SEPARATION OF AQUEOUS DYE-SALT SOLUTIONS BY NANOFILTRATION.
ANALYSIS OF NEGATIVE SALT REJECTION

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The process of desalination of aqueous dye-salt solutions by polymeric nanofiltration membranes using commercially available modules was studied. The influence of dye and salt concentration on the salt rejection and flux as well as comparison of individual NF membranes for desalting purposes is presented. Extended Spiegler–Kedem model including Donnan exclusion mechanism and the term of concentration dependence of salt permeability was used for prediction of salt rejection. The experimental results show negative salt rejections during the desalination and the dependence of this phenomenon on permeate flux. It was also shown that the extended Spiegler–Kedem model including Donnan exclusion mechanism can satisfactorily predict salt rejections even at high concentration typical of desalting process. From among the membranes used in this work membrane PES 10 has been chosen as the most suitable for desalination of the given type of dye.

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Introduction

Nanofiltration (NF) membranes are a new class of membranes which have properties between those of ultrafiltration (UF) and reverse-osmosis (RO) membranes. Their separation mechanisms involve both steric (sieving) effects and electrical (Donnan) effects. This combination allows NF membranes to be effective for a range of separation of mixtures of organic solutes (either neutral or charged) and salts.

The ability to predict the process performance of NF membrane separations would be very useful for planning and optimisation of the processes. Such prediction would ideally utilize available physical property data of a process stream and a membrane.

In this article, an example of such prediction will be presented for the separation of dye-salt solutions using NF membranes. This kind of membranes is especially suited for such process since, through the combination of steric and Donnan effects, the dye will be highly rejected while the salt may even be negatively rejected (concentrated in the permeate).

Two main approaches have been used thus far to model the transport of ionic species through NF membranes. One approach is based on the extended Nernst–Planck equation [1]. Through this approach, a system containing any number of n ions can be described using a set of $(3n + 2)$ equations. In this approach, it is assumed that the flux of every ion through the membrane is induced by pressure, concentration and electrical potentials. This model describes the transport of ions in terms of an effective pore radius r_p (m), an effective membrane thickness/porosity ratio $\Delta x/A_k$ (m) and an effective membrane charge density X_d (mol m^{-3}). Such a model requires many experiments for determination of this structural parameters and it is hard to solve.

The second approach is through the Spiegler–Kedem model. This black-box approach allows the membranes to be characterised in terms of salt permeability P_S and reflection coefficient σ. This model is limited to binary salt systems, and in the limiting case to a binary salt system in the presence of completely rejected organic ion [2,3]. In this work Spiegler–Kedem model was used for description of salt transport through NF membranes, even at high concentrations typical for industrial desalination of organic dyes.

Theoretical

Salt Rejection of a Single Electrolyte

Salt rejection of a single electrolyte has been described by Spiegler and Kedem [4] by the following three transport coefficients: water permeability L_p, salt

permeability P_S and reflection coefficient σ. For the curve describing salt rejection as a function of flow, the salt can be treated as a single electroneutral species.

Assuming linear local equations for volume and salt flows, these authors derived an expression of salt rejection R_S as a function of volume flux J_V. The local flux equations are

$$ J_V = -L_P \left(\frac{dp}{dx} - \sigma \frac{d\pi}{dx} \right) \tag{1} $$

$$ J_S = -P \frac{dc_S}{dx} + (1 - \sigma)c_S J_V \tag{2} $$

where salt rejection R_S is defined by the salt concentrations c_{SF} and c_{SP} in the feed and permeate streams, respectively

$$ R_S = 1 - \frac{c_{SP}}{c_{SF}} \tag{3} $$

and

$$ c_P = \frac{J_S}{J_V} \tag{4} $$

With constant fluxes, constant coefficients P and σ and with condition (4), integration of Eq. (2) through the membrane thickness yields

$$ \frac{J_V(1 - \sigma)\Delta x}{P} = \ln \frac{c_{SP}\sigma_S}{c_{SP} - c_{SF}(1 - \sigma_S)} \tag{5} $$

and then salt rejection can be expressed as

$$R_S = \frac{(1 - F)\sigma_S}{1 - \sigma_S F} \tag{6}$$

where

$$F = e^{-J_V A}, \quad A = \frac{1 - \sigma_S}{P}\Delta x = \frac{1 - \sigma_S}{P_S} \tag{7}$$

where P is the local salt permeability and P_S is overall salt permeability.

