preparation

Polymer	Melt temperature (°C)	Young modulus (MPa)	Density (g/cm^3)
Low density polyethylene (LDPE)	111	200	0.924
High modulus polymer (HMP)	124	400	0.915

Table 4
Composition of laboratory heterogeneous membranes

Membrane code	Anion-exchange resin (wt.%)				Polyethylene (wt.%)	
	Mega standard	Purolite A420S	Purolite A600	Purolite A532	LDPE	HMP
M1	60				40	
M2	30	30			40	
M3		60			40	
M4			60		40	
M5	15	15	30		40	
M6				60	40	
M7	15	15		30	40	
M8	62					38

2.3. Characterization of membranes

Eq. (2) was used for the calculation of ideal selectivities ($a_{i/j}$) of investigated ion-exchange membranes.

$$a_{i/j} = \frac{R_{Ai}}{R_{Aj}} = \frac{R_{Si}}{R_{Sj}} \tag{2}$$

where R_{Ai} and R_{Aj} are areal resistances, and R_{Si} and R_{Sj} are specific resistance (resistivity) of the membrane for ions i and j, respectively.

Eq. (2) is an analogy of Eq. (3) for the calculation of ideal selectivities ($a_{i/j}$) of gas separation membranes [13].

$$a_{i/j} = \frac{P_i}{P_j} \tag{3}$$

where P_i and P_j are gas membrane permeabilities of gases i and j, respectively.

Electrochemical resistance of investigated membranes was determined by a standard potentiometric compensation method [14]. The electrochemical resistance for compensation method is calculated by the following Eqs. ((4)–(7)), where R_j^s is the resistance without membrane, R_j^s is the resistance with membrane, and R_{Aj} the is a real resistance of membrane, U_{meas} is the measured potential under the current, U_{as} is the asymmetric potential measured without applied current, A_m is the active sample area, Th_j the is sample thickness, index s—solution, m—membrane, and j—solution type. The (1,2) and (2,1) means sequence of saturated calomel electrode. Scheme and real cell is shown in Fig. 2.

$$R_j^s = \frac{\left|U^s_{meas.}(1,2) - U^s_{as}(1,2)\right|_j + \left|U^s_{meas.}(2,1) - U^s_{as}(2,1)\right|_j}{2I} \tag{4}$$

$$R_j^{s+m} = \frac{\left|U^{s+m}_{meas.}(1,2) - U^{s+m}_{as}(1,2)\right|_j + \left|U^{s+m}_{meas.}(2,1) - U^{s+m}_{as}(2,1)\right|_j}{2I} \tag{5}$$

$$R_{A,j} = \left(R_j^{s+m}(1) - \bar{R}^s\right)A_m \tag{6}$$

$$R_{S,j} = \frac{R_{Aj}}{Th_j} \tag{7}$$

Electrochemical resistance of investigated membranes was measured in 0.5 M solutions of NaCl, KCl, $NaNO_3$, Na_2SO_4, $CaCl_2$, $MgCl_2$, and Na_2HPO_4, respectively.

3. Results and discussion

Values of areal resistances and selectivities of commercial anion-exchange membranes measured in different solutions are presented in Tables 5 and 6.

Heterogeneous membranes AM(H)-PES (Mega a.s.) exhibited significantly higher values of areal resistance than homogeneous membranes AEM I and II (FUJI), but lower than homogeneous membranes AR 103 QDP (GE). All investigated homogeneous anion-exchange membranes showed a higher selectivity to monovalent ions than heterogeneous ones, but this was not the case of bivalent ions selectivity (see Table 6).

The surface modification of AM(H)-PES membrane, both by a plasmatic hydrophilization and by a treatment with a fuming sulfuric acid, had only a negligible effect on the values of areal resistance and selectivities. This can be explained by the mechanism of ion transport through the membrane. The scheme in Fig. 3, which is generally valid for both the cation- and anion-exchange membranes, shows the influence of both non-conducting and conducting domains on transport of ions. It can be seen that both plasma modification and sulfonation affect, in particular, the non-conducting domains on the surface of membrane. Conductive channels inside the membrane are not modified and therefore the transport of ions through the membrane is not affected.

