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Effect of temperature on ion transport in nanofiltration membranes: Diffusion, convection and electromigration

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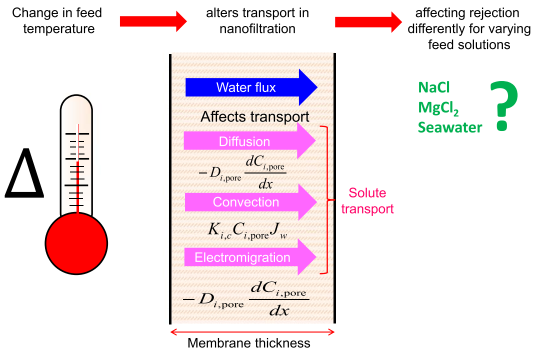
GRAPHICAL ABSTRACT



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ABSTRACT

Nanofiltration performance as a function of feed temperature is relevant to several industrial settings including pretreatment for scale control in thermal desalination. Understanding of solute transport as a function of temperature is critical for effective membrane and system design. In this study, nanofiltration is modeled at 22, 40 and 50 °C using the Donnan Steric Pore Model with dielectric exclusion (DSPM-DE). This modeling includes the temperature dependence of the three modes of solute transport, namely the convective, electromigrative, and diffusive modes, and the three mechanisms of solute exclusion, namely Donnan, steric, and dielectric exclusion. The effect of temperature is captured through the variation of membrane parameters and solvent and ionic mobilities with temperature. We compare the most abundant ionic compound in natural water, sodium-chloride with magnesium-chloride to portray how the salt passage and rejection change for a 1:1 salt compared to a 2:1 salt, and we analyze Arabian Gulf seawater to understand how rejection of scale-forming ions, such as Mg^{2+} and Ca^{2+}, is affected by feed temperature. In all cases, solute transport increases with temperature, attributed predominantly to the cumulative effect of membrane parameters and only to a small extent (up to 5%) to the solvent viscosity and ion diffusivity together.

1. Introduction

1.1. Significance of nanofiltration for elevated feed temperatures

In a world where water-scarcity is a burgeoning issue, methods of water-treatment and reuse that are economic and minimize energy consumption are of vital importance for the safekeeping of the environment [1]. Nanofiltration (NF) is a pressure driven membrane-based desalination technique. The pore sizes of NF membranes are between that of reverse osmosis (RO) and ultrafiltration (UF) membranes [2–6]. NF has the unique capability to

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Nomenclature

A_k	porosity of membrane
C	concentration, mol m^{-3}
C_X	membrane volumetric charge density, mol m^{-3}
d	thickness of a single water molecule (0.28 nm), nm
D	solute diffusivity, m^2 s^{-1}
F	Faraday's constant, C eq^{-1}
j	solute flux, mol m^{-2} s^{-1}
J_w	solvent permeation flux, m s^{-1}
K_c	hindrance factor for convection
K_d	hindrance factor for diffusion
N_c	number of components in the mixture
r_{pore}	pore radius of membrane, m
R	universal gas constant, J mol^{-1} K^{-1}
T	temperature, K
x	distance normal to membrane, m
Δx	membrane active layer thickness, m
z	valence of species

Greek symbols

ε	dielectric constant of medium
ε^*	dielectric constant of oriented water layer inside pores
λ	ratio of solute Stokes radius to pore radius
ν	kinematic viscosity, m^2 s^{-1}
ρ	density, kg m^{-3}
Φ_i	steric partitioning factor
Φ_B	Born solvation factor for partitioning
ψ	membrane potential, V

Subscripts

D	Donnan potential
i	solute species
m	feed-membrane interface
p	permeate just outside the membrane
$pore$	inside pore
w	solvent
∞	bulk