In a mixture of electrolytes, the interactions between different ions can be very important and the behaviour of mixed solutions in NF cannot be predicted from the coefficients describing each salt separately. The differences in mobilities of ions lead to an electric field, which influences the velocity of each ion. Thus one needs to analyse all ion fluxes together. This analysis for the mixture of two electrolytes with common permeable counter ion and two co-ions, which are the rejected and the permeable ion respectively, is presented below.

Salt Permeation in Presence of Retained Organic Ions

Consider a system (Fig. 1) which consists of semipermeable membrane separating two aqueous solutions with mixed electrolyte sharing a common permeable cation 1 and two anions of which anion 2 is permeable through the membrane and anion 3 is fully rejected.

For the sake of simplicity let us consider a mixture of a mono-monovalent salt (NaCl) and a multifunctional organic anion X^{v-} containing v negatively charged groups per molecule in a sodium salt form.

The two electrolytes are fully dissociated as shown in Eqs (8) and (9).

$$NaCl \rightleftharpoons Na^+ + Cl^- \tag{8}$$

$$Na_v X \rightleftharpoons vNa^+ + X^{v-} \tag{9}$$

feed solution · membrane · permeate solution

(1) Na$^+$

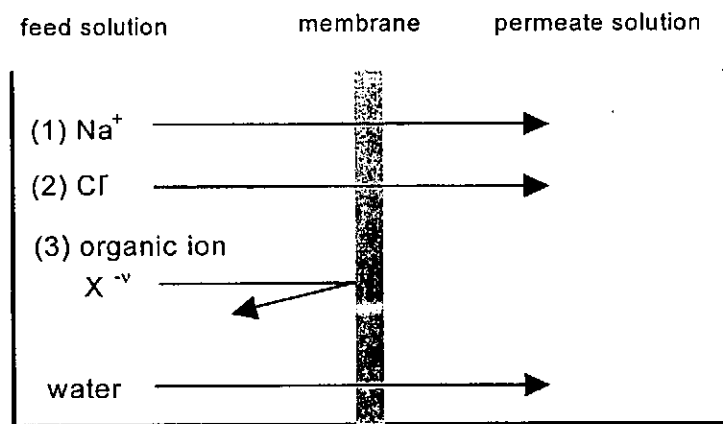(2) Cl$^-$

(3) organic ion

X$^{-\nu}$

water

Fig. 1 Scheme of the system

If we consider the salt as a single electroneutral species we can express the condition of equilibrium between feed solution and the solution inside the membrane.

$$(a_1 a_2)_F = (a_1 a_2)_M \tag{10}$$

In the feed solution containing a nonpermeable multifunctional organic anion at a concentration C_x, $[\text{g l}^{-1}]$ the following conditions of electroneutrality can be written for each phase

$$[\text{Cl}^-]_F = c_{SF} \tag{11}$$

$$[\text{X}^{\nu-}]_F = C_{xF} \tag{12}$$

$$[\text{Na}^+]_F = c_{SF} + \nu C_{xF} \tag{13}$$

$$[\text{Cl}^-]_M = [\text{Na}^+]_M = c_{SM} \tag{14}$$

Assuming equilibrium on the membrane solution interface, approximating activities with concentrations and substituting Eqs (11), (13) and (14) into Eq. (10) one obtains the value of salt concentration inside the membrane on the feed side

$$c_{SM} = c_{SF}\left(1 + \frac{\nu C_{xF}}{c_{SF}}\right)^{0.5} \tag{15}$$

In the presence of Donnan exclusion forces, induced by the impermeable organic ions, the salt transport across the membrane proceeds as if the membrane were exposed to a salt solution having a concentration c_{SM} instead of c_{SF}. Thus the value of c_{SM} and not that of c_{SF} determines the driving force for the salt passage and should be used as boundary condition during the integration of Eqs (1) and (2).

Then the expression for salt rejection in the presence of retained organic ion can be written as

$$R_S = \frac{(1 - \sigma_S F) - (1 - \sigma_S)\left(1 + \frac{\nu C_{xF}}{c_{SF}}\right)^{0.5}}{1 - \sigma_S F} \tag{16}$$

Concentration Dependence of the Solute Permeability

The concentration dependence of the solute permeability was proposed by Schirg and Widmer [3] as a power-law model

$$P = \alpha c_F'^{\beta} \tag{17}$$

where c_F' is the concentration of the permeable component in the feed $[\text{g l}^{-1}]$,
α – coefficient for salt permeability $[\text{m s}^{-1} \text{g}^{-\beta} \text{l}^{\beta}]$,
β – coefficient for concentration dependence of salt permeability.

