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The effect of membrane characteristics on nanofiltration membrane performance during processing of practically saturated salt solutions

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ABSTRACT

Information on the effect of membrane characteristics on the performance of nanofiltration membranes during processing of concentrated sodium chloride solutions is scarce. This hampers membrane selection for these applications. In this study nanofiltration membranes, ranging from very tight to very open, have been evaluated for processing of sodium chloride solutions obtained from solution mining. Sulfate retention of these membranes is inversely related to their pore radius obtained from membrane characterization. The chloride retention during nanofiltration of practically saturated salt solutions is a function of the sulfate concentration difference between concentrate and permeate. The observed relation is explained by the small sodium chloride chemical potential difference between concentrate and permeate, indicating low membrane resistance for sodium chloride transport. This is concluded from the sodium chloride concentration product ratios of permeate over concentrate, which were found to be between 0.9 and 1 for all membranes evaluated. This ratio is proportionally related to the membrane pore radius obtained from characterization. Based on the results the sulfate and chloride retention of nanofiltration membranes for processing of saturated sodium chloride solutions can now be obtained from a simple characterization experiment.

1. Introduction

Nanofiltration is a pressure driven membrane technology with membrane characteristics in between those for reverse osmosis and ultrafiltration [1]. This technology is commonly applied in amongst others the water production industry, in the food industry and the chemical industry [1]. One of the applications for which nanofiltration membranes are suitable is the separation of di-valent from mono-valent anions in an aqueous solution. One of the best known examples is the separation of sulfates from chlorides. Other technologies, e.g. liquid–liquid extraction, are being explored for the separation of sulfates from chlorides as well [2]. Yet, nanofiltration is (still) the preferred option for this application. Usually studies that report about this application deal with solutions containing low sulfate and chloride concentrations studied for modeling purposes. However, industrial applications often deal with the separation of more concentrated solutions, such as sea water (for off-shore applications) [3], depleted brines in the chlor/alkali industry (for more efficient sulfate purging) [3], practically saturated brines that are produced in the salt industry [4,5] (e.g. for production of sodium sulfate crystals or processing of other salt brine streams) and, as recently reported, for treating reverse osmosis concentrates obtained from processing of sea water [6,7].

For these types of applications only limited information is available in open literature and there is a lack of fundamental understanding of the performance of nanofiltration membranes for processing of these concentrated salt solutions. Bargeman et al. [5] have made a first effort to relate the chloride retention obtained during processing of salt plant mother liquor to the difference in sulfate concentration between retentate and permeate for NF-270 and Desal 5DK nanofiltration membranes. Although they have obtained a nice relation between the two, fundamental understanding of this relation has not been given. Furthermore, a broad range of nanofiltration membranes with molecular weight cut-offs (MWCO) ranging from 200 Da to 1000 Da are commercially available. It is unclear whether this relation obtained for NF-270 and Desal 5DK applies to other nanofiltration membranes as well. Because of this lack of information selection of a proper membrane for the required application is not straightforward. The objective of this work is to improve the fundamental understanding of processing of nearly saturated sodium chloride solutions with nanofiltration membranes and to facilitate the selection of these membranes for practical applications. Therefore a range of nanofiltration membranes based on different polymers and with different MWCO (as reflected by differences in average pore radii) have been evaluated. The membranes have been characterized with pure water and model solutions containing a single neutral solute to obtain pore radius and

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effective membrane thickness, and model solutions containing a single salt. The retention characteristics of the membranes obtained during single salt solutions experiments have been related to the obtained pore radii of the membranes. Subsequently, sulfate retentions obtained during nanofiltration of practically saturated salt solutions originating from solution mining have been related to the pore radii from the characterization experiments, and chloride retentions have been related to the difference in sulfate concentrations between retentate and permeate for all evaluated membranes. Obtained results have furthermore been explained by thermodynamic considerations.

2. Theoretical considerations

2.1. Determination of the pore radius and effective thickness during membrane characterization

The extended Nernst–Planck description is most often used to interpret the flux and retention results obtained from nanofiltration experiments. Therefore this description was used in the current study as well to obtain membrane pore radii and effective thicknesses from characterization experiments using single solute glycerol, glucose or sucrose solutions. The mean pore radius and effective thickness reported in this study were obtained using the equations described in [8,9] and below.