The values of areal resistances and selectivities of anion-exchange membranes prepared in laboratory conditions within this work are shown in Tables 7 and 8, respectively. These laboratory anion-exchange membranes contain four types of anion exchangers (Table 2). Three of the resins are of the same type but differ in the degree of crosslinking. Determinations of electrochemical properties showed that the degree of crosslinking had a very small effect on the values of the areal resistances and selectivities.

The fourth resin, containing tributyl ammonium chloride groups, is more selective to nitrates than sulfates according to the manufacturer (Technical list from http://purolite.com/). A high affinity of this resin for nitrate ions brought about a slowdown in the transport of all ions through the membrane M6 by nitrate absorption on the conductive centers and thus blocking the transport. The membrane containing this resin showed the highest areal resistances in all investigated solutions.

The matrix of membranes M1–M7 is the LDPE and that of membrane M8 of HMP, which is a HMP

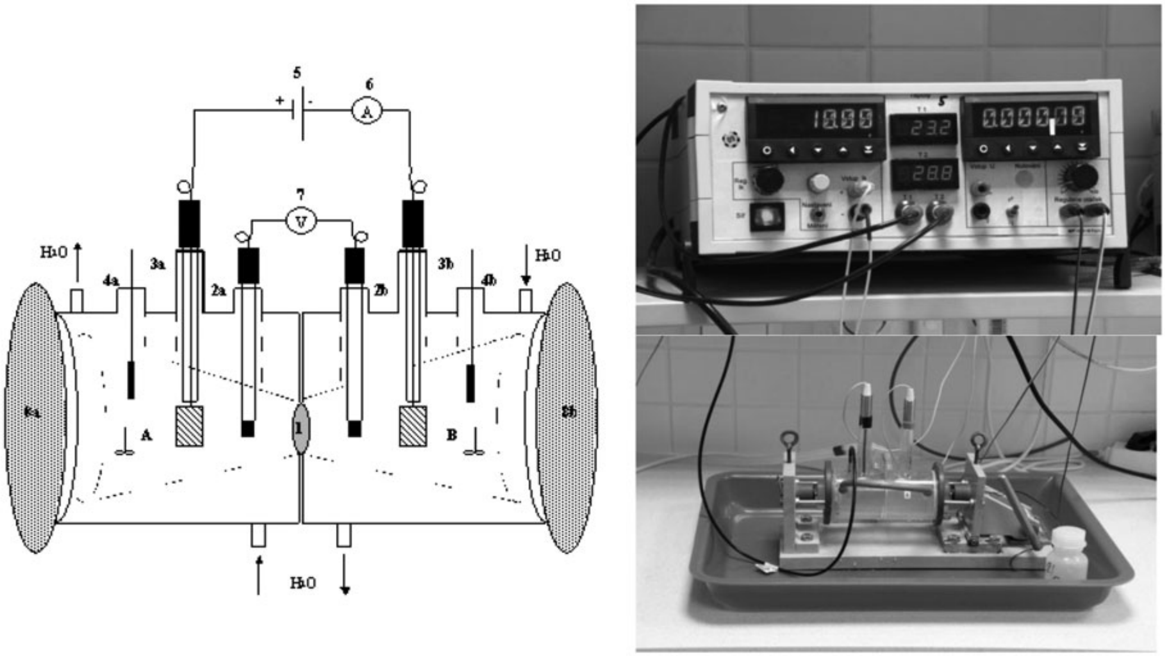


Fig. 2. Scheme of measuring cell (left) and real cell with a galvanostat (right).