After introducing of Eq. (17) into Eq. (6), the retention for single electrolyte can be written as

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$$R_S = 1 - \frac{1 - \sigma_S}{1 - \sigma_S \exp\left(\dfrac{(\sigma_S - 1)J_V}{\alpha c_F'^{\beta}}\right)} \tag{18}$$

Similarly, introducing Eq. (17) into Eq. (16), the salt retention for the system with retained organic ion can be expressed as

$$R_S = 1 - \frac{(1 - \sigma_S)\left(1 + \dfrac{\nu M_S C_{xF}}{M_x c_{SF}'}\right)^{0.5}}{1 - \sigma_S \exp\left(\dfrac{(\sigma_S - 1)J_V}{\alpha_S c_{SF}'^{\beta_S}}\right)} \tag{19}$$

Experimental

The batch experimental set-up was used. Both permeate and retentate streams were returned to keep the concentration and volume constant during the experiments. All experiments were carried out at 20 °C and the constant feed flow-rate 500 l h^{-1}.

Membranes: composite, polyamide, polyethersulphone

Table I List of membranes used

Membrane	Producer	Module type	Area, m^2	Material
Desal 5 DK	Desal	spiral wound	2.51	polyamide
Desal 5 DK	Desal	disc	1.00	polyamide
PES 10	Hoechst	spiral wound	1.60	polyethersulphone
NF 45	FILMTEC	spiral wound	2.00	polyamide

Feeds: aqueous salt solutions, mixed aqueous dye-salt solutions (Acid Red 357)
Determination of concentration: the dye concentrations were determined by means of a spectrophotometer (wavelength 494 nm), the salt concentrations in feed were determined by potentiometric titration and those in permeate by measuring

electrical conductivity.

Determination of flux: by measuring of the time needed to fill up the 100 ml container with the permeate.

Pure Water Flux

The pure water flux as the function of the trans-membrane pressure (0.3, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.5 MPa) was measured for every membrane.

Flux and Salt Rejection in Single Salt Solutions

The flux and the permeate concentration for various feed concentrations and for various trans-membrane pressures (0.8, 1.0, 1.2 and 1.5 MPa) were measured for NaCl and $MgSO_4$ single salt solutions.

Flux, Salt and Dye Rejection in Mixed Dye-Salt Solutions

In the case of Desal 5DK-DM, the flux and the permeate concentrations of NaCl and dye were measured for various feed concentrations (10.2, 48.8, 102.5, 136.8, 191.1 g l^{-1} of dye and 2.5, 5.0, 10.0, 25.0, 50.0 g l^{-1} of NaCl) under the constant trans-membrane pressure of 1.5 MPa. The separation ability of several other membranes for dye-salt solutions was compared at concentration 102.5 g l^{-1} of dye and at the same NaCl concentrations as in the case of Desal 5DK-DM.

Results and Discussion

Pure Water Flux

By integration of Eq. (1) we can obtain the linear dependence between flux and trans-membrane pressure ΔP for pure water transport ($\Delta \pi = 0$). The slope of this line (L_p) is therefore an important parameter for every membrane reflecting ability of water permeability.

Figure 2 shows that membranes Desal 5DK-SM, Desal 5DK-DM and FILMTEC NF 45 possess similar flux-pressure dependences and therefore similar values of the water permeability (Table II). Obviously, the water permeability of PES 10 is approximately three times higher than water permeability of the other membranes. This can be due to the more open structure of this membrane, which approaches an UF membrane. But the open structure may cause the insufficient

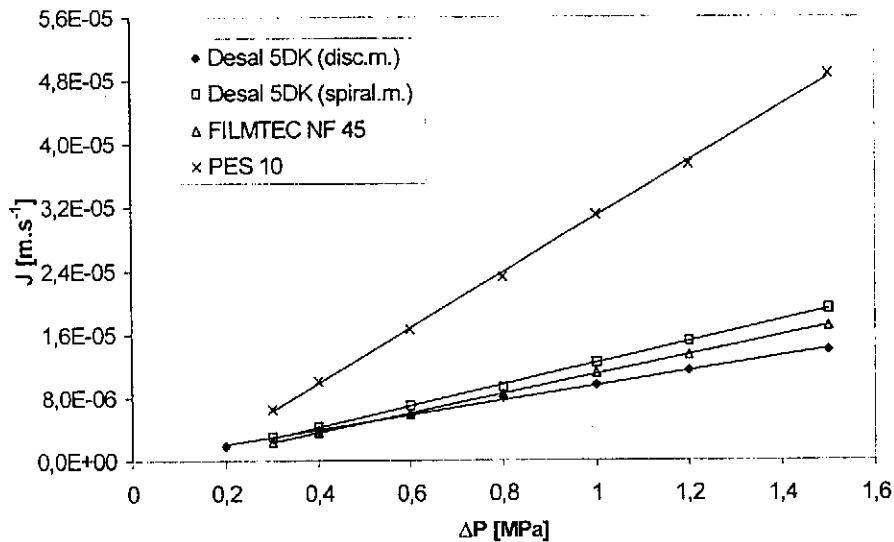retention of the dye in the case of the dye-salt separation.