For uncharged solutes such as glycerol, glucose or sucrose, the transport through the membrane is governed purely by diffusive and convective flows. Consequently, the Nernst–Planck equation yields

$$j_i = -D_{i,p}\frac{dc_i}{dx} + K_{i,c}c_i\nu \tag{1}$$

where

$$D_{i,p} = K_{i,d}D_{i,\infty} \tag{2}$$

$K_{i,d}$ and $K_{i,c}$ account for the hindrance due to diffusion and convection respectively, and can be related to the hydrodynamic coefficients K^{-1} (enhanced drag) and G (lag coefficient) according to the following equations [8]:

$$K^{-1}(\lambda, 0) = 1.0 - 2.3\lambda + 1.154\lambda^2 + 0.224\lambda^3 \tag{3}$$

$$G(\lambda\ , 0) = 1.0 + 0.054\lambda - 0.988\lambda^2 + 0.441\lambda^3 \tag{4}$$

where

$$\lambda = \frac{r_s}{r_p} \tag{5}$$

In Eq. (5) r_s represents the solute radius and r_p the mean pore radius of the membrane.

In our approach it is assumed that the solute velocity was fully developed [8] and the solute velocity had a parabolic profile of the Hagen–Poiseuille type. Thus the hindrance factors become [8]

$$K_{i,d} = K^{-1}(\lambda, 0) \tag{6}$$

$$K_{i,c} = (2 - \Phi)G(\lambda, 0) \tag{7}$$

where

$$\Phi = (1 - \lambda)^2 \tag{8}$$

Eq. (1) can be expressed in terms of real rejection of the solute by the membrane as

$$R_{real} = \frac{C_{i,m} - C_{i,p}}{C_{i,m}} = 1 - \frac{K_{i,c}\Phi}{1 - \exp(-Pe_m)[1 - \Phi K_{i,c}]} \tag{9}$$

where the Peclet number Pe_m is defined as

$$Pe_m = \frac{K_{i,c}J}{K_{i,d}D_{i,\infty}}\frac{\Delta x}{A_k} \tag{10}$$

where J represents the permeate flux in $m^3\,m^{-2}\,s^{-1}$, $D_{i,\infty}$ is the bulk diffusivity in $m^2\,s^{-1}$ and $\Delta x/A_k$ is the effective membrane thickness (m).

To properly calculate the pore radius of the different membranes from single neutral solute solution experiments concentration polarization at the membrane surface was taken into account as well. The relation between the real retention and the observed retention can be obtained from [8,9]

$$\ln\left(\frac{1 - R_{obs}}{R_{obs}}\right) = \ln\left(\frac{1 - R_{real}}{R_{real}}\right) + \frac{J}{k} \tag{11}$$

where the observed retention (in the remainder of this work referred to as retention) is defined as

$$R_{obs} = 1 - \frac{C_p}{C_c} \tag{12}$$

Since cross-flow operation was used in this study, the correlation for the mass transfer coefficient k as proposed in [8] for dead end stirred cell operation could not be used. Consequently, we assumed the mass transfer coefficient k to be equal to the ratio of the diffusion coefficient at infinite dilution D_∞ over the film thickness δ. On the basis of earlier studies in the DSS labstak at similar flow-rate [10] a constant value for the film thickness of $\delta = 2.0 * 10^{-5}$ m has been selected.

Furthermore, in the approach described in [8,9], the effective membrane thickness $\Delta x/A_k$ was obtained from the Hagen–Poiseuille equation using the pure water flux of the membrane

$$\frac{J_w}{\Delta P} = \frac{r_p^2}{8\eta(\Delta x/A_k)} \tag{13}$$

where $J_w/\Delta P$ is the pure water permeance in $m\,s^{-1}\,kPa^{-1}$ and η is the dynamic viscosity of the solution in kPa s.

2.2. Thermodynamic considerations for sodium chloride salting-out by sodium sulfate during nanofiltration operation processing nearly saturated salt solution

In earlier work [5] the retention of NF-270 and Desal 5DK for chloride during nanofiltration of saturated mother liquor brines (with very high sulfate concentrations in the solution) was shown to be negative and a function of the difference in sulfate concentration between concentrate and permeate. The observed effect is ascribed to the salting-out effect on (sodium) chloride due to the presence of (sodium) sulfate. Salting-out is a well-known phenomenon in extraction and crystallization processes, where the solubility of a specific salt is reduced e.g. by the addition of a common-ion salt (Le Chatelier's principle), leading to crystallization. Similarly, during nanofiltration of salt solutions practically saturated in sodium chloride, the concentration of sodium sulfate in the retentate leads to salting-out of sodium chloride due to common ion effects. This salting-out effect can either lead to sodium chloride crystallization in the retentate, or to sodium chloride passage through the semi-permeable nanofiltration membrane. Since the retention of the nanofiltration membranes at high NaCl concentrations is close to 0 for single salt solutions, and long term nanofiltration operation for salt solutions saturated in both sodium chloride and sodium sulfate is possible [5], which would not be expected for situations where crystals are produced in the retentate, it is assumed that the primary salting-out effect is the transport through the nanofiltration membrane. Salting-out of the sodium chloride for practically saturated sodium chloride solutions is a thermodynamic phenomenon. In nanofiltration processes per definition the chemical potential of the permeate is lower than the chemical potential of the concentrate due to transport related resistances. This means that the following