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Mechanisms of transfer of ionic solutes through composite polymer nano-filtration membranes in view of their high sulfate/chloride selectivities

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ABSTRACT

A number of nano-filtration membranes exhibit quite high rejections of sulfates (98–99%) accompanied by quite moderate rejections (sometimes as low as 10–20% and even less) of chlorides from highly concentrated electrolyte solutions like sea water or various brines. In this communication, it is shown that this phenomenon can hardly be explained within the scope of commonly accepted model of nano-filtration where the barrier layer is considered a nano-porous medium, and, accordingly, there is a considerable convective coupling between the transfers of solutes and solvent. The very high experimentally observed sulfate/chloride selectivities turn out hardly reconcilable with the quite moderate values of rejection of NaCl.

It is suggested that this phenomenon can be explained by the solution-diffusion mechanism of solute transfer across very thin and practically non-porous barrier layers. The approach of rejection to non-100% apparent saturation values observed experimentally can be explained by the concentration polarization.

To verify this hypothesis, studies have been carried out of pressure-driven rejection of various single-salt electrolyte solutions (NaCl, Na_2SO_4 and $CaCl_2$) by two commercial composite nano-filtration membranes (NF270 and NF200) in a cross-flow setup equipped with GE SEPA™ CF II test cell with the possibility of independent variation of trans-membrane pressure difference and cross-flow velocity. The experimental data could be very well fitted by the solution-diffusion-film model, the stagnant layer diffusion permeability depending in a reasonable way on the cross-flow velocity and solute bulk diffusion coefficient.

Keywords: Membrane; Nano-filtration; Sulfate; Chloride; Solution-diffusion-film model; DSP model; Spiegler-Kedem model

1. Introduction

It has been observed experimentally that various polymer NF membranes systematically reject sulfates up to 98–99% from concentrated electrolyte solutions like seawater. At the same time, the rejection of chloride ions is quite low. This very high sulfate rejection from concentrated electrolyte solutions is useful for a number of practical applications, e.g., the sulfate removal from sea water before its further desalination

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by reverse osmosis/distillation [1], prior to its injection in the oil extraction process [2], or the sulfate removal from brines in chlor-alkali electrolysis [3].

Usually, the sulfate/chloride selectivity in NF is explained by a negative membrane fixed charge. This mechanism is usually evoked within the scope of the so-called Donnan-Steric-Partition model (DSPM) where the membrane active layer is considered a nano-porous medium [4–6]. An alternative approach to the modelling of NF is the use of solution-diffusion model coupled with the film model to account for concentration polarization [2,7]. To our knowledge, this latter approach has not, yet, been used to explain the high sulfate/chloride selectivity. Meanwhile, as is shown in this communication, this model appears to be more suitable for the interpretation of this phenomenon.

The available literature experimental data on the sulfate rejection from concentrated electrolyte solutions (see, e.g., [1,3]) were obtained just at single values of trans-membrane pressure difference and in membrane modules where the concentration polarization can be fairly strong and, additionally, its extent can vary considerably along the module. This makes difficult a quantitative interpretation of these data and calls for systematic measurements performed under more controlled conditions.

2. Theory

Usually, NF is modeled within the scope of the so-called DSPM. Mathematically, it is implemented by means of a system of extended Nernst-Planck equations. In general case of electrolyte solutions containing more than two ions, this system of equations can be solved only numerically. However, in the particular case of binary electrolytes (single salts), there is just one equation, which can be solved in quadratures. As demonstrated in [8], the general features of this solution are very similar to those of the classical Spiegler-Kedem model. Minor quantitative differences are related to the fact that actually the phenomenological coefficients (the salt reflection coefficient and the membrane solute permeability) depend on the reference salt concentration inside the membrane whereas within the scope of classical Spiegler-Kedem approach they are assumed to be constant. However, usually these minor differences cannot be reliably identified in view of the finite accuracy and imperfect reproducibility of experimental data. Therefore, basically, it appears to be quite acceptable to interpret experimental dependences of salt rejection on the trans-membrane volume flow within the scope of Spiegler-Kedem approach. The phenomenological coefficients obtained in this way can further be interpreted within the scope of mechanistic model(s). Just this approach will be used in this communication.

