

# NF- and RO- Membranes in Drinking Water Production

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## ABSTRACT

The paper presents results of the tests carried out on selected membranes produced by Osmonics Inc. (USA). The efficiency of membrane water softening was evaluated on the basis of the permeate flux obtained and additional physico-chemical analyses conducted in raw water and permeate. Transport-separation properties of the membranes examined were determined with reference to the tested solutions of NaCl and MgSO<sub>4</sub>. The next stage of the research dealt with membrane filtration of natural waters characteristic of high degree of hardness. The tests carried out indicated that membranes may be applied to the softening of water for drinking and household purposes.

## KEY WORDS

Membrane techniques, water treatment, water softening, NF, RO

## INTRODUCTION

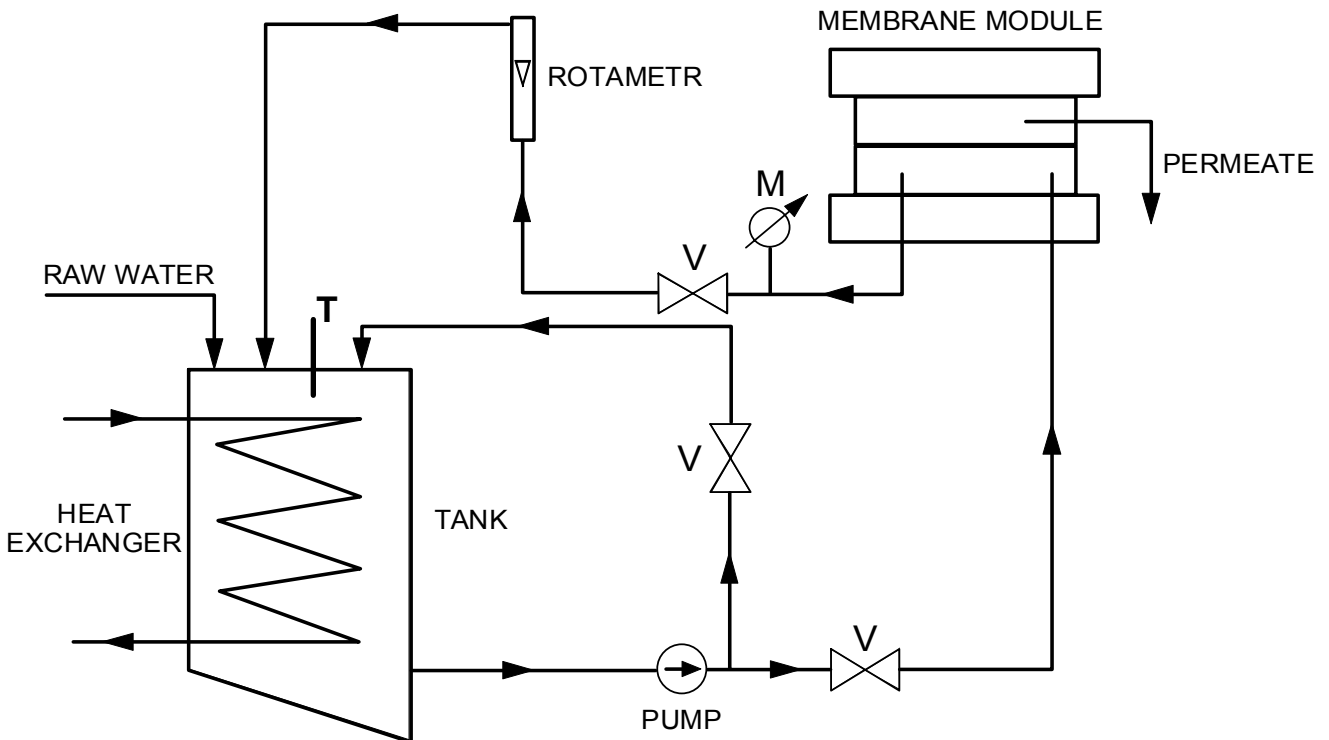
In accordance with the Decree of Health and Social Welfare Minister no. 82 dated 4th September 2000 item 937, drinking water and water for economic purposes should be characterised by hardness (CaCO<sub>3</sub>) 60-500mg/dm<sup>3</sup>. The consumption of underground water has recently increased while water quality has become worse as a result of rapid industry and agriculture development. An increasing demand for high quality water observed during the expansion of civilization creates at the same time a necessity of rationalization of hard and very hard water softening processes. The rationalization refers to the water tapped in Poland. In recent years the membrane techniques become the alternative for conventional water treatment processes. The membranes used in high pressure techniques like: reverse osmosis and nanofiltration (RO, NF) make the removal of small-molecule substances (e.g. salt, organic compounds) possible.

