Available online at www.sciencedirect.com

Journal of Membrane Science 247 (2005) 11–20

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Nanofiltration of multi-component feeds. Interactions between neutral and charged components and their effect on retention

G. Bargeman[a,c,*], J.M. Vollenbroek[b,c], J. Straatsma[c], C.G.P.H. Schroën[d], R.M. Boom[d]

[a] *Akzo Nobel Chemicals Research Arnhem, P.O. Box 9300, 6800 SB Arnhem, The Netherlands*
[b] *Nestle PTC Konalfingen, 3510 Konalfingen, Switzerland*
[c] *NIZO Food Research, P.O. Box 20, 6710 BA Ede, The Netherlands*
[d] *Wageningen University, Food and Bioprocess Engineering Laboratory, P.O. Box 8129, 6700 EV Wageningen, The Netherlands*

Received 19 December 2003; received in revised form 30 May 2004; accepted 30 May 2004

Abstract

Membrane characterization and modeling of membrane processes are essential steps in the development and implementation of new membrane filtration processes. The generalized Maxwell–Stefan equation is frequently used to describe these processes. However, predictive modeling on the basis of characterization experiments using single solutes is still troublesome in a lot of cases. Consequently, a better understanding of the effect of the interaction between different components on the membrane separation characteristics is required. In this work, four well-known commercially available membranes, Desal 5DK, Desal 5DL, Desal G5, NTR-7450, and a newly introduced membrane NF have been characterized. The pore radii of these membranes determined from glucose retention experiments increase in the following sequence: Desal 5DK $\approx$ NF $<$ Desal 5DL $<$ Desal G5 $<$ NTR-7450. The pore radii and effective membrane thickness determined on the basis of glycerin experiments are within 6% of those determined using glucose. The presence of salt ions, especially of those for which the membranes show low retention, leads to reduction of the retention of neutral components (glucose). The retention reduction, at maximum 10% (absolute) in this study, depends on the membrane selected. For NF and Desal 5DK a high glucose retention drop coincides with a high concentration of the anion salt (Cl^-) ions in the permeate, independent of the cation salt ion used. This phenomenon can be explained by several hypotheses. One of these, supported by generalized Maxwell–Stefan model calculations, is that the presence of a pore size distribution leads to the observed shift in selectivity. In the presence of salt ions in the pores, the flux through small pores is reduced to a larger extent than that in bigger pores. Consequently, the retention for glucose drops and a shift in the apparent pore radius is determined. Regardless of the mechanism that causes the reduction of the glucose retention, it is essential that this effect is incorporated in predictive models for nanofiltration to predict the loss of organic components to the permeate sufficiently accurately, since this loss may affect permeate disposal costs or product yield.

Keywords: Maxwell–Stefan; Characterization; Membrane; Salt; Glucose; Glycerin

1. Introduction

Nanofiltration membranes are a relatively new class of membranes, with properties in between those of ultrafiltration (UF) and reverse osmosis (RO) membranes. These membranes are amongst others used in the food industry for the demineralization of whey and UF whey permeates [1]. The availability of a fundamental mathematical model that would predict the separation efficiency and the capacity of a nanofiltration membrane for industrial processes would facilitate the development of new processes and the design of nanofiltration installations. Several (e.g. extended Nernst–Planck and Maxwell–Stefan) models have been or are being developed for this purpose [2–10]. In these models generally steric hindrance (sieving effect), Donnan exclusion [2,3], dielectric exclusion [4,11] and/or increased solute solvation energy are assumed to be responsible for the retention of solutes by nanofiltration membranes [12].

One of the most fundamental ways to predict the transport through a nanofiltration membrane is by means of a model using the generalized Maxwell–Stefan (GMS) equations [13]. In these equations, the diffusive movement of

---

* Corresponding author. Tel.: +31 318 659565; fax: +31 318 650400.
E-mail address: gerrald.bargeman@akzonobel-chemicals.com (G. Bargeman).

0376-7388/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2004.05.022

a species is described as a result of the friction of that species with all the other components in the system. This generalized Maxwell–Stefan description attracted increased attention [8–10] after several empirical relations to calculate all the friction coefficients in a multi-component system became available in the 1990s [14–16].

The parameters required in a Maxwell–Stefan (or extended Nernst–Planck) model to describe the sieving effect and Donnan exclusion are the mean pore radius, the effective membrane thickness, and the surface charge density [2,4,5]. These parameters are usually obtained by fitting the model to solute retentions and membrane fluxes measured in membrane characterization experiments using pure water, single salt, and single sugar solutions [8]. When dielectric exclusion or changes in solvent structure are taken into account as well, the number of model parameters involved will of course increase [12].

With several models, e.g. the Maxwell–Stefan model as proposed by Straatsma et al. [8], the membrane performance for processing a solution containing a mixture of salts can be fitted well. However, generally the results cannot be predicted on the basis of the parameters obtained in membrane characterization experiments with single component solutions. Clearly, the interactions between different components and the membrane, and their effect on the separation characteristics of nanofiltration membranes, are not yet sufficiently understood [8]. In this study the membrane characteristics and the interactions between different components on the separation efficiency for five commercially available nanofiltration membranes have been investigated to get a better insight into these phenomena. Special attention has been paid to the effect of salt ions on the retention of neutral components. To evaluate the experimental results the Maxwell–Stefan model as proposed by Straatsma et al. [8] has been used. The description of concentration polarization, not used in the original Straatsma et al.'s model [8], has now been implemented.

2. Theoretical background

The Maxwell–Stefan equation of a species i, worked out for one transport direction (y) is:

$$-\frac{\mathrm{d}\mu_i}{\mathrm{d}y} - V_{\mathrm{m},i}\frac{\mathrm{d}P}{\mathrm{d}y} - z_i F\frac{\mathrm{d}\Phi}{\mathrm{d}y} = \sum_{j=1}^{n}(x_j\zeta_{i,j}(u_i - u_j)) \qquad (1)$$

Straatsma et al. [8] have applied the Maxwell–Stefan equations to the interfaces at both sides of the membrane boundary and the membrane layer itself. A fourth transport layer, a stagnant layer where concentration polarization takes place, was described mathematically, but was not yet implemented in the model [8]. The common form of the Maxwell–Stefan Eq. (1) has now been implemented in Straatsma et al.'s model [8] to describe the transport through this layer.