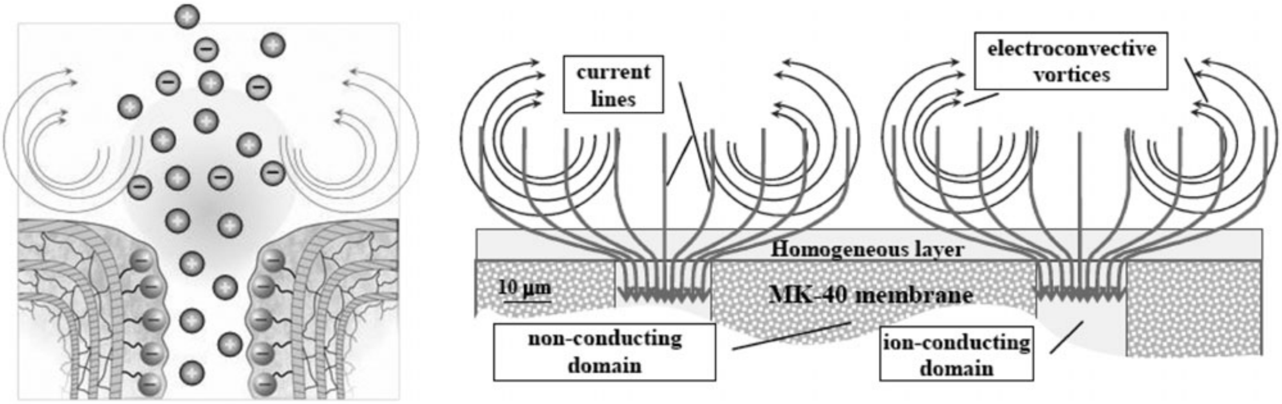
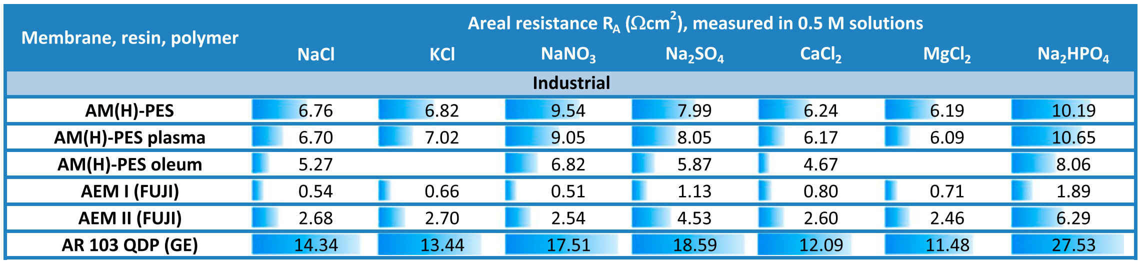


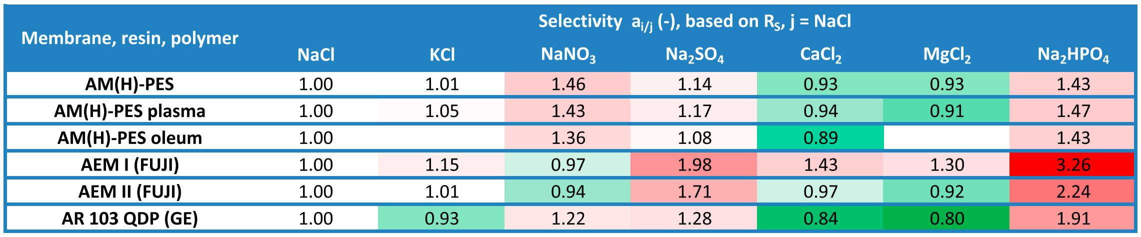
Fig. 3. Scheme of electroconvective vortices for cation-exchange membrane, left unmodified, right surface modified by homogeneous layer (source presentation Victor Zabolotsky, Victor Nikonenko, Effect of membrane surface properties on the membrane behavior in electrodialysis, Permea 2009).