The nanofiltration membranes act like a sieve against large particles and large pore sizes enable relatively high flows of 10<sup>-6</sup>m/s. The selectivity of nanofiltration membranes depends largely upon the groups capable of decomposition which give the surface area certain static charge [1]. The application of nanofiltration to the softening of water intended for drinking produces a product of highest quality i.e. water of required mineral composition: abounding in cations and anions indispensable to the proper growth and functioning of organisms and devoid of the ions which bring about its excessive hardness. One of the advantages is the possibility to combine membrane processes with traditional methods used for water treatment.

## EXPERIMENTAL

### APPARATUS AND MEMBRANES

A schematic of the apparatus used in the research is presented in Fig 1.



**Figure 1 Schematic of pilot installation on a large-laboratory scale for the examination of membrane filtration**

The basic element of the installation is the membrane module produced by Osmonics Inc., type SEPA CF-HP, high-pressure version, adjusted for carrying out reverse osmosis and nanofiltration. The module used flat membranes in the form of rectangular sheets. Effective membrane area was 155 cm<sup>2</sup>. The fluid that underwent membrane filtration was pumped with a circulation pump (piston, high-pressure pump). The suction tube ramified into a by-pass and main tube. The by-pass is directly linked through a cut-off valve with a tank for the fluid circulating in the module, and the main tube was linked through another valve with the membrane module. Two types of membranes SEPA CF produced by Osmonics Inc. were used in the experiment: DS-51-DL and DS-3-SE.

### METHODOLOGY OF MEMBRANE TESTING AND MEMBRANE FILTRATION OF WATERS

Transport properties of the tested membranes - DS-51-DL, DS-3-SE - and filtration efficiency of natural waters were determined calculating the volumetric flux of deionized water that passed through a membrane at constant process parameters. Retention coefficients of Mg<sup>2+</sup> and Cl<sup>-</sup> ions for 0.5% solutions of NaCl and MgSO<sub>4</sub> were determined. Membrane filtration for those solutions was carried out for 3.5 hours

The membrane filtration was carried out for 5 hours at constant process parameters, i.e. working pressure 2 MPa (for DS-51-HL) and 3 MPa (for DS-3-SE), feed flow over the membrane surface 1 m/s, medium temperature 25 °C. Four types of natural waters characterized by different total hardness ( $H_{tot}$ ) were used in the experiment. The membrane filtration was carried out for 5 hours at constant process parameters.

Testing of the membranes and filtration of the natural waters were conducted applying the batch mode and receiving similar volumes of each 500cm<sup>3</sup> of permeate. Half of the volume of each permeate was introduced into the feed tank so that it could not get thick while the other half was used to carry out analytical determinations. All the research cycles were repeated to confirm the results obtained.