For the calculation of the solute concentration at the membrane surface, the layer thickness is required. This thickness strongly depends on the flow intensity along the membrane and membrane characteristics like porosity and roughness [17]. On the basis of the film model theory [18], the thickness can be calculated from:

$$Sh = \frac{kL}{D} = \frac{L}{\delta_1} \qquad (2)$$

Many empirical correlations have been proposed to calculate the Sherwood number (*Sh*) [19]. One of the most popular correlations for turbulent flow is described by [19]:

$$Sh = 0.023Re^{0.8}Sc^{0.33} \qquad (3)$$

The concentration polarization layer thickness (δ_1) calculated for the flat sheet membranes used in our experiments varied from 1×10^{-5} to 3×10^{-5} m. Because the exact flow characteristics of the membrane module used are insufficiently known and would require a separate study to determine, we have used 2×10^{-5} m as an estimate for the concentration polarization layer thickness in the updated (GMS) model for all experiments described.

As in the original Straatsma et al.'s model the membrane charge Q_m has been calculated using the Freundlich isotherm [8]:

$$Q_\mathrm{m} = Q_0\left(\sum_i |z_i|\, x_i\right)^{K_\mathrm{s}} \qquad (4)$$

3. Experimental work

3.1. Membranes

Retention experiments were carried out with five different commercially available nanofiltration membranes (Desal 5DK, Desal 5DL, Desal G5, NF, and NTR-7450). Desal 5DK and Desal 5DL (Osmonics, USA) are three-layer thin film polysulfone based membranes with a polyamide top layer. Desal G5 (Osmonics, USA) is a two-layer thin film polysulfone based membrane with a polyamide top layer. NF (DOW Chemicals, USA) is a three-layer polysulfone based membrane with a polypiperazine top layer. This membrane was introduced recently and replaces the well known NF-45 and NF-70 membranes. NTR-7450 (Nitto Denko, Shiga, Japan) is a sulfonated polyethersulfone membrane. The molecular weight cut-offs (MWCO) of these membranes as reported by the suppliers are listed in Table 1.

3.2. Model solutions

The neutral solutes used in the experiments were glucose (Brunschwig Chemie, The Netherlands) and glycerin (Sigma, USA). The salts used were NaCl, KCl, and $CaCl_2$ (Merck, Germany). The properties of the neutral solutes and the salts are listed in Table 2. All feeds used in the test were obtained by dissolving these components in RO permeate of tap water (see Section 3.5).

Table 1
Molecular weight cut-off (MWCO) of nanofiltration membranes as reported by suppliers

Membrane	MWCO (Da)
Desal 5DK	200
Desal 5DL	400
Desal G5	1000
NF	<200
NTR-7450	1000

3.3. Apparatus

Retention experiments were carried out using a DDS Lab 20 unit as described by van der Horst et al. [7]. The experiments were performed in batch circulation mode, recycling both the retentate and permeate to the feed tank. Four membranes at maximum were placed in series, each membrane having a surface area of 0.036 m^2. From top to bottom in the module the following membranes were installed: Desal 5DK, NF, Desal 5DL, and NTR-7450. Desal G5 was tested separately. The solute concentrations in the feed to the last membrane in the series, as determined on the basis of mass balance and solute balance calculations, differed by less than 2% from those of the feed to the first membrane in the series. Furthermore the cross-flow velocity was practically constant throughout the module (see Section 3.5). Therefore the position of the membrane in the module had no significant effect on the results obtained.

3.4. Analyses

Glucose concentrations were measured with a polarimeter from Perkin-Elmer. Glycerin concentrations were analyzed by HPLC using a Carbohydrates-Pb column (Varian) and refractive index detection. The salt concentrations were analyzed by conductivity measurements with a Metrohm conductometer.

3.5. Experimental conditions

Prior to the experiments the membranes were pre-compacted by increasing the pressure to 40 bar and maintaining circulation operation at this pressure, until the flux of the individual membranes remained constant for at least 30 min. During pre-compaction at a temperature of 20 °C, RO permeate of tap water was used as feed.

Table 2
Diffusivities and Stokes radii of ions and neutral solutes

Ions/solutes	AW or MW ($g\,mol^{-1}$)	D_∞ ($m^2\,s^{-1}$) × 10^{-9}	r_s (nm)
K^+	39.1	1.95	0.125
Na^+	23	1.33	0.161
Cl^-	35.5	2.03	0.106
Ca^{2+}	40	0.78	0.233
Glycerin	92	0.81	0.264
Glucose	180	0.60	0.360

AW: atomic weight, MW: molecular weight.

The temperature and cross-flow velocity during all experiments were 20.0 ± 0.5 °C and 0.9 $m\,s^{-1}$, respectively. Since the combined permeate flow of the membranes was always less than 5% of the retentate flow, the cross-flow velocity was practically equal for all membranes. The pressure-drop along the module was below 0.1 MPa in all cases.

Pure water fluxes were measured using RO permeate of tap water to determine the permeability of individual membranes. The pressure was varied between 0.2 and 4.0 MPa.

Retention experiments were carried out at outlet pressures ranging from 0.2 to 3 MPa. After each pressure adjustment, at least 30 min was allowed for equilibrium to be reached. At each pressure, the temperature, permeate flux, and permeate composition were determined.

Retention experiments with solutions containing neutral components (glucose or glycerin) were carried out to determine, in combination with the results of the pure water flux experiments, the pore radius and the effective thickness of the membranes. Feed solutions contained 1.5 $g\,kg^{-1}$ glucose or 3 $g\,kg^{-1}$ glycerin. The glucose concentrations of the permeates and retentate were measured (see Section 3.4) directly and the samples were put back in the feed tank to keep the feed composition unchanged. To investigate whether the two neutral solutes would affect each other's retention, an experiment with 1.5 $g\,kg^{-1}$ glucose and 1.5 $g\,kg^{-1}$ glycerin was carried out.

To investigate the influence of the presence of salts on the glucose retention, experiments were carried out using feeds with a glucose concentration of 1.5 $g\,kg^{-1}$ in combination with NaCl, $CaCl_2$ or KCl. The salt concentrations used in these tests were 0.01–1.0, 0.005–0.05, and 0.1 M for NaCl, $CaCl_2$, and KCl, respectively. During the entire set of experiments only one flat sheet per membrane type was used. Prior to the experiments with different solutions pure water fluxes of the individual membranes were determined at 1 and 2 MPa to evaluate whether the membrane had changed or fouling had occurred during the previous experiment. Since the variation in the pure water flux of the individual membranes was 10% at maximum (and in most cases far less) during the entire experimental program, it is assumed that the condition of the membranes did not change significantly. Furthermore, the variation in the pure water flux of the individual membranes did not show a specific (e.g. reducing) trend with progressing of the experimental program, apart from NTR-7450, for which a gradual reduction of the pure water flux with progressing of the run was observed.