Fig. 2 Flux as a function of trans-membrane pressure for pure water

Table II Coefficients of extended Spiegler–Kedem model for the transport of NaCl for various
membranes

Membrane	$L_p,$ $\mathrm{m\ s^{-1}\ Pa^{-1}}$	σ	$\alpha,$ $\mathrm{m\ s^{-1}\ g^{-\beta}\ l^{\beta}}$	β
Desal 5DK-DM	9.311×10^{-12}	0.4940	1.957×10^{-6}	0.9449
Desal 5DK-SM	1.354×10^{-11}	0.8238	5.053×10^{-6}	0.4381
FILMTEC NF	1.225×10^{-11}	0.5828	4.386×10^{-6}	0.2663

Flux and Salt Rejection in Single Salt Solutions

Figure 3 depicts dependence of the flux on the trans-membrane pressure for NaCl
solutions with various salt concentrations. As can be seen this dependence for
every salt concentration shows a straight line course. Thus we can assume that the
concentration polarization has no significant influence and, therefore, we can
consider the bulk concentration equal to that on the membrane wall [5], which is
required in model equations.

Experimental data rejection-flux can be evaluated by extended Spiegler–
Kedem model to obtain parameters σ, α and β (Fig. 4).

The membrane PES 10 was not included in Table II because this membrane

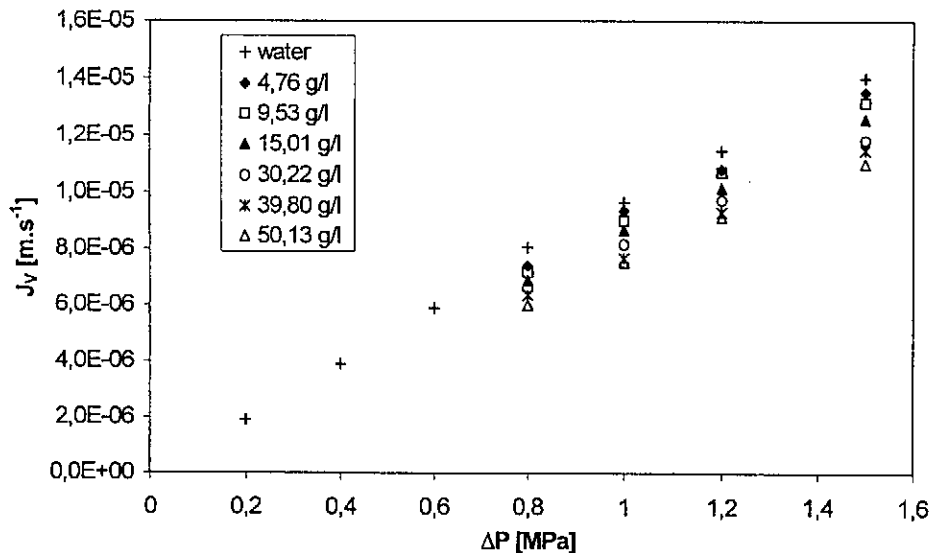Novák R. *et al.*/Sci. Pap. Univ. Pardubice Ser. A 7 (2001) 201–216

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Fig. 3 Flux as a function of trans-membrane pressure for NaCl solutions with various salt concentrations (Desal 5DK-DM)

did not show a typical course of the rejection-flux dependence. These differences are caused by different nature of this membrane close to UF type and, therefore, the transport through this membrane cannot be described by Spiegler–Kedem model.

Table II shows that the water permeability and the salt permeability exhibit the same trend for various membranes (L_p and α). The parameter σ means the maximum rejection attainable on a given membrane (at the lowest concentration and the highest pressure). The parameter β expresses the concentration dependence of the salt permeability. The analysis of experimental data for separation of $MgSO_4$ by the Spiegler–Kedem model is less interesting because all membranes except for PES 10 showed rejection almost equal to unity.