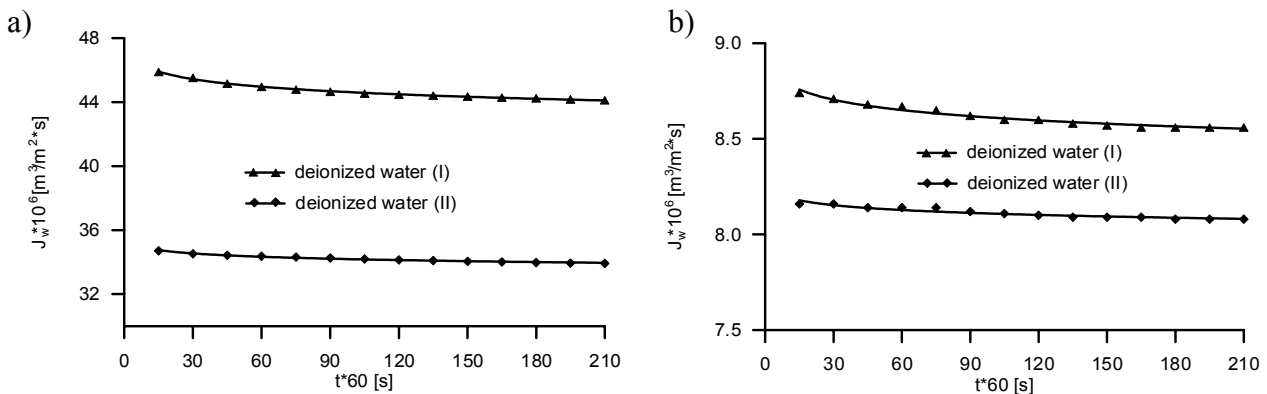
### ANALYTICAL CONTROL OF THE PROCESS

Each research cycle dealt with determination of the amounts of Cl<sup>-</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and total (H<sub>tot</sub>) and carbonate hardness (H<sub>C</sub>) in the raw water and averaged permeate sample. Concentration of magnesium, calcium and determination of total hardness were carried out applying the complexometric titration with EDTA, while concentration of the chlorides was determined applying titration by Mohr. Retention coefficients R were calculated using the following equation:  $R = (1 - \frac{C_p}{C_n}) \cdot 100$  [%], where: C<sub>p</sub> - concentration of the substance in the permeate, C<sub>n</sub> - concentration of the substance in the raw water.

## RESULTS AND DISCUSSION

### MEMBRANE TESTING

The results of the tests show that the efficiency of the membrane DS-51-HL (approx. 45·10<sup>-6</sup> m<sup>3</sup>/m<sup>2</sup>s) is several times higher than that of the membrane DS-3-SE for deionized water flux (J<sub>w</sub>) was equal to 8.5·10<sup>-6</sup> m<sup>3</sup>/m<sup>2</sup>s (Fig.2a, b – deionized water I).



**Figure 2 Time dependence of volume flux through:**  
**a) Membrane DS.-51-HL b) membrane DS.-3-SE;**  
**the feed: deionized water**

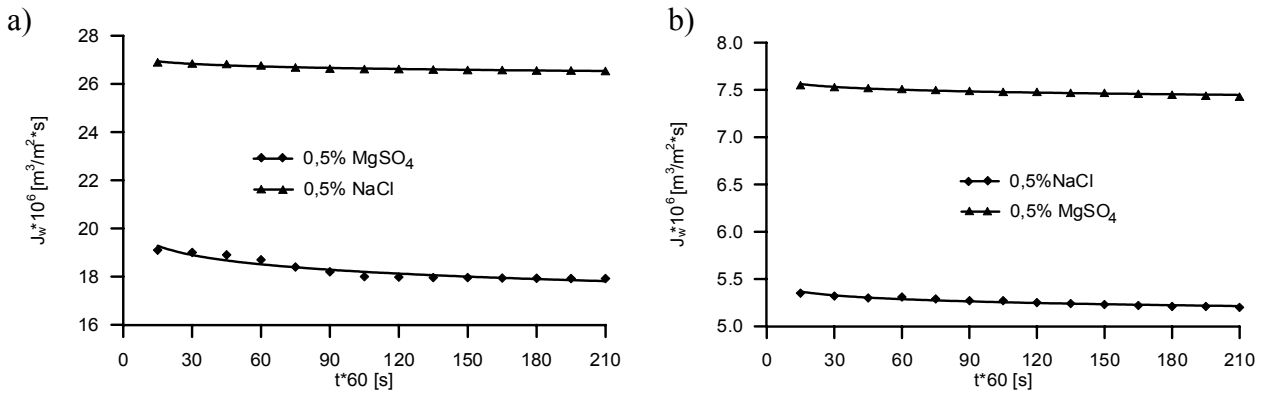
Basing on the obtained results of investigation there has been made a test of water membrane filtration process modelling. The selection of appropriate mathematical models is not easy in case of high – pressure processes for water as a multiplied by solution .

The application of half – empirical mass transport models has been proposed. There have been observed that both membranes (DS-51-HL and DS-3-SE) used in the experiments showed slightly higher deionized water flux (J<sub>w</sub> – deionized water I) at first tests, in comparison with the J<sub>w</sub> of deionized water (II) after multiple exploitation of the given membrane (Fig. 2). This fact shows a partial (irrevocable) pores blocking (fouling), which influenced a slight reduction of water filtration process efficiency.

Analysis of the retention coefficients of Cl<sup>-</sup> and Mg<sup>2+</sup> ions obtained during testing the membranes with model solutions of the salts reveals the following effects concerning

the removal of those ions: for DS-51-HL membrane:  $R_{Cl} = 10\%$ ,  $R_{Mg} = 80.7\%$ , and for DS-3-SE membrane:  $R_{Cl} = 89\%$ ,  $R_{Mg} = 97\%$ . These results suggest that the (DS-51-HL) is nanofiltration membrane due to the varied degree of monovalent and bivalent ions retention and (DS-3-SE) is RO-membrane due to the similar degree of monovalent and bivalent ions retention.