Table 5
Areal resistance of commercial anion-exchange membranes in different solution



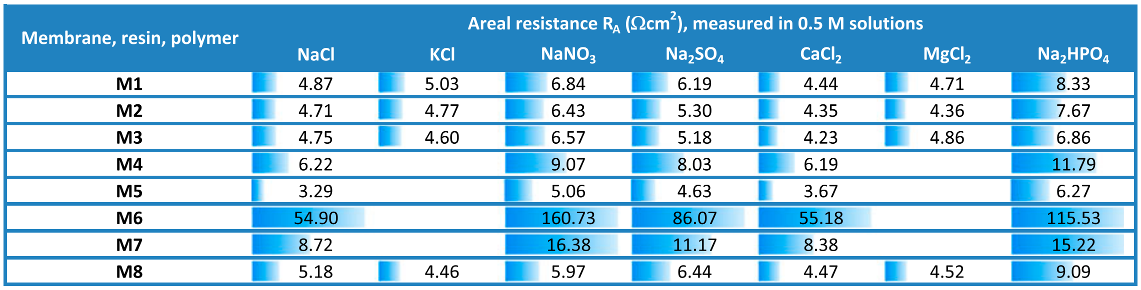
Membrane, resin, polymer	Areal resistance R_A (Ωcm^2), measured in 0.5 M solutions						
	NaCl	KCl	$NaNO_3$	Na_2SO_4	$CaCl_2$	$MgCl_2$	Na_2HPO_4
			Industrial				
AM(H)-PES	6.76	6.82	9.54	7.99	6.24	6.19	10.19
AM(H)-PES plasma	6.70	7.02	9.05	8.05	6.17	6.09	10.65
AM(H)-PES oleum	5.27		6.82	5.87	4.67		8.06
AEM I (FUJI)	0.54	0.66	0.51	1.13	0.80	0.71	1.89
AEM II (FUJI)	2.68	2.70	2.54	4.53	2.60	2.46	6.29
AR 103 QDP (GE)	14.34	13.44	17.51	18.59	12.09	11.48	27.53

Table 6
Selectivity coefficient of tested commercial anion-exchange membranes based on specific resistance comparison



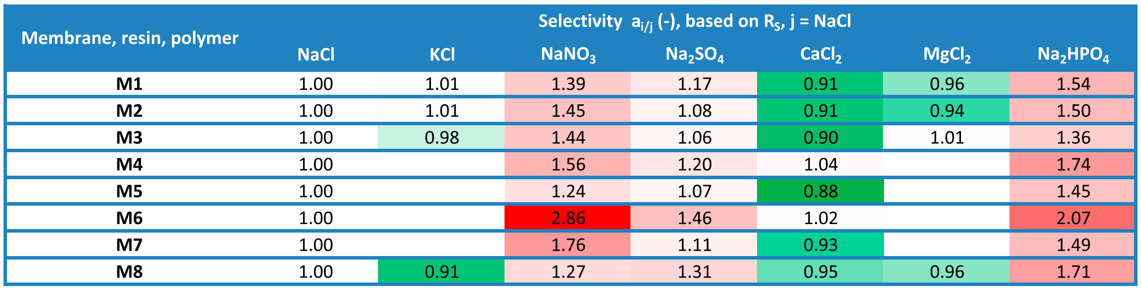
Membrane, resin, polymer	Selectivity $a_{i/j}$ (-), based on R_S, j = NaCl						
	NaCl	KCl	$NaNO_3$	Na_2SO_4	$CaCl_2$	$MgCl_2$	Na_2HPO_4
AM(H)-PES	1.00	1.01	1.46	1.14	0.93	0.93	1.43
AM(H)-PES plasma	1.00	1.05	1.43	1.17	0.94	0.91	1.47
AM(H)-PES oleum	1.00		1.36	1.08	0.89		1.43
AEM I (FUJI)	1.00	1.15	0.97	1.98	1.43	1.30	3.26
AEM II (FUJI)	1.00	1.01	0.94	1.71	0.97	0.92	2.24
AR 103 QDP (GE)	1.00	0.93	1.22	1.28	0.84	0.80	1.91