Flux, Salt and Dye Rejection in Mixed Dye-Salt Solutions

The aim of these experiments was to find the dependence of salt and dye rejections on the salt and dye concentrations. In every experiment carried out in this work the dye rejection was very high and almost equal to unity. The lowest value of the dye rejection observed was 0.9988. The salt rejection as a function of dye and salt concentrations is plotted in Fig. 5.

It can be seen that the salt rejection decreases with decreasing salt concentration and with increasing dye concentration, corresponding to Donnan
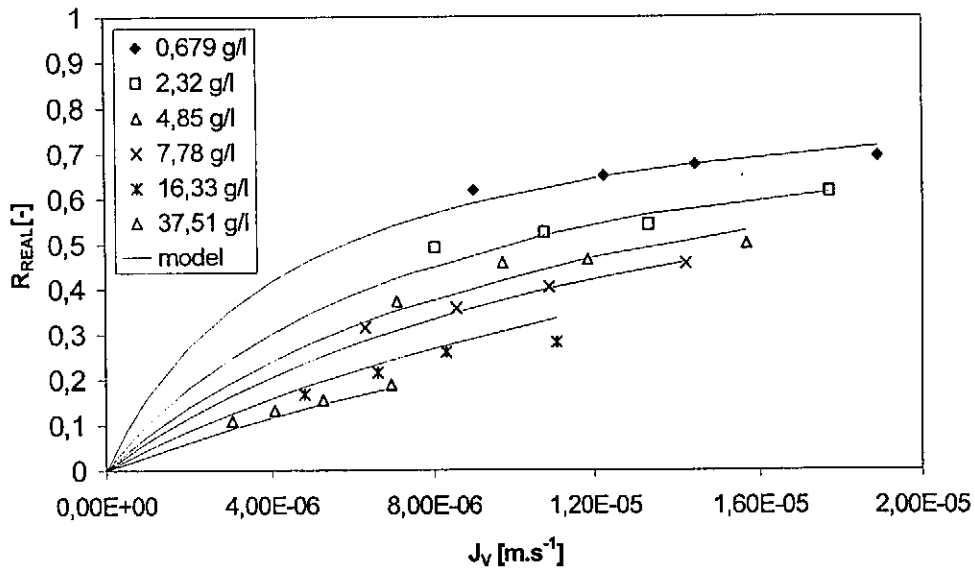
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Fig. 4   Rejection of NaCl as a function of flux for various salt concentrations (Desal 5DK-SM)
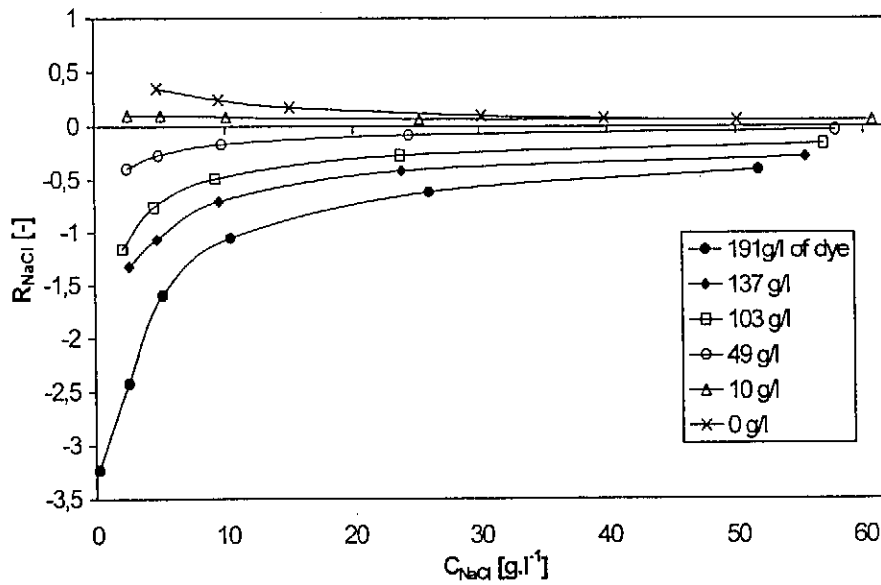