As shown, for example, in [9], there is a model-independent relationship

$$T_s \equiv 1 - \sigma_s = \tau_+ t_- + \tau_- t_+ \tag{1}$$

relating the salt transmission coefficient (one minus reflection coefficient) to the so-called ion transmission (entrainment) coefficients $\tau_\pm$ [9], and the ion transport numbers in the membrane phase, $t_\pm$, defined as

$$t_\pm \equiv \mp \frac{Z_\pm P_\pm}{Z_+ P_+ - Z_- P_-} \tag{2}$$

where $Z_\pm$ are the ion charges, and $P_\pm$ are the membrane diffusion permeabilities with respect to corresponding ions. Within the scope of the so-called homogeneous model

$$\tau_i = \alpha_i \Gamma_i \tag{3}$$

where Γ_i is the distribution coefficient and α_i is the hindrance coefficient.

$$P_i = \frac{f}{L} \cdot D_i \Gamma_i \tag{4}$$

where f is the active porosity (including the pore tortuosity), L is the membrane thickness, D_i is the effective ion diffusion coefficient including the effects of hindrance. The distribution coefficients must satisfy the condition of electric neutrality of membranes phase.

In the estimates below, the effects of steric exclusion and hindrance were taken into account by means of the well-known relationships reported by Deen [10] (see also [6]) and derived for a model of straight cylindrical capillaries.

In the solution-diffusion model, it is assumed that there is no convective coupling between the trans-membrane solute transfer and the volume flow. The trans-membrane solute transport occurs only via diffusion, and the following relationship applies

$$J_s \equiv J_V c_s'' = P_m \left(c_s' - c_s'' \right) \tag{5}$$

where J_V is the trans-membrane volume flow, c_s'' is the permeate concentration, P_m is the membrane diffusion (solute) permeability, and c_s' is the solute concentration at the membrane feed surface. From Eq. (5), for the intrinsic rejection, we obtain

$$R_{\text{int}} \equiv 1 - \frac{c_s''}{c_s'} = \frac{J_V/P_m}{1 + J_V/P_m} \tag{6}$$

It can be shown that accounting for the concentration polarization within the scope of film model

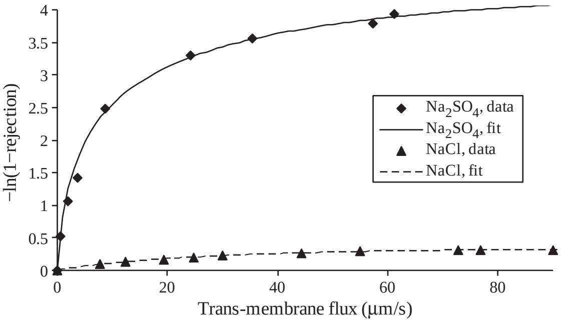

Fig. 1. Rejection of 0.45 M NaCl and 0.22 M Na_2SO_4 solutions by NF270 membrane and the Spiegler-Kedem fits; cross-flow velocity 1 m/s. The logarithmic scale is used to make better visible the behavior of rejections approaching 100%.

(solution-diffusion-film model, SDFM) leads to the following

$$R_{\text{obs}} = \frac{\frac{J_V}{P_m}\exp\left(-\frac{J_V}{P_\delta}\right)}{1+\frac{J_V}{P_m}\exp\left(-\frac{J_V}{P_\delta}\right)} \tag{7}$$

where R_{obs} is the observable rejection, and P_δ is the diffusion permeability of unstirred layer.