Furthermore, it has been observed that high values of the flow are typical of NaCl filtration and low values the filtration of  $MgSO_4$  (Fig.3).



**Figure 3 Time dependence of volume flux through:**  
**a) Membrane DS-51-HL b) membrane DS-3-SE;**  
**feed 0.5%NaCl, 0.5% MgSO<sub>4</sub>**

This phenomenon can be explained (partly at least) by the different osmotic pressure differences,  $\Delta\pi$ , of the feed and permeate solutions developed during the filtration of NaCl and  $MgSO_4$ . Using the layer model of concentration polarisation for the calculation of the salt concentration near the surface of membrane:

$$c_{s,f}^{(m)} = c_{s,p} + (c_{s,f} - c_{s,p}) \exp\left(J_v \frac{l_p}{D_s}\right) \quad (1),$$

necessary for the calculation of  $\Delta\pi$ :

$$\Delta\pi \approx 2RT(\phi_f c_{s,f}^{(m)} - \phi_p c_{s,p}) \quad (2),$$

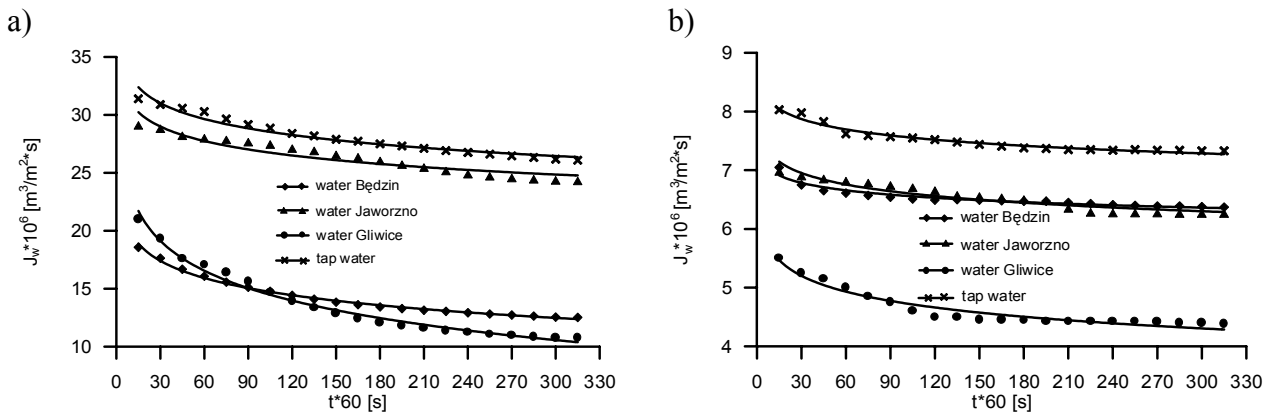
It has been estimated that for DS-3-SE  $\Delta\pi$  is equal ca. 0.44 (NaCl) and 0.10 MPa ( $MgSO_4$ ), whereas for DS-5-DK:  $\Delta\pi = 0.08$  (NaCl) and 0.16 MPa ( $MgSO_4$ ). Thus, remembering that  $\Delta p = 2$  MPa the effective force ( $\Delta p - \Delta\pi$ ) is substantially higher in the first case for  $MgSO_4$ , whereas in the second case – for NaCl.

For the interpretation of retention coefficients the model based on the extended Nerst – Planck equation and the Donnan equation has been applied [2].

According to the model the concentration of fixed charges in the pore solution,  $\bar{c}_m$ , for DS-51-DK is 0.5 M as calculated from the NaCl data, assuming  $r_p = 1$  nm,  $l_p = 50$   $\mu$ m. Using the  $MgSO_4$  data, however, the model calculations yield one hundred times higher values of  $\bar{c}_m$ . These unexpectedly high values of  $\bar{c}_m$  mean that the steric effect, larger for  $MgSO_4$ , plays here the important role (the radii of ions calculated from their mobilities are 0.348 ( $Mg^{2+}$ ) vs. 0.184 ( $Na^+$ ), 0.231 ( $SO_4^{2-}$ ) vs. 0.121 ( $Cl^-$ ) nm). In the case of DS-3-SE for both electrolytes the calculated  $\bar{c}_m$  is also much too high (ca. 20 M). Here for the explanation of salt rejection the surface force-pore model of Matsuura and Sourirajan can be applied [3,4].