Dimensionless parameters

$R_{C/E}$	ratio between the convective and electromigrative terms
$R_{E/D}$	ratio between the electromigrative and diffusive terms

preferentially remove multivalent ions [7,8]. In several applications, water temperature varies from point-to-point in the treatment plant or changes over time [9]. For example, NF-MSF (nanofiltration with multistage flash) and NF-MSF-RO (nanofiltration with multistage flash and reverse osmosis), are widely studied applications of NF in hybrid with thermal desalination systems where feed (seawater or brackish water) temperature changes over the year and the performance of the nanofiltration membrane changes noticeably with temperature [10]. Nanofiltration also has other high temperature applications: in the textile industry, water used for bleaching and dyeing may reach temperatures up to 90 °C; in the pulp and paper industry, the water temperature is often above 60 °C [11]. Water temperature is usually reduced before membrane treatment. This practice requires expenditure on heat exchangers and also creates energy costs due to the inefficiencies of the heat exchangers [12]. Thus, by designing NF membranes for optimal performance at above ambient temperature, capital costs and energy consumption in heat-exchangers, dependence on other energy-intensive water-treatment methods such as RO, and the use of chemical additives to remove scale-forming ions can be reduced significantly [13]. Detailed modeling of nanofiltration (NF) with variation in feed temperature is necessary to achieve this, as the rejection of undesired components can vary significantly as a result of changing temperature.

1.2. The DSPM-DE model of nanofiltration

This work uses the Donnan Steric Pore Model with Dielectric Exclusion (DSPM-DE) to analyze the temperature dependence of nanofiltration. This model has been used widely into recent times to model and explain nanofiltration performance using a variety of feed solutions with success [14–19]. DSPM-DE is a comprehensive model for nanofiltration. As the name suggests, the model provides information regarding the magnitudes of the different modes of solute exclusion occurring at the membrane-solution interfaces, namely steric exclusion (size-based exclusion at the pore opening), Donnan effect (repulsion or attraction effect due to membrane potential) and dielectric exclusion (resistance to the solute entering the membrane pores due to an energy barrier associated with shedding of the solute hydration shell in order to enter the pore) [20–22]. The model uses the Nernst-Planck equation to describe solute transport through the membrane and hence provides information on the individual modes of transport within the membrane, namely diffusion (movement of solute down a concentration gradient), convection (solute transported by bulk fluid motion) and electro-migration (ion movement due to the membrane potential gradient). As inputs to this model, the membrane is characterized by certain structural parameters (pore radius and effective active layer thickness) and electrical parameters (membrane charge and pore dielectric constant) [21,23]. These nanofiltration membrane properties are affected by experimental conditions such as feed composition, pH, concentration and temperature [24,25,10]. An understanding of how membrane properties affect the modes of solute exclusion and solute transport for different solutes is important in order to gain intuition about nanofiltration. Such understanding will ultimately allow one to gain intuition of how experimental conditions such as temperature affect rejection and solvent flux characteristics of nanofiltration membranes.

1.3. Conventional understanding of the effect of temperature on nanofiltration

Usually, water flux through nanofiltration membranes increases with increase in temperature, while uncharged solute rejection reduces with increase in temperature and the variation of charged solute rejection with temperature depends on the ion and the membrane used. Although experimental evidence for these observations is abundant in literature, the understanding of how the membrane itself changes and related modeling work is missing in literature. For instance, from the study of Manttari et al. [11] on the nanofiltration of glucose and pulp mill effluent over a temperature range of 25 °C to 65 °C using several different membranes, the authors found that the rejection of uncharged solutes decreased by ~20% from 20 °C to 55 °C and the overall rejection of the ionic species remained almost unchanged (at ~90%) over the same range of temperature. Schaep et al. [26] experimentally studied the nanofiltration of ground water using the UTC-20 NF membrane over a temperature range of 10 °C to 30 °C and found that water flux at 30 °C is 1.5 times that at 10 °C. In their study, the rejection of monovalent ions (sodium, chloride and potassium) decreased significantly over the given range of temperature, while the rejection of divalent ions (calcium, magnesium and sulfate) was barely affected by temperature, showing only a slight increase with increase in temperature [26]. In another study by Nilsson et al. [27], the Alfa Laval NFT-50 nanofiltration membrane was used over a temperature range of 20 °C–50 °C keeping solvent flux constant, and the results showed that the rejection