As reported in the literature [7], the solute (diffusion) permeability of NF membranes increases rather strongly with feed concentration. Then, logically, the solute permeability should also be considered a function of reference concentration inside the membrane, which is disregarded in Eqs. (5)–(7). This dependence can be taken into account, for example, for this functional form [8]

$$P_m(c) = P_m(c_0)\cdot\left(\frac{c}{c_0}\right)^a \tag{8}$$

where c_0 is an arbitrary concentration, a is a parameter quantifying the rate of concentration dependence. By using Eq. (8), this implicit relationship can be obtained between the observed rejection and the trans-membrane volume flow

$$J_V\cdot\frac{1+a}{P_m(c')}=(1-R_{\text{obs}})^a\left\{\left[1+\left(\frac{R_{\text{obs}}}{1-R_{\text{obs}}}\right)\cdot\exp\left(\frac{J_V}{P_\delta}\right)\right]^{a+1}-1\right\} \tag{9}$$

3. Experimental

We used a cross-flow setup equipped with a commercially available test cell (GE SEPA™ CF II) with a spacer-filled rectangular feed channel and the possibility of independent variation of trans-membrane pressure difference and cross-flow velocity.

The membranes were NF270 and NF200 (Dow-Filmtec).

4. Results and discussion

Fig. 1 shows experimental data on the rejection of NaCl and Na_2SO_4 from rather concentrated single-salt solutions. The feed concentrations were selected in such a way that the concentrations of counter-ions (that is cations assuming a negatively charged membrane) were the same. The cross-flow velocity in these measurements was 1 m/s and the channel height was ca. 1 mm. At such cross-flow rates and channel dimensions (especially in spacer-filled channels), it is customary to consider concentration polarization negligible [11]. Fig. 1 also shows the results of Spiegler-Kedem fits of experimental data. The fitted model parameters are listed in Table 1.

As far as the parameters of Spiegler-Kedem fit are concerned, the principal message of Table 1 is that the reflection coefficient of Na_2SO_4 is too close to unity to be compatible with the relatively small reflection coefficient of NaCl. Indeed, the limiting selectivity defined as

$$S \equiv \frac{1-\sigma_{\text{NaCl}}}{1-\sigma_{\text{Na}_2\text{SO}_4}} \tag{10}$$

is as high as ca. 53 in this case. Fig. 2 shows the results of theoretical estimates of limiting selectivity as a function of reflection coefficient of NaCl within the scope of DSP model. The plots have been calculated for various constant values of pore size and variable fixed charge density. The peculiar dependence of NaCl reflection coefficient on the fixed charge density is caused by the fact that due to the lower mobility of sodium ions, the reflection coefficient decreases with the fixed charge density at its low to moderate values (and may even become negative in not too narrow pores).

Fig. 2 shows that the largest selectivity compatible with $\sigma_{\text{NaCl}} = 0.282$ is ca. 4.4, which is more than one order of magnitude smaller than the value estimated from the experimental data. Of course, with decreasing pore size and/or increasing fixed charge density the selectivity can be made as high as needed. However, with this the reflection coefficient of NaCl will also be made too large as compared to the value estimated from the experimental data. Of course, it can be speculated that because of some reason the fixed charge density was just higher in the case of sodium sulfate. However, it should be kept in mind that the high sulfate/chloride selectivities reported in the literature occurred in mixed solutions where the fixed charge density was the same for all the ions.

Table 1
Parameters of Spiegler-Kedem (S-K) and SDFM fits of experimental data shown in Fig. 1

Solute	Reflection coefficient (S-K)	Solute permeability (S-K) (μm/s)	Solute permeability (SDFM) (μm/s)	P_δ (SDFM) (μm/s)
NaCl	0.282	21.8	86.5	86.5
Na_2SO_4	0.9864	0.76	0.69	85

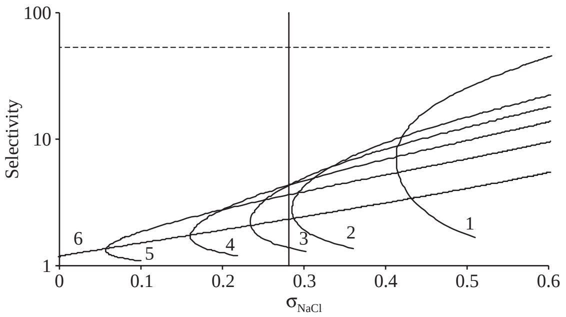

Fig. 2. Limiting selectivity Na_2SO_4 vs. NaCl (defined by Eq. (10)) as a function of reflection coefficient of NaCl calculated by means of DSPM; the pore diameters: 0.74 nm (1); 0.92 nm (2); 1.02 nm (3); 1.23 nm (4); 1.84 nm (5); ∞ (6). The vertical and horizontal lines correspond to the values of NaCl reflection coefficient and of Na_2SO_4/NaCl selectivity determined from experimental data by means of Spiegler-Kedem model.