4. Results and discussion

4.1. Pure water permeabilities of the membranes

On the basis of pure water flux measurements, the permeabilities determined for NTR-7450, Desal 5DL, NF, De-

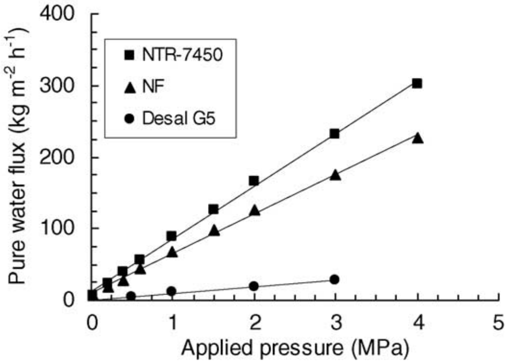

Fig. 1. Pure water flux as a function of the applied pressure.

sal 5DK, and Desal G5 are $2.05\cdot\times\ 10^{-11}$, $1.58\cdot\times\ 10^{-11}$, $1.53\cdot\times\ 10^{-11}$, $1.42\cdot\times\ 10^{-11}$, and $0.25\cdot\times\ 10^{-11}\ \mathrm{m\,s^{-1}\,Pa^{-1}}$, respectively (see Fig. 1 for pure water permeabilities of NTR-7450, NF, and Desal G5). The pure water permeability obtained for Desal 5DK is reasonably in line with those reported by Bowen and Mohammad [20] and Straatsma et al. [8]. Hagmeyer and Gimbel [4] presented permeabilities for Desal 5DK that are more in line with those of Desal 5DL as found by Bowen and Mohammad [20] and in this study (see Table 3). The pure water permeability determined in this study for NTR-7450 is around 30% lower than that reported by Bowen and Mohammad [20]. Schaep et al. [21] presented a pure water permeability 2.5 times higher than that found by Bowen and Mohammad. Possible explanations for these differences in pure water permeabilities may be differences in pre-compaction procedures of the membranes (not always presented by the various authors), measurement of the pure water permeability at only one pressure in other studies, the module configuration used and the representativeness of the small membrane sheets used.

4.2. Membrane characterization using uncharged solutes

The glucose retentions for Desal 5DK, NF, and Desal 5DL are significantly higher than those for Desal G5 and NTR-7450 (Figs. 2 and 3), as expected on the basis of the MWCO values reported by the suppliers for these membranes (see Table 1). Surprisingly, there is a significant difference in glucose retention between Desal G5 and NTR-7450, despite the similar MWCO (1 kDa) as reported by their suppliers.

Table 3
Pure water permeabilities reported for Desal 5DK, Desal 5DL, and NTR-7450

Membrane	Pure water permeability ($\mathrm{m\,s^{-1}\,Pa^{-1}}$)	Reference
Desal 5DK	$1.4\cdot\times\ 10^{-11}$	Bowen and Mohammad [20]
Desal 5DK (first batch)	$2.2\cdot\times\ 10^{-11}$	Hagmeyer and Gimbel [4]
Desal 5DK (second batch)	$1.7\cdot\times\ 10^{-11}$	Hagmeyer and Gimbel [4]
Desal 5DK	$1.3\cdot\times\ 10^{-11}$	Straatsma et al. [8]
Desal 5DK	$1.5\cdot\times\ 10^{-11}$	This work
Desal 5DL	$2.1\cdot\times\ 10^{-11}$	Bowen and Mohammad [20]
Desal 5DL	$1.6\cdot\times\ 10^{-11}$	This work
NTR-7450	$2.6\cdot\times\ 10^{-11}$	Bowen and Mohammad [20]
NTR-7450	$6.4\cdot\times\ 10^{-11}$	Schaep et al. [21]
NTR-7450	$2.1\cdot\times\ 10^{-11}$	This work

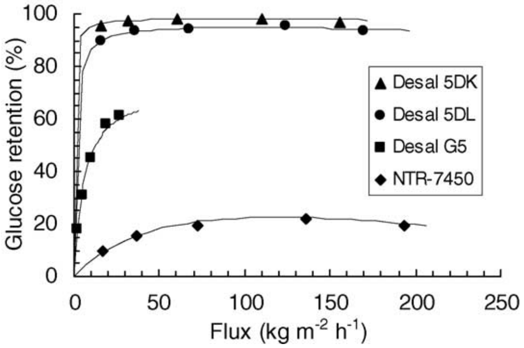

Fig. 2. Glucose retention as a function of flux for Desal 5DK, Desal 5DL, Desal G5, and NTR-7450. Symbols are measured results; lines are model fitted curves.

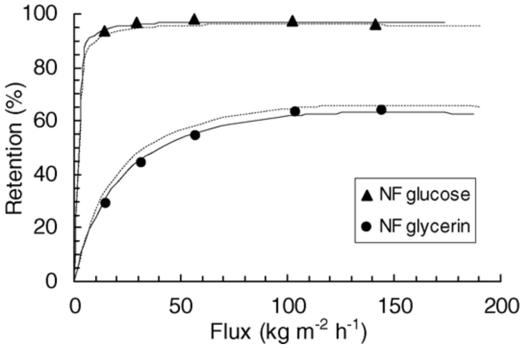

Fig. 3. The retention of the NF membrane for glucose and glycerin as a function of the permeate flux. Uninterrupted lines are based on the fitted r_p and δ_m. Dashed lines are model predictions based on the r_p and δ_m fitted for the other component.

The mean pore size (r_p) and the effective membrane thickness ($\delta_m = d_m\tau/\varepsilon$) for the membranes, calculated through fitting of the experimental flux and glucose retention results using the four layer (including concentration polarization) GMS model, are listed in Table 4. In this fitting procedure the effect of the membrane charge and the electrical forces on the transport of this neutral component are neglected ($z_i = 0$

Table 4
Results of membrane characterization with uncharged solutes

Membrane	Glucose		Glycerin	
	r_p (nm)	δ_m (μm)	r_p (nm)	δ_m (μm)
NTR-7450	1.34	11.69	–	–
Desal G5	0.84	40.54	–	–
Desal 5DL	0.45	2.54	–	–
NF	0.43	2.47	0.44	2.62
Desal 5DK	0.42	2.59	0.44	2.74

in Eq. (4)). Desal 5DK and NF have the smallest pore size, whereas Desal 5DL appears to be slightly more open. The effective membrane thickness for these three membranes is practically equal. The high flux of Desal 5DL as compared to Desal 5DK and NF is therefore mainly due to the bigger main pore radius of Desal 5DL. The fitted mean pore radius and effective membrane thickness for Desal 5DK and NF as obtained from glycerin retention experiments deviate by less than 6% from those determined on the basis of glucose experiments (see Table 4). The retention data for NF using a solution containing 1.5 g kg^{-1} glucose and a solution containing 3.0 g kg^{-1} glycerin are shown in Fig. 3. The continuous lines are the fitted flux retention curves for glycerin and glucose resulting in the r_p and δ_m as listed in Table 4. The dashed lines show the model predictions for the uncharged solutes on the basis of the r_p and δ_m determined using the other uncharged solute. As can be seen from Fig. 3, the solute retention can be predicted sufficiently accurately, even when a pore radius and effective membrane thickness determined for the other neutral solute are used. The marginal difference in the membrane characteristics found from the glucose and glycerin characterization may be due to a slight deviation of the actual Stokes radius for glucose and/or glycerin from the theoretical values as given in Table 2.