Fig. 5   Salt rejection as a function of salt concentration for different dye concentrations (Desal 5DK-DM, 1.5MPa)
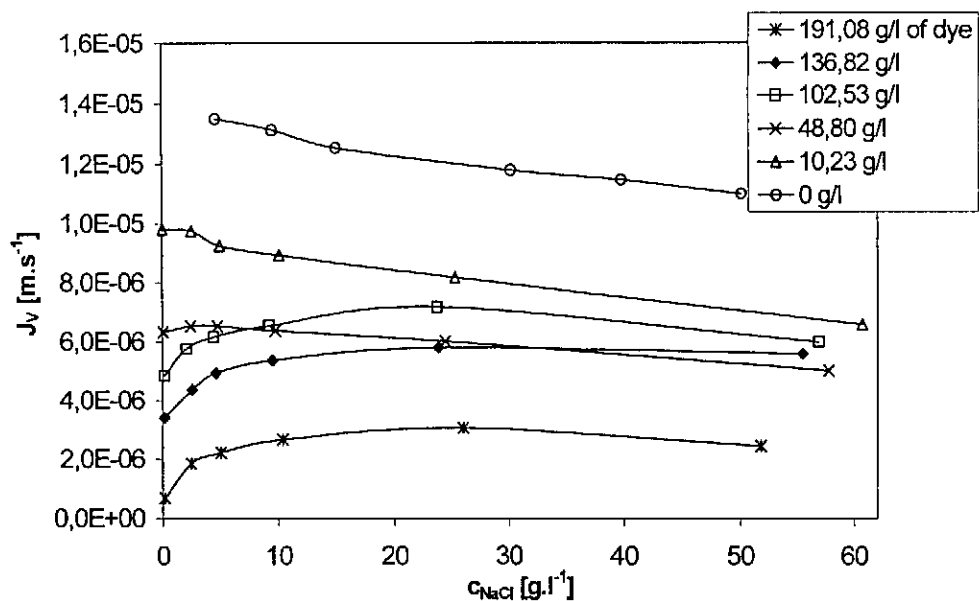
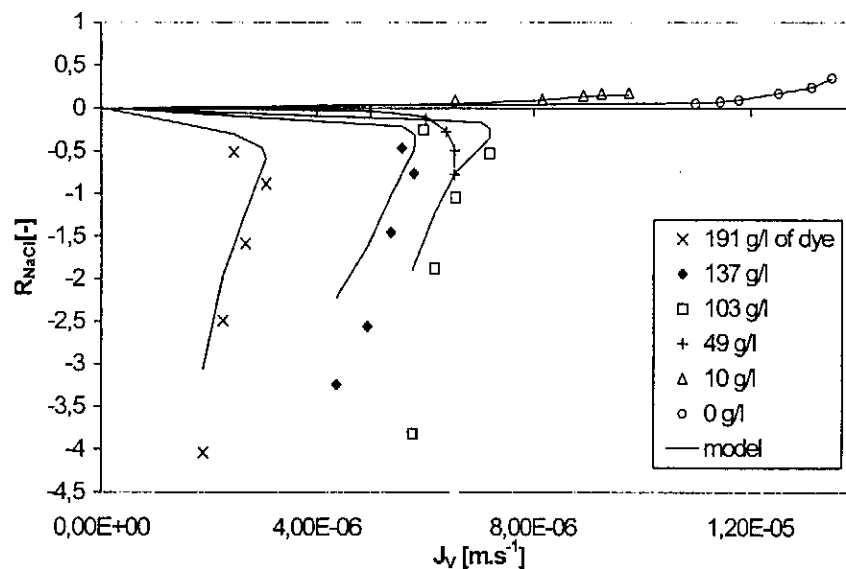Fig. 6 Flux as a function of salt concentration for different dye concentrations (Desal 5DK-DM, 1.5MPa)

Fig. 7 Salt rejection as a function of flux for different dye concentrations (Desal 5DK-DM, 1.5 MPa), σ_{NaCl} = 0.4241, α_{NaCl} = 2.989×10^{-6} and β_{NaCl} = 0.6898

equilibrium (Eq. 15).

In the case of solution without the dye or with low dye content (positive rejections) we can observe the typical decline of salt rejection with increasing salt concentration. At higher dye content we can observe an increase in salt rejection with increasing salt concentration due to a shift of Donnan equilibrium [6].

From Fig. 6 it is obvious that the salt content also affects the flux. In the case of single salt solution (without dye) we can see a typical decrease in flux with increasing salt content. In the case of mixed dye-salt solutions we can observe initial increase in flux followed by a decrease after a maximum has been reached. The initial increase in flux at high dye concentration and low salt concentration is due to negative rejection (see Fig. 5), which causes the reverse osmotic pressure difference between permeate and feed side of the membrane ($\Delta\pi > 0$). This reverse osmosis pressure difference enhances the driving force of the process (Eq. (1)), thus increasing the flux.