The model used above does not account for a pore size distribution. Any such distribution would give rise to a further decrease in the selectivity at a given reflection coefficient of one of the solutes, and the calculated values would be even further from estimated from experiment.

Dielectric exclusion is another possible mechanism of ion rejection in NF [12]. In this case, the excess solvation energy (responsible for the ion exclusion) is proportional to the square of ion charge [12], and, thus, is essentially larger for double-charge ions (sulfates) than for single-charge ones (chlorides). However, due to the condition of electric neutrality of membrane phase, in the case of (1:2) electrolytes the potentially strong exclusion of double-charge ions cannot manifest itself in full, and the logarithm of distribution coefficient of salt (for neutral membranes) turns out proportional to $Z_+|Z_-|$ [13]. Therefore, the transmission coefficient (proportional to the distribution coefficient in this case) of (1:2) salt is roughly proportional to the square of transmission coefficient of (1:1) salt. Accordingly, for $\sigma_{NaCl} = 0.282$, we could expect $\sigma_{Na_2SO_4} \approx 0.5$, which is very far from the value estimated from the experiment.

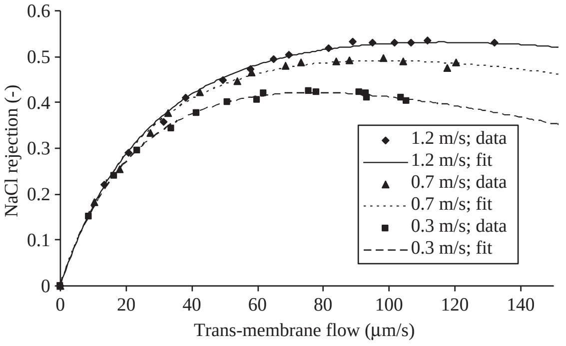

Fig. 3. Rejection of 0.085 M NaCl solution by NF270 membrane at various cross-flow velocities; solution-diffusion-film-model fits.

The experimental data shown in Fig. 1 could be equally well fitted by means of SDF model (the plots are not shown since they practically coincide with the Spiegler-Kedem fits). The corresponding parameters are also listed in Table 1. It is seen that to fit the experimental data, the membrane solute permeability for Na_2SO_4 has to be assumed to be more than two orders of magnitude lower than that for NaCl. However, in contrast to the reflection coefficients, such a large difference is quite compatible with the high solute permeability for NaCl. Indeed, the solute permeability is directly proportional to an effective diffusion coefficient (including distribution coefficient) and inversely proportional to the active layer thickness. In dense (and, possibly, cation-exchange) media, one can expect the effective diffusion coefficient of Na_2SO_4 to be much smaller than that of NaCl. Logically, this has to be accompanied by a quite low effective diffusion coefficient of NaCl. Nonetheless, the membrane solute permeability for the latter may well be quite high due to the small active layer thickness. This explanation is in agreement with the findings of [14] where it is reported that the active layers of NF membranes are essentially thinner than those of RO membranes.

To additionally check the applicability of SDF model, we have performed measurements of rejection of NaCl and $CaCl_2$ as a function of trans-membrane volume flow at various cross-flow velocities. The

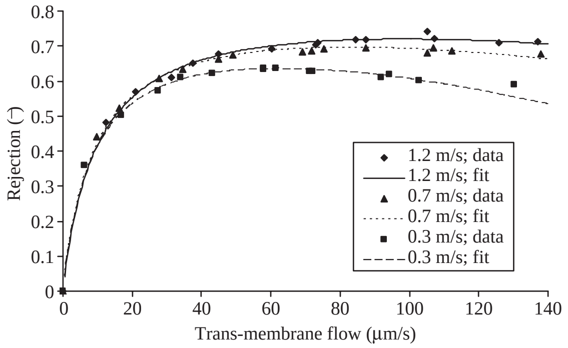

Fig. 4. Rejection of 0.029 M $CaCl_2$ solution by NF270 membrane at various cross-flow velocities; solution-diffusion-film-model fits.