The mean pore radius determined for Desal 5DK is slightly lower (0.42 nm versus 0.46 nm) than previously reported by Straatsma et al. [8], using their three-layer model. The current result is considered to be more accurate, since more experimental data points were used, especially at relatively low fluxes, and concentration polarization is now taken into account. Bowen and Mohammad [20] reported pore radii for Desal 5DK and Desal 5DL in excess of 0.5 nm. In their estimation the pore size was based on an assumed MWCO for these membranes of 225 Da. Furthermore, concentration polarization was not taken into account in their calculation.

Desal G5 and NTR-7450, both reported by the manufacturers to have a MWCO of 1 kDa, are the most open membranes. Desal G5 has a very low permeate flux compared to NTR-7450. This is partly caused by a lower mean pore size, but mainly by a much higher effective membrane thickness (see Table 4). The mean pore radius for NTR-7450 is slightly lower than that reported by Bowen and Mohammad ($r_p = 1.41$ nm [20]). Schaep et al. [21] reported mean pore radii for NTR-7450 of 0.55, 0.71, and 0.80 nm for solutions containing galactose, maltose, and raffinose, respectively. Timmer et al. reported a lower pore radius for NTR-7450 (0.76 nm [22] and 0.82 nm [23]) on the basis of Paselli MD6 (glucose polymers with a sugar radius between 0.5 and 1.2 nm) solution experiments and using the well-known Ferry equation. Also Wang et al. [24] reported a pore radius (0.70 nm) more in line with that found by Timmer et al. [22] and Schaep et al. [21]. The reason for the large spread in reported pore radii is not known.

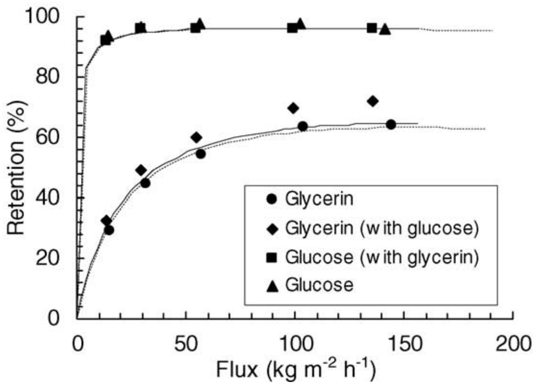

Fig. 4. Measured (symbols) and predicted glycerin and glucose retention for NF. Predicted values for single sugar (glycerin or glucose) solutions presented with dashed lines; predicted values for mixed sugar (glycerin and glucose) solutions presented with full lines.

4.3. *Prediction of retention for a solution containing glycerin and glucose*

The glucose and glycerin retention for NF and Desal 5DK predicted for a 1.5 g kg^{-1} glucose solution, a 3.0 g kg^{-1} glycerin solution, and a solution containing 1.5 g kg^{-1} glucose and 1.5 g kg^{-1} glycerin on the basis of average pore radius and effective membrane thickness as determined using a 3.0 g kg^{-1} glycerin solution are shown in Figs. 4 and 5, respectively. For both membranes the measured glucose retention with or without glycerin being present in the solution is predicted well by the model. This retention is hardly influenced by the presence of glycerin (see Figs. 4 and 5). The glycerin retention appears to be higher when part of the glycerin is replaced by glucose. The model predicts a higher glycerin retention, since the friction between glycerin and glucose in the solution and in the membrane pores is higher than the friction between individual glycerin molecules, but the observed difference is higher than predicted by the model, especially for NF.

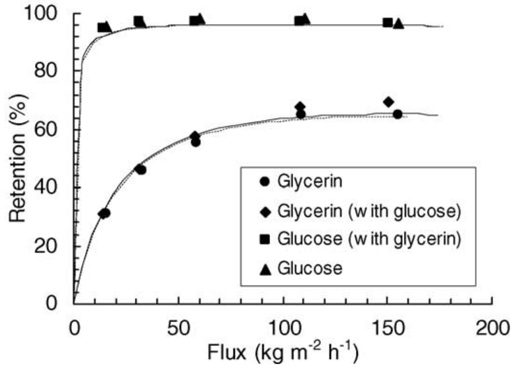

Fig. 5. Measured (symbols) and predicted glycerin and glucose retention for Desal 5DK. Predicted values for single sugar (glycerin or glucose) solutions presented with dashed lines; predicted values for mixed sugar (glycerin and glucose) solutions presented with full lines.

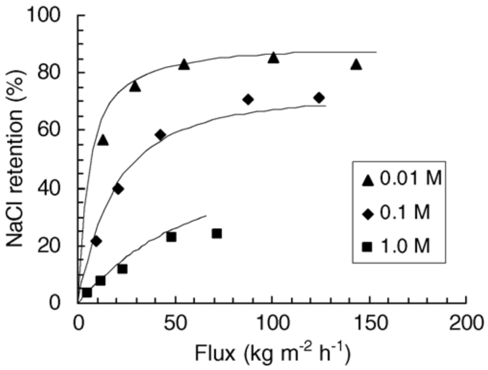

Fig. 6. NaCl retention for NF as a function of flux at different NaCl concentrations in the presence of 0.15% glucose, using $Q_0 = -1.9 \cdot \times 10^4\,\mathrm{mol\,m^{-3}}$, and $K_s = 0.17$. Lines represent model predictions.

