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Rejection of minor ionic solutes in nanofiltration. Influence of solution composition

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Nanofiltration (NF) is a membrane separation process used in water treatment for ion separations, taking advantage of different selectivities toward various ions, higher fluxes and lower energy requirements than in reverse osmosis (RO). In order to improve the quality of produced water or extend the options of concentrate revalorization, there is a need to understand and optimise the rejection of not only major components (eg. NaCl or MgSO<sub>4</sub>) but also of minor components, like ammonium, bromide, iodide etc. from seawater, brines or brackish waters.

The selectivity of ion rejection by NF membranes has been studied theoretically and experimentally. The theoretical analysis has been carried out within the scope of solution-diffusion-film model recently extended to electrolyte mixtures [1].

Experimental data have been obtained with two commercial NF membranes (NF270, Dow Chemical and TFCS, Koch Membrane) which were tested at various trans-membrane pressures and at constant cross-flow velocity in a cross-flow test cell. Several representative combinations of dominant salts (NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>) and trace ions (Na<sup>+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Br<sup>-</sup>, I<sup>-</sup>) have been used.

The rejection of ions crucially depends on their “environment”, that is the nature of dominant salt as can be observed in Fig.1. The dramatic differences in the rejections can be explained by the spontaneously arising electric fields. These fields increase the flux of “slower” ions and reduce that of more “rapid” ones of dominant salts. They give rise to negative rejections of “rapidly-permeating” ions present as relatively small additions to well-rejected dominant salts.

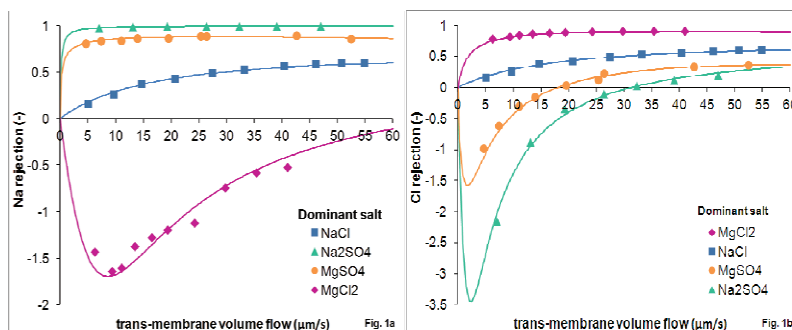


Fig.1 Rejection of Na<sup>+</sup> and Cl<sup>-</sup> against trans-membrane volume flow by NF270 membrane (Dow Chemical); cross-flow rate 1 m/s, concentrations of dominant salts 100 mM; relative concentrations of traces ca. 0.5%; the lines are theoretical fits.

Fig. 1a shows the rejections of  $\text{Na}^+$  as a part of dominant NaCl, as a part of dominant  $\text{Na}_2\text{SO}_4$ , as the trace added to  $\text{MgCl}_2$  and as the trace added to  $\text{MgSO}_4$ . The intrinsic membrane permeability to sulphates is very low and, thus, lower than to  $\text{Mg}^{2+}$  and  $\text{Na}^+$ . Therefore, in dominant  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$  the electric field retards cations and makes the rejection of  $\text{Na}^+$  relatively high. In dominant NaCl the direction of electric field is the same but its magnitude is essentially smaller because of the much higher membrane permeability to  $\text{Cl}^-$ . In dominant  $\text{MgCl}_2$  the membrane permeability to  $\text{Mg}^{2+}$  is lower than to  $\text{Cl}^-$ . Therefore, the electric field accelerates cations, which makes the rejection of  $\text{Na}^+$  negative.

Fig. 1b shows the rejections of  $\text{Cl}^-$  as a part of dominant NaCl, as a part of dominant  $\text{MgCl}_2$ , as the trace added to  $\text{MgSO}_4$  and as the trace added to  $\text{Na}_2\text{SO}_4$ . In both sulphate-containing dominant salts ( $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$ ) the electric field accelerates anions such as  $\text{Cl}^-$  and makes their rejection negative at small to intermediate trans-membrane volume flows. However, the double-charge dominant magnesium cations make this field weaker. Accordingly, the negative rejections of chloride ions in dominant  $\text{MgSO}_4$  are noticeably less pronounced than in dominant  $\text{Na}_2\text{SO}_4$ .

As a result of theoretical interpretation the intrinsic membrane permeabilities to ions have been estimated for various solution chemistries. Information on the ionic permeabilities is useful for the optimization of membrane performance in electrolyte mixtures. Predictive modelling of NF is important for the optimization and scale-up of its applications.

## References

[1] A. Yaroshchuk, et al. (2011). Solution-diffusion-film model for the description of pressure-driven trans-membrane transfer of electrolyte mixtures: One dominant salt and trace ions. *Journal of Membrane Science*, 368, 192 – 201.

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