The experimental dependence of the salt rejection on flux can be evaluated by the extended Spiegler–Kedem model (Fig. 7) in order to obtain the parameters σ_{NaCl}, α_{NaCl} and β_{NaCl}. These parameters are characteristic of the transport of NaCl through the given membrane and also of the given dye in feed solution. The meaning of individual parameters is the same as that in the case of single salt transport.

Figure 7 depicts the experimental dependence of the salt rejection on the flux. The curves represent the course of salt rejection as a function of the flux for a given dye content in the feed. The pressure difference was kept constant during all experiments and flux was changed by changing salt content in the feed (changing osmotic pressure difference).

It can be seen from Fig. 7 that the extended Spiegler–Kedem model is not able to fit rejection-flux data so accurately as it was in the case of the single salt transport. But taking into account the range of rejection values, we can consider prediction by this model still satisfactory.

The coefficient α is approximately 1.5 times higher than in the case of the separation of single NaCl solution, which reflects the fact that the presence of the dye enhances the salt permeability through the membrane [6].

The comparison with other membranes was carried out in order to determine the most suitable one. As seen in Fig. 8 membranes Desal 5DK-DM and PES 10 have the best course of dependence of salt rejection as a function of concentration but PES 10 shows the highest flux (Fig. 9). The best comparison of given membranes is provided by the salt transport parameter $J_V(1 - R_S)$, which is in fact the relative salt flux (Eq. (20)).

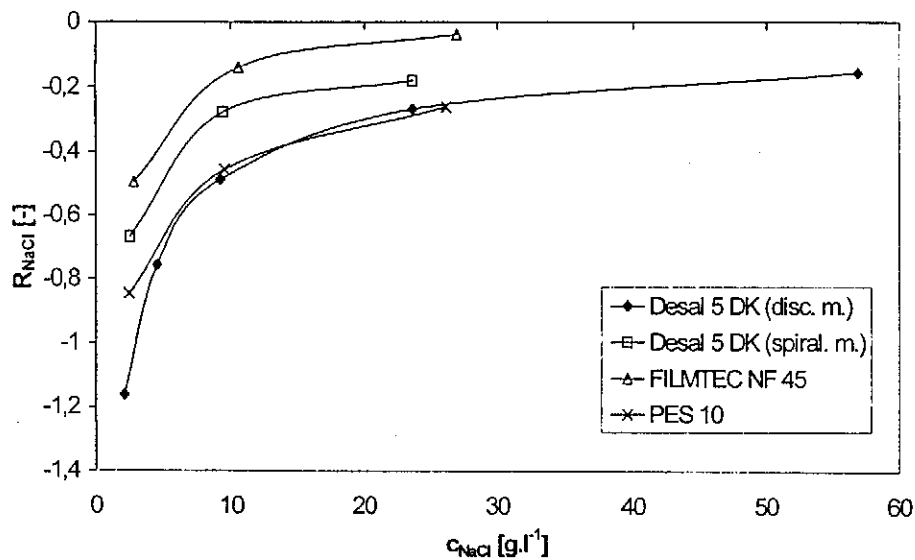$$\frac{J_S}{c_{SF}} = J_V \frac{c_{SP}}{c_{SF}} = J_V(1 - R_S) \tag{20}$$

Fig. 8 Comparison of rejection-NaCl concentration dependence for various membranes at dye concentration 100 g l^{-1} (1.5 MPa)
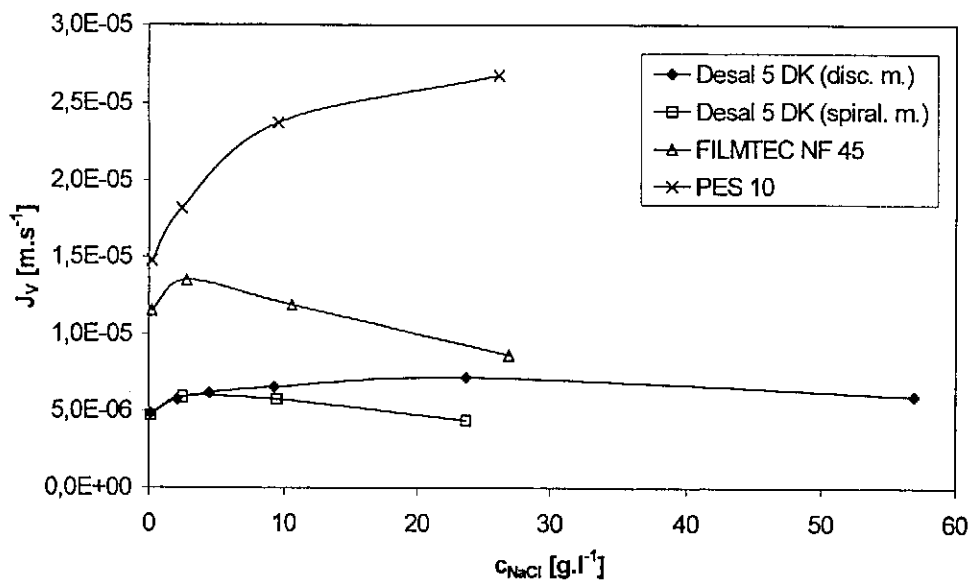