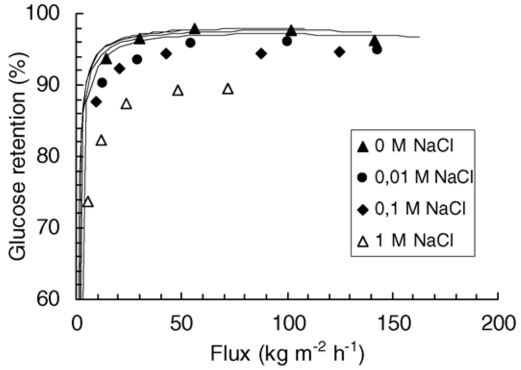

Fig. 7. Glucose retention for NF as function of the flux for feeds containing glucose and NaCl with different NaCl concentrations (see legends). Continuous lines are model predictions using $r_p = 0.43\,\mathrm{nm}$, $Q_0 = -1.9 \cdot \times 10^4\,\mathrm{mol\,m^{-3}}$, and $K_s = 0.17$.

4.4. *The effect of salt on glucose retention*

The effect of the presence of salt in the feed solution on the membrane characteristics for NF, Desal 5 DK and NTR-7450 was determined by measuring glucose retentions in the presence of different salts and using different salt concentrations. The salt retentions were measured as well, to determine the charge characteristics of the membrane, required for the prediction of the glucose retention in the presence of salt. Generally, the NaCl retention decreases with increasing salt concentration (see, e.g. Fig. 6). The Freundlich parameters Q_0 and K_s (see Section 2) fitted for each membrane using the mean pore size obtained from glucose experiments without salt (Table 4) are summarized in Table 5. The measured NaCl retentions could be fitted well (see Fig. 6 for the fit results for NF).

The measured glucose retentions for NF using a $1.5\,\mathrm{g\,kg^{-1}}$ glucose feed solution with different NaCl concentrations are compared with model predictions (using $r_p = 0.43\,\mathrm{nm}$, $\delta_m = 2.47\,\mu\mathrm{m}$, $Q_0 = -1.9 \cdot \times 10^4\,\mathrm{mol\,m^{-3}}$, and $K_s = 0.17$) in Fig. 7. The model predicts the observed flux decrease when higher salt concentrations are used (see Table 6); however, calculated fluxes still deviate by up to around 20% from measured flux values. An increase in salt concentration increases the membrane charge density and consequently the friction between the components (including water) in the membrane. This results in a lower flux. On the basis of the model predictions it is expected that an increase in NaCl concentration would cause a slight increase of the glucose retention (see Fig. 7). However, the experimental results show an opposite effect. Not only the salt retention, but also the glucose retention gradually decreases with increasing NaCl concentration. For a feed solution containing 1.0 M NaCl, the decrease in glucose retention, as compared to a solution without NaCl, is as high as 10%.

Table 5
Freundlich parameters used in the model

Membrane	Salt	Q_0 ($\mathrm{mol\,m^{-3}}$)	K_s
Desal 5DK	NaCl	-3.5×10^4	0.3
	KCl	-4.1×10^4	0.3
	$CaCl_2$	5.5×10^6	0.6
NF	NaCl	-1.9×10^4	0.17
	KCl	-2.1×10^4	0.17
	$CaCl_2$	1.6×10^5	0.6
NTR-7450	NaCl	-1.9×10^3	0.16
	KCl	-1.5×10^3	0.16
	$CaCl_2$	-1.3×10^3	0.16

The decrease in glucose retention at increasing NaCl concentration can only be described accurately by adjusting the value of the mean pore size of the membranes in the model. The fitted values for the mean pore size and the effective membrane thickness for the different membranes at different NaCl concentrations are shown in Table 7. For all three membranes tested the fitted pore sizes increase when the NaCl concentration is increased. For NTR-7450 this increase in pore size is relatively large, whereas for Desal 5DK only a minor increase is found, since the glucose retention for the latter membrane is less dependent on the salt content of the feed. Vellenga and Trägård [25] also studied the effect of combined sugar and salt solutions on the sugar retention for Desal 5 (DS5). They did not observe any effect of the presence of NaCl on the sugar retention for Desal 5. This may seem to contradict with the results found in this study, however it should be noted that they used sucrose/NaCl mixtures in their study. Sucrose has a higher molecular weight than glucose and therefore shows much higher retention. It is therefore expected that a slight increase in mean pore size as

Table 6
Measured and predicted (using $r_p = 0.43\,\mathrm{nm}$, $Q_0 = -1.9 \cdot \times 10^4\,\mathrm{mol\,m^{-3}}$ and $K_s = 0.17$) fluxes for NF at $P = 30\,\mathrm{bar}$

NaCl concentration (M)	Predicted flux ($\mathrm{kg\,m^{-2}\,h^{-1}}$)	Measured flux ($\mathrm{kg\,m^{-2}\,h^{-1}}$)	Deviation (%)
0	163	141	−16
0.01	140	143	2
0.1	108	124	13
1.0	55.2	71.9	23

Table 7
Results of membrane characterization with 1.5 g kg^{-1} glucose in the presence of different NaCl concentrations

NaCl concentration (M)	NTR-7450		NF		Desal 5DK	
	r_p (nm)	δ_m (μm)	r_p (nm)	δ_m (μm)	r_p (nm)	δ_m (μm)
0	1.34	11.7	0.43	2.47	0.42	2.59
0.01	1.70	18.4	0.45	2.62	0.43	2.66
0.1	2.30	33.0	0.46	2.69	0.43	2.66
1.0	2.25	31.7	0.48	2.84	0.44	2.74

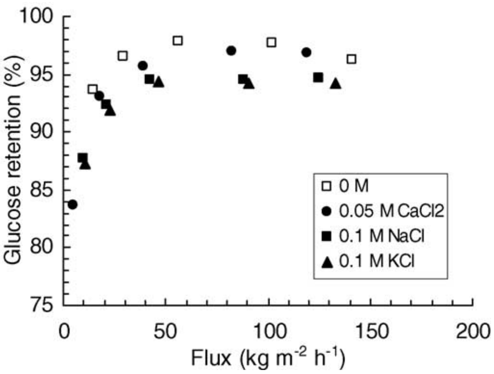

Fig. 8. Glucose retention for feeds containing, apart from 0.15% glucose, different salts (see legends) as function of the flux for NF.

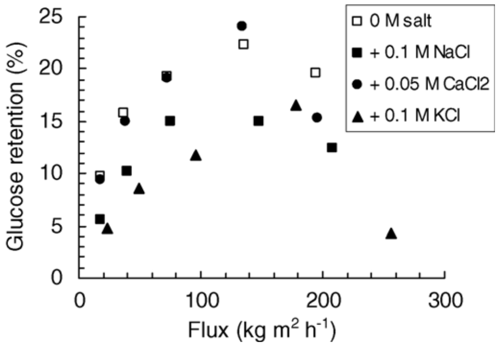

Fig. 9. Glucose retention for feeds containing, apart from 0.15% glucose, different salts (see legends) as function of the flux for NTR-7450.

consequence of an increased amount of NaCl in the feed (as found for Desal 5DK in this study) affects the glucose retention to a larger extend than the sucrose retention. Since the glucose retention for Desal 5DK only changed little when 1.0 M NaCl was added to the solution, an unchanged sucrose retention would not be unexpected. Vellenga and Trägård [25] also reported that the observed high retention of sucrose could have hidden influences on transport phenomena.