Table 7
Areal resistance of laboratory anion-exchange membranes in different solution



Membrane, resin, polymer	Areal resistance R_A (Ωcm^2), measured in 0.5 M solutions						
	NaCl	KCl	$NaNO_3$	Na_2SO_4	$CaCl_2$	$MgCl_2$	Na_2HPO_4
M1	4.87	5.03	6.84	6.19	4.44	4.71	8.33
M2	4.71	4.77	6.43	5.30	4.35	4.36	7.67
M3	4.75	4.60	6.57	5.18	4.23	4.86	6.86
M4	6.22		9.07	8.03	6.19		11.79
M5	3.29		5.06	4.63	3.67		6.27
M6	54.90		160.73	86.07	55.18		115.53
M7	8.72		16.38	11.17	8.38		15.22
M8	5.18	4.46	5.97	6.44	4.47	4.52	9.09

Table 8
Selectivity coefficient of tested laboratory anion-exchange membranes based on specific resistance comparison



Membrane, resin, polymer	Selectivity $a_{i/j}$ (-), based on R_S, j = NaCl						
	NaCl	KCl	$NaNO_3$	Na_2SO_4	$CaCl_2$	$MgCl_2$	Na_2HPO_4
M1	1.00	1.01	1.39	1.17	0.91	0.96	1.54
M2	1.00	1.01	1.45	1.08	0.91	0.94	1.50
M3	1.00	0.98	1.44	1.06	0.90	1.01	1.36
M4	1.00		1.56	1.20	1.04		1.74
M5	1.00		1.24	1.07	0.88		1.45
M6	1.00		2.86	1.46	1.02		2.07
M7	1.00		1.76	1.11	0.93		1.49
M8	1.00	0.91	1.27	1.31	0.95	0.96	1.71

(Tables 3 and 4). We assumed that a matrix polymer with a high Young modulus can reduce porosity and the water swelling of the membrane. A decrease in swelling may have a negative effect on the conductivity of the membrane and, on the other hand, may increase membrane selectivity. However, the comparison of water swelling and electrochemical properties of M1, M3, and M8 membranes (Tables 7 and 9) shows that the areal resistances of the three membranes were not significantly different despite

Table 9
Relative water content of selected membrane samples

Membrane (resin/polymer ratio)	M1 (60/40)	M3 (60/40)	M8 (62/38)
Relative water content (rel wt.%)	51.5	71.5 (38.8%)	42.7 (−17.1%)
Relative water content based on pure dry resin (rel. wt.%)	85.8	119.2 (38.8%)	68.9 (−19.7%)

their different water swelling. Only, the membrane with a reduced water swelling (M8) was a little more selective to monovalent ions (Table 8).

4. Conclusions

(1) Surface modification of heterogeneous anion-exchange membranes by plasma or by sulfonation had a negligible effect on membrane areal resistance and selectivities.
(2) Homogeneous anion-exchange membranes are more selective to monovalent ions than heterogeneous ones.
(3) Heterogeneous anion-exchange membranes with a matrix of a HMP swell little in water.
(4) Heterogeneous anion-exchange membranes with a decreased swelling in water have an increased selectivity to monovalent ions.
(5) Heterogeneous anion-exchange membranes containing an anion-exchange resin with a high affinity to nitrates have a very high areal resistance in the presence of nitrates.

Acknowledgment

This work was supported by the Ministry of Industry and Trade of the Czech Republic within the framework of the project "Special membrane for the development and intensification of electro membrane technologies" program TIP No FR-TI4/507 using the infrastructure of the Membrane Innovation Centre (No. CZ 1.05/2.1.00/03.0084).

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