Four types of waters characterised by different total hardness ( $H_{tot}$ ) were used in the experiment. They were the well waters taken from Jaworzno ( $H_{tot} \approx 500 \text{ mg CaCO}_3/\text{dm}^3$ ), Będzin ( $H_{tot} > 500 \text{ mg CaCO}_3/\text{dm}^3$ ) and Gliwice ( $H_{tot} > 600 \text{ mg CaCO}_3/\text{dm}^3$ ), and the tap water for comparison.

In the case of both DS-51-DK and DS-3-SE membranes the highest  $J_w$  is observed for the tap water and the well water from Gliwice characterised by the lowest total hardness  $H_{tot}$  (Figs.4a, 4b).



**Figure 4 Volumetric permeate flux with respect to time:**  
a) membrane DS-51-HL b) membrane DS-3-SE

The dependence of volume flow on time can be approximated by the logarithmic function  $J_v = a \log(t) + b$ . The parameters of that function, including the determination coefficient  $R^2$ , for the investigated membrane systems have been listed in Table 1.

**Table 1 Time dependence of  $J_v$ ,  $J_v = a \log(t/\text{min}) + b$ , and the determination coefficient  $r^2$  for membranes DS-51-HL i DS-3-SE**

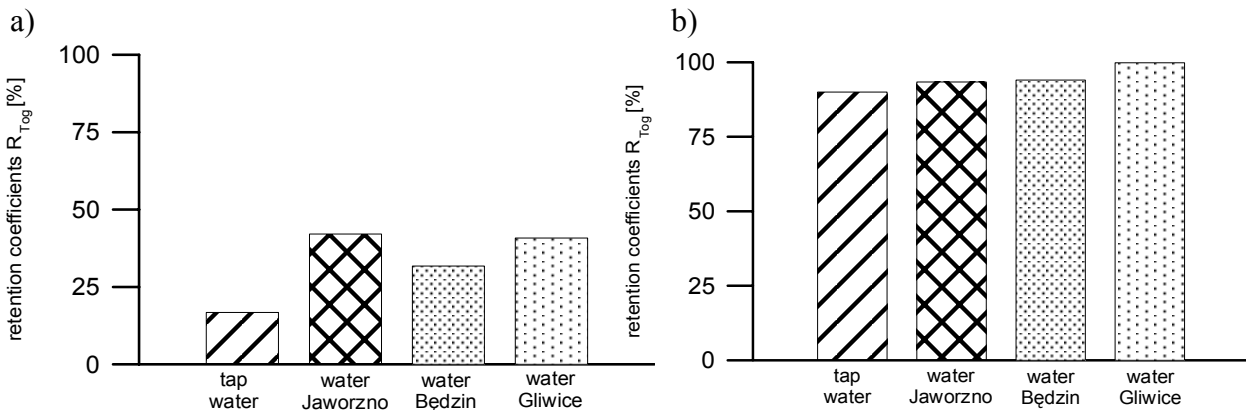
Water	Membrane DS.-51-HL	Membrane DS-3-SE
	$J_w \cdot 10^6 = a \cdot \log(t) + b$	$J_w [\text{m}^3/\text{m}^2 \cdot \text{s}] \quad t[\text{min}]$
Tap	$J_w = -1.98295 \cdot \log(t) + 37.7703$	$J_w = -0.253556 \cdot \log(t) + 8.73457$
Jaworzno	$J_w = -1.80032 \cdot \log(t) + 35.1362$	$J_w = -0.282854 \cdot \log(t) + 7.91341$
Będzin	$J_w = -3.72053 \cdot \log(t) + 31.7824$	$J_w = -0.389027 \cdot \log(t) + 6.52227$
Gliwice	$J_w = -2.14213 \cdot \log(t) + 24.6905$	$J_w = -0.183157 \cdot \log(t) + 7.40608$
Determination coefficient $r^2$		
Tap	0.957743	0.959282
Jaworzno	0.895493	0.898017
Będzin	0.994467	0.937019
Gliwice	0.994467	0.924129

Figs. 5 and 6 illustrate retention coefficient of  $H_{tot}$  and Cl<sup>-</sup>.

During the processes of the membrane softening, it was observed that the highest retention coefficients  $H_{tot}$  were obtained while filtering very hard waters (well water from Gliwice).