When glucose solutions containing $CaCl_2$ or KCl are used, a reduction of the glucose retention as compared to a situation where salt is absent is also observed (see Figs. 8 and 9 for NF and NTR-7450, respectively). In the presence of 0.05 M $CaCl_2$ this reduction is small for NF, whereas for 0.1 M KCl the decline in glucose retention (approximately 5%) is only marginally higher than that found for a glucose solution containing 0.1 M NaCl. For NTR-7450 a similar pattern is observed. The presence of 0.05 M $CaCl_2$ in the 0.15% glucose solution hardly affects the glucose retention, whereas the presence of 0.1 M KCl in the 0.15% glucose solution reduces the glucose retention to 50% of the retention found for the 0.15% glucose solution that does not contain any salt. The mean pore size and the effective membrane thickness, fitted on the basis of glucose retention in the presence of different salts at equal chloride concentration in the feed, are summarized in Table 8.

For all three membranes addition of salts result in an increase in the fitted mean pore size (r_p) as compared to the mean pore size fitted with only glucose. The smallest effect is seen in the presence of $CaCl_2$. For Desal 5DK only a minor increase is observed for all three salts. Simultaneously measured salt retentions for NF using solutions containing 1.5 g kg^{-1} glucose and 0.1 M Cl^- are shown in Fig. 10. The $CaCl_2$ retention for NF is considerably higher than that for NaCl and KCl. Since the glucose retention reduction, when $CaCl_2$ is added to the solution, is relatively low as compared to addition of NaCl and KCl, apparently there is a positive correlation between the glucose and salt retention (Figs. 8 and 10) at similar Cl^- concentration in the feed. Independent of the Cl^- concentration in the feed and the type of cation used, for NF and Desal 5DK the decline in glucose retention (and consequently the fitted mean pore radius) appears to correlate well with the Cl^- concentration

Table 8
Results of membrane characterization with 1.5 g kg^{-1} glucose in the presence of different salts

Salt	NTR-7450		NF		Desal 5DK	
	r_p (nm)	δ_m (μm)	r_p (nm)	δ_m (μm)	r_p (nm)	δ_m (μm)
0.1 M NaCl	2.30	33.0	0.46	2.69	0.43	2.66
0.05 M $CaCl_2$	1.45	13.6	0.44	2.54	0.43	2.66
0.1 M KCl	>3	>55	0.47	2.77	0.44	2.74

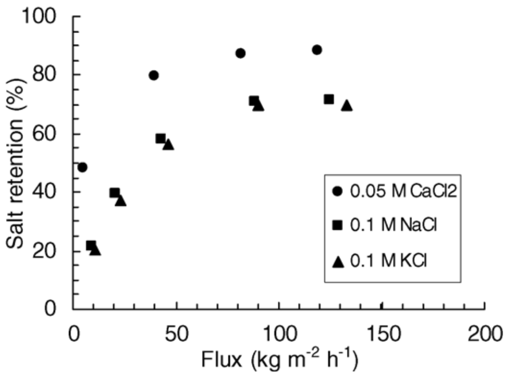

Fig. 10. The salt retention for different salts as a function of the flux for NF using feeds containing salt and 0.15% glucose.

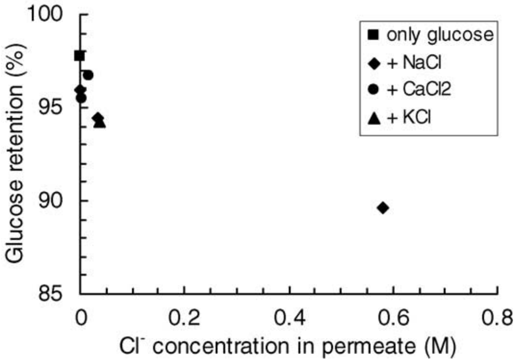

Fig. 11. Glucose retention as a function of the chloride concentration in the permeate for NF at $J = 75 \pm 5\,\mathrm{kg\,m^{-2}\,h^{-1}}$ using feeds containing either glucose, glucose with KCl, glucose with NaCl or glucose with $CaCl_2$ (see legends).

in the permeate (see Fig. 11 for NF and Fig. 12 for Desal 5DK, where glucose retentions at a permeate flux of 75 ± 5 $\mathrm{kg\,m^{-2}\,h^{-1}}$ are shown as a function of the Cl^- concentration in the permeate). For both NF and Desal 5 DK the presence of relatively low Cl^- concentrations in the permeate already leads to a significant decrease of the glucose retention. For NTR-7450, the relation between glucose retention and Cl^- concentration in the permeate, as found for NF and Desal 5DK, is less evident. The Cl^- concentration in the permeate increases when KCl is used instead of NaCl, giving lower glucose retention (see Fig. 9), as for the other two membranes (see Figs. 10 and 11). However, for a glucose solution containing 0.05 M $CaCl_2$ a relatively low Cl^- concentration in the permeate, as compared to those for 0.1 M NaCl and 0.1 M KCl containing solutions, is found at low flux only. At high flux operation relatively low $CaCl_2$ retention and consequently relatively high Cl^- concentrations in permeate (as compared to those for NaCl and KCl) are found. Despite these high Cl^- concentrations in permeate the glucose retention is hardly different from that found for the glucose feed without salt added (see Fig. 9).

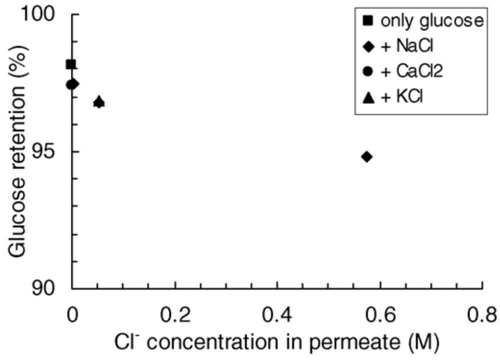

Fig. 12. Glucose retention as a function of the chloride concentration in the permeate for Desal 5DK at $J = 75 \pm 5\,\mathrm{kg\,m^{-2}\,h^{-1}}$ using feeds containing either glucose, glucose with KCl, glucose with NaCl or glucose with $CaCl_2$ (see legends).