Fig. 9 Comparison of flux-NaCl concentration dependence for various membranes at dye concentration 100 g l^{-1} (1.5 MPa)
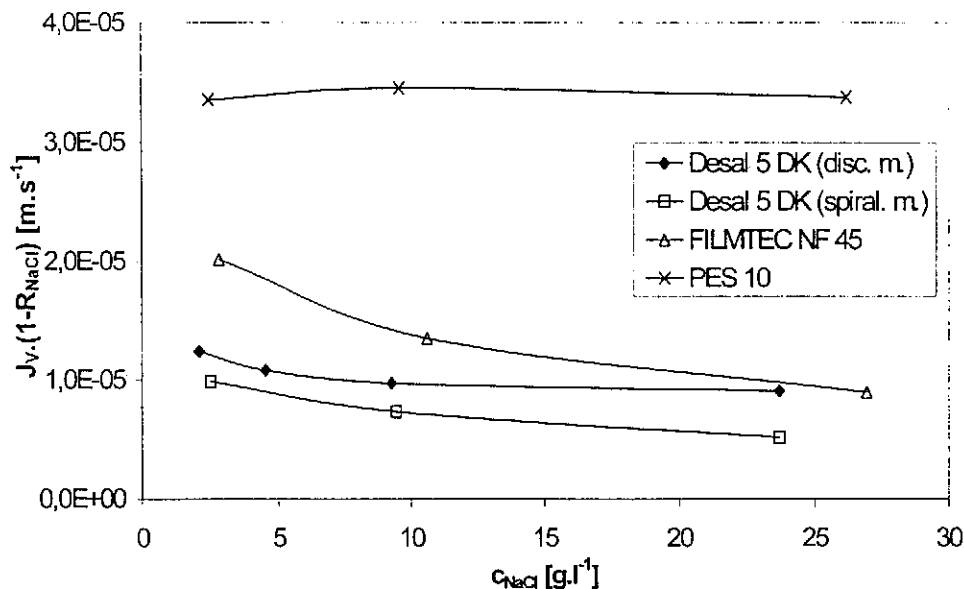
Fig. 10 Comparison of the salt transport parameter-NaCl dependence for various membranes at dye concentration 100 g l^{-1} (1.5 MPa)

Figure 10 depicts this salt transport parameter as a function of the salt concentration in the bulk. It is obvious from this picture that membrane PES 10 has the best salt fluxes and it is, therefore, the most suitable membrane for desalination of this dye.

Conclusion

The introduction of a power-law term for the concentration dependence of salt permeability in the Spiegler–Kedem model allows a very good prediction of rejection of nanofiltration membranes for single salt solutions depending on the feed concentration and permeate flux.

In the case of separation of mixed dye-salt solutions the extended Spiegler–Kedem model including Donnan equilibrium term (the Perry–Linder model) and the power-law concentration dependence term can be used for satisfactory prediction of the salt rejection even at high dye concentrations typical of industrial desalination processes.

From among membranes used in this work, membrane PES 10 has been chosen as the most suitable for desalination purposes.

Acknowledgements

Symbols

c'_{SF} salt concentration in the feed, g l^{-1}
c'_{SP} salt concentration in the permeate, g l^{-1}
c'_{SM} concentration of the salt inside the membrane on the feed side, g l^{-1}
J_V flux, m s^{-1}
J_S salt flux, m s^{-1}
L_P water permeability, m s^{-1} Pa^{-1}
P_S permeability, m s^{-1}
R_S salt rejection
σ reflection coefficient
α coefficient for salt permeability, m s^{-1} g^{-1} l^{β}
β coefficient for concentration dependence of salt permeability

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