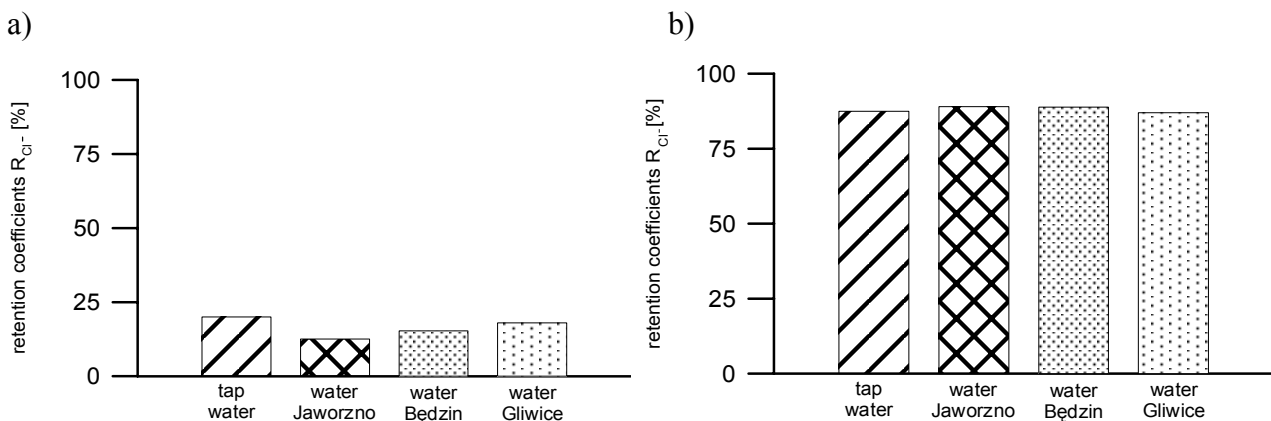
The highest values of retention coefficient of total hardness,  $H_{tot}$ , were obtained while filtering the hard waters through the DS-3-SE membrane (Fig. 5). The rejection coefficient (R) of ions contributing to the total hardness has exceeded 80% for this membrane.

Retention coefficients of  $H_{\text{Tot}}$  was  $<50\%$  for well water filtering by the use membrane DS-51-HL. This membrane can be recommended for the production of potable and household water.



**Figure 5 Retention coefficients of  $H_{\text{Tot}}$ :**  
a) membrane DS-51-HL b) membrane DS-3-SE

Analysing the parameters of the hard waters after the filtration through the DS-3-SE membrane one can state that none of them meets the requirements of the Decree because of low concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. In order to make this water potable, it might be mixed with the water treated by other (e.g. conventional) methods.



**Figure 6 Retention coefficients of  $\text{Cl}^-$  ions :**  
a) membrane DS-51-HL b) membrane DS-3-SE

The another aim of the work was the mathematical description ( of NF- and RO- process of natural waters) by use extended Nerst – Planck equation.

## CONCLUSIONS

- 1) It has been observed that DS-51-DK is a typical nanofiltration membrane and can be recommended for the production of potable and household water. The total hardness of permeate has not exceeded the permissible value for drinking water.
- 2) It has been proved the reverse osmosis process is not favourable for the production of drinking water because of too high retention of micro and macro elements. These elements are responsible for the water health virtues. The water softened on RO membranes can be mixed with the water by softened other methods.
- 3) The model based on the extended Nernst-Planck equation and the Donnan equation can quantitatively be fitted to the experimental data, however, the obtained values of

model parameters indicate that in the case of RO membranes another mechanism than the Donnan exclusion is responsible for the high retention of ions.

### List of symbols

$c_{s,f}$ ,  $c_{s,p}$  – concentrations of electrolyte in the feed and permeate ( $\text{mol}\cdot\text{m}^{-3}$ ),  
 $\bar{c}_i$ ,  $\bar{c}_m$  – concentrations of ion  $i$  and of the fixed charges (moles per  $\text{m}^3$  of pore solution),  
 $D_s$  – bulk diffusivity ( $\text{m}^2\cdot\text{s}^{-1}$ ),  
 $J_w$  – volume flux (based on membrane area) ( $\text{m}\cdot\text{s}^{-1}$ ),  
 $l_p$  – thickness of polarisation layer (m),  
 $R$  – gas constant ( $=8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  
 $T$  – absolute temperature (K),  
 $\pi$  – osmotic pressure ( $\text{N}\cdot\text{m}^{-2}$ ),  
 $\phi_f$ ,  $\phi_p$  – osmotic coefficients of the feed and permeate solutions,

### ACKNOWLEDGEMENTS

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