Several hypothetical explanations can be given for the observed effect of salt on glucose retention. Two of these will be discussed in more detail. The presence of high salt concentrations in the pores of the membrane generally results in a higher surface charge in the membrane pores, as predicted by the model. Furthermore, a higher concentration of counter-ions will be present in the electrical double layer in the pores. The higher repulsion forces, due to the presence of these charges, may result in swelling of the pores (higher pore radii) and consequently lead to reduced retention of neutral components. An exception in swelling behavior may be NTR-7450. Schaep et al. [3] found that the charge of this membrane was very low and practically independent of the concentration of the di-valent cation, using feed solutions with $MgCl_2$ concentrations ranging between 25 and 375 $\mathrm{mol\,m^{-3}}$. The membrane was charged and this charge depended on the concentration when a feed solution containing a monovalent cation (50–750 $\mathrm{mol\,m^{-3}}$ NaCl) was used. Provided that the use of $CaCl_2$ shows the same behavior as $MgCl_2$, the relatively low membrane charge and consequently similar swelling behavior as for glucose solutions without salt added, may explain the unchanged glucose retention when $CaCl_2$ is added to the glucose solution and the relatively large change in glucose retention when KCl or NaCl are added to the glucose solution.

Another hypothetical explanation is that the observed phenomenon is caused by the presence of a pore size distribution in the membrane. When salt is added to the feed, the flux of the membrane is reduced. The effect of the addition of 1.0 M NaCl on the reduction of the flux as compared to a situation where no NaCl is present in the feed is shown in Figs. 13 and 14 for NF with varying pore radius. One case (see Fig. 13) represents a situation where the membrane charge per volume Q_0 was assumed to be independent of the pore radius, whereas the other (more likely) case (see Fig. 14) assumes that the membrane charge per surface area of the pore ($Q_{a,0} = r_p Q_0/2$) is independent of the pore radius. As can be seen from Figs. 13 and 14, this flux decrease as a consequence of salt addition is relatively high for low pore radii. Consequently, the larger pores contribute more to the permeate flux when a feedstock containing salt is used. Since these larger pores have lower glucose retention than

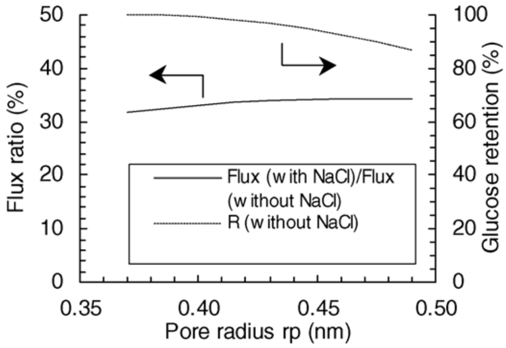

Fig. 13. The calculated effect of the pore radius on the flux ratio (the flux in the presence of 1.0 M NaCl over the flux without the presence of NaCl) and glucose retention (without NaCl) for NF at $P = 30$ bar using a 0.15% glucose solution, assuming Q_0 to be independent of the pore size.

the smaller pores (see Figs. 13 and 14), reduced glucose retention is possible and consequently a shift in the apparent pore radius to higher values may result. A similar effect of the pore size distribution on retention has been reported by Bowen and Welfoot [26].

Regardless of the possible explanation, the observed effect of salts on the retention of uncharged solutes can be of great importance for several industrial applications, e.g. the desalination of carboxymethylinulin [27]. When the effect of salt on the retention of uncharged product components during desalting using a nanofiltration membrane is not taken into account properly in the selection of the membrane, higher than anticipated product losses and permeate discharge costs may be encountered. Therefore, for industrial application studies the effect of salt on the retention of neutral components has to be incorporated in the model predictions or application tests with the industrial feed, under conditions where only interpolation of the results is required to predict commercial operation, should be carried out.

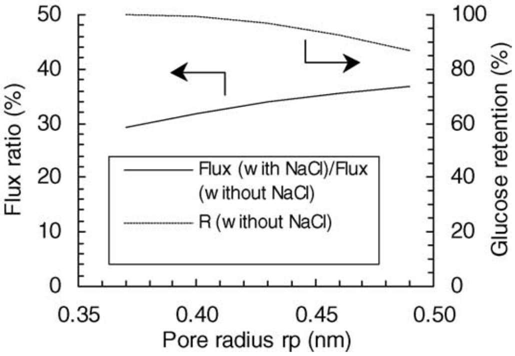

Fig. 14. The calculated effect of the pore radius on the flux ratio (the flux in the presence of 1.0 M NaCl over the flux without the presence of NaCl) and glucose retention (without NaCl) for NF at $P = 30$ bar using a 0.15% glucose solution, assuming $Q_{a,0}$ to be independent of the pore size.

5. Conclusions

For nanofiltration membranes the addition of salt ions to a glucose solution can result in reduction of the glucose retention. This reduction is membrane specific and furthermore depends on the retention of the salt ion added. A low salt ion retention results in a higher decrease in glucose retention. For addition of NaCl, $CaCl_2$, and KCl, the retention drop is a function of the Cl^- concentration in the permeate for Desal 5DK and NF. This function is independent of the cation used. The observed effect is important for prediction of membrane performance during the demineralization of sugar solutions. However, it is not well described by a predictive model on the basis of the Maxwell–Stefan equation, which uses only pore size exclusion, Donnan exclusion, and average pore size to describe the separation process.

The reduced glucose retention in the presence of salt can be described well when the pore radius value substituted in the model is increased. Several hypotheses are available to explain the observed phenomenon. An example is that the glucose retention reduction is caused by an increased effective average pore size, as a consequence of higher repulsion forces between the double layers in the pores when the concentration of ions and therefore the membrane charge, as is predicted by the model, is increased. Another possible explanation is the presence of a pore size distribution. The Maxwell–Stefan model shows that the addition of salt with relatively low retention reduces the flux of the small pores to a higher extent than the larger pores. Thus the retention of glucose is determined to a larger extent by the larger pores and reduces when salt is added. This explains why in experiments where salts with low retention characteristics are present, the glucose retention drop is relatively large and a larger pore size estimate in the Maxwell–Stefan model is required to predict the glucose retention more accurately.