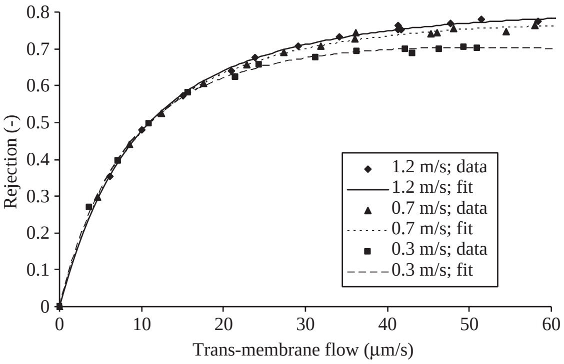

Fig. 5. Rejection of 0.085 M NaCl solution by NF200 membrane at various cross-flow velocities; solution-diffusion-film-model fits.

experimental data and the SDFM fits are shown in Figs. 3–5. The fitted parameters are listed in Table 2.

The data can be remarkably well fitted by using the same values of membrane solute permeability and parameter *a* independent of cross-flow velocity (in agreement with the physics of the model), and the diffusion permeabilities of unstirred layer correlate with the cross-flow velocity in a reasonable way. Strictly speaking, for given solute, cross-flow velocity and feed spacer, the diffusion permeability of unstirred layer had to be the same independent of the membrane used, which is not quite the case for the data obtained with NF270 and NF200 membranes. However, one should keep in mind that due to some particularities of the test cell design with membranes of slightly different thicknesses, the channel height could, probably, not be kept exactly the same for two different membranes. This could give rise to some differences in the cross-flow hydrodynamics.

The negative value of parameter *a* fitted for $CaCl_2$ may reflect the fact that the rejection of $CaCl_2$ solutions by polymer NF membranes surprisingly increases with the feed concentration and not decreases as it does in NaCl solutions. This kind of behavior has already been reported in the literature [11].

Negative rejections of ions have often been observed in NF/RO of electrolyte mixtures at small to moderate trans-membrane volume flows (see, e.g. [15–17]). Typically this occurred for less charged ions in the presence of prevailing amounts of more charged ions of the same sign. Negative rejections have also been observed for very mobile ions (typically H^+) in the presence of less mobile ions of the same sign. Within the scope of solution-diffusion model, this can be explained by the action of electric field of trans-membrane diffusion potential, which arises due to the difference in the membrane permeabilities to cations and anions of prevailing salt. The field of diffusion potential accelerates the less permeating ions of prevailing salt (to keep the trans-membrane electric current equal to zero) but also other ions of the same sign present in the feed. If the membrane permeability to those ions is sufficiently high, their rejection turns out negative. This phenomenon will be quantitatively considered within the scope of SDF model in the following publication.

5. Conclusions

According to the hypothesis put forward in this communication, the reflection coefficients for both NaCl and Na_2SO_4 are equal to one (solution-diffusion mechanism of trans-membrane solute transfer) and the experimentally observed high sulfate/chloride selectivity is explained by the very large difference in the membrane solute permeabilities with respect to NaCl and Na_2SO_4. For this large difference to occur, the membrane specific solute permeability to NaCl has to be sufficiently low. This, however, does not give rise to high rejections at realistic trans-membrane volume flows due to the small active layer thickness. The theoretically high rejections at very high trans-membrane volume flows are unachievable because of concentration polarization. On the other hand, in the case of Na_2SO_4, these almost 100% rejections are reached already at moderate trans-membrane flows due to the low membrane solute permeability.

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Table 2
Parameters of SDF model fitted to the data shown in Figs. 3–5

Membrane/solute	P_m (μm/s)	a	Cross-flow (m/s)	P_δ (μm/s)
NF270, 0.085 M NaCl	46.5	0.56	1.2	150
			0.7	125
			0.3	96
NF270, 0.029 M $CaCl_2$	11.5	−0.3	1.2	77
			0.7	65.5
			0.3	50
NF200, 0.085 M NaCl	12.0	0.68	1.2	128
			0.7	110
			0.3	75

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