Nomenclature

d_m	thickness of the membrane layer (m)
D_∞	diffusion coefficient ($m^2\,s^{-1}$)
F	Faraday constant ($C\,mol^{-1}$)
J	permeate flux ($kg\,m^{-2}\,h^{-1}$)
J_w	pure water permeate flux ($kg\,m^{-2}\,h^{-1}$)
k	mass transfer coefficient ($m\,s^{-1}$)
K_s	model constant Freundlich equation
L	length (m)
P	pressure (Pa)
Q_0	model constant Freundlich equation ($mol\,m^{-3}$)
$Q_{a,0}$	membrane charge constant based on pore surface area ($mol\,m^{-2}$)
Q_m	membrane charge concentration based on pore volume ($mol\,m^{-3}$)

r_s	Stokes radius of ions and solutes (m)
R	rejection (%)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
u	diffusive velocity ($\mathrm{m\,s^{-1}}$)
V_m	molar volume ($\mathrm{m^3\,mol^{-1}}$)
x	mole fraction
y	co-ordinate in the membrane (m)
z	ion valence

Greek letters

δ_l	thickness concentration polarization layer (m)
δ_m	effective membrane thickness (m)
ε	membrane porosity
Φ	electrical potential ($\mathrm{J\,C^{-1}}$)
μ	chemical potential ($\mathrm{J\,mol^{-1}}$)
τ	membrane tortuosity
ζ	diffusive friction coefficient ($\mathrm{kg\,s^{-1}\,mol^{-1}}$)

Subscripts

i	ith component
j	jth component

References

[1] G. Bargeman, M.J.K. Timmer, H.C. van der Horst, Applications in the food industry, in: A. Schaefer, A.G. Fane, T.D. Waite (Eds.), Nanofiltration—Principles and Applications, Elsevier, Amsterdam, 2003, accepted for publication.

[2] W.R. Bowen, A.W. Mohammad, N. Hilal, Characterization of nanofiltration membranes for predictive purposes—use of salts, uncharged solutes and atomic force microscopy, J. Membr. Sci. 126 (1997) 91.

[3] J. Schaep, C. Vandecasteele, A.W. Mohammad, W.R. Bowen, Modelling the retention of ionic components for different nanofiltration membranes, Sep. Purif. Technol. 22–23 (2001) 169.

[4] G. Hagmeyer, R. Gimbel, Modelling the salt rejection of nanofiltration membranes for ternary ion mixtures and for single salts at different pH values, Desalination 117 (1998) 247.

[5] W.R. Bowen, H. Mukhtar, Characterization and prediction of separation performance of nanofiltration membranes, J. Membr. Sci. 112 (1996) 263.

[6] Y. Garba, S. Taha, N. Gondrexon, G. Dorange, Ion transport modelling through nanofiltration membranes, J. Membr. Sci. 160 (1999) 187.

[7] H.C. van der Horst, J.M.K. Timmer, T. Robbertsen, J. Leenders, Use of nanofiltration for concentration and demineralization in the dairy industry: model for mass transport, J. Membr. Sci. 104 (1995) 205.

[8] J. Straatsma, G. Bargeman, H.C. van der Horst, J.A. Wesselingh, Can nanofiltration be fully predicted by a model? J. Membr. Sci. 198 (2002) 273.

[9] T.R. Noordman, P. Vonk, V.H.J.T. Damen, R. Brul, S.H. Schaafsma, M. de Haas, J.A. Wesselingh, Rejection of phosphates by a ZrO_2 ultrafiltration membrane, J. Membr. Sci. 135 (1997) 203.

[10] T.R. Noordman, High flux membrane filtration, Ph.D. thesis, University of Groningen, 1994.

[11] A.E. Yaroshchuk, Dielectric exclusion of ions from membranes, Adv. Coll. Interface Sci. 85 (2000) 193.

[12] A.E. Yaroshchuk, V. Ribitsch, The use of trace ions for advanced characterization of transport properties of NF membranes in electrolyte solutions: theoretical analysis, J. Membr. Sci. 5149 (2001) 1.

[13] E.A. Mason, H.K. Lonsdale, Statistical–mechanical theory of membrane transport, J. Membr. Sci. 51 (1990) 1.

[14] J.A. Wesselingh, R. Krishna, Mass Transfer, Ellis Horwood, Chichester, UK, 1990.

[15] J.A. Wesselingh, P. Vonk, G. Kraaijeveld, Exploring the Maxwell–Stefan description of ion exchange, Chem. Eng. J. 57 (1995) 75.

[16] J.A. Wesselingh, A.M. Bollen, Multicomponent diffusitives from the free volume theory, Trans. IChemE 75A (1997) 590.

[17] P. Vonk, Diffusion of large molecules in porous structures, Ph.D. thesis, University of Groningen, Groningen, The Netherlands, 1994.

[18] R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, Wiley, New York, 1960.

[19] V. Gekas, B. Hallström, Mass transfer in the membrane concentration polarisation layer under turbulent cross-flow. Part 1. Critical literature review and adaptation of existing Sherwood correlations to membrane operations, J. Membr. Sci. 30 (1987) 153.

[20] W.R. Bowen, A.W. Mohammad, Characterization and prediction of nanofiltration membrane performance—a general assessment, Trans. IChemE 76A (1998) 885.

[21] J. Schaep, C. VandeCasteele, A.W. Mohammad, W.R. Bowen, Analysis of the salt retention of nanofiltration membranes using the Donnan-steric partitioning pore model, Sep. Sci. Technol. 34 (1999) 3009.

[22] J.M.K. Timmer, M.P.J. Speelmans, F. Donkers, H.C. van der Horst, Mass transfer of amino acids through nanofiltration membranes, in: A.J.B. Kemperman, G.H. Koops (Eds.), Progress in Membrane Science and Technology, Book of Abstracts, Euromembrane'97, Enschede, The Netherlands, 22–27 June 1997, Dinkeldruk Oldenzaal, The Netherlands, p. 459.

[23] J.M.K. Timmer, Properties of nanofiltration membranes model development and industrial application, Ph.D. thesis, Technical University of Eindhoven, Eindhoven, The Netherlands, 2001.

[24] X.-L. Wang, T. Tsuru, M. Togoh, S.-I. Nakao, S. Kimura, Evaluation of pore structure and electrical properties of nanofiltration membranes, J. Chem. Eng. Jpn. 28 (1995) 186.

[25] E. Vellenga, G. Trägårdh, Nanofiltration of combined salt and sugar solutions: coupling between retentions, Desalination 120 (1998) 211.

[26] W.R. Bowen, J.S. Welfoot, Modelling of membrane nanofiltration—pore size distribution effects, Chem. Eng. Sci. 57 (2002) 1393.

[27] J. Houwing, R. Jonker, G. Bargeman, J.G. van Doorn, M.A. Jansens, M.P.J. Dohmen-Speelmans, H.C. van der Horst, Ontzouten en concentreren van carboxymethylinuline (CMI) met nanofiltratie, Procestechnologie 3 (2001) 23.