



Selective rejection of ions and correlation with surface properties of nanofiltration membranes



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ABSTRACT

The selective ions permeation through nanofiltration (NF) membranes is the rationale of its application in different fields. However, the correlation of selectivity with membranes properties such as hydrophilicity, surface free energy and electrokinetic potential is not completely understood. Three negatively charged commercial NF membranes (NP010, NP030 and NF90) were characterized by scanning electronic microscopic (SEM), contact angle and zeta potential measurements. The rejection of salts typically present in seawater (NaCl, Na₂SO₄, MgSO₄, K₂SO₄, and CaSO₄) was evaluated at various transmembrane pressures. Sieve mechanisms, ionic electrical exclusion, dielectric effects and permeate flux coupling of ions to keep electroneutrality contribute simultaneously to ions selective rejection. Permeation with mixture of mono and divalent ions through membranes with higher pore size, NP010 and NP030, showed that high sulfate exclusion leads to increase in the rejection of all cations present in the solution. Conversely, for NF90 membrane steric effects are predominant and high sulfate rejection leads to reduction of monovalent ions rejection.

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1. Introduction

Nanofiltration (NF) is a relatively new technique among all pressure-driven membrane separation technologies, being currently used for water treatment, seawater desalination, solvent recovery and removal of solutes from complex process streams [1–4]. Mostly, NF membranes are a thin film composite with pore sizes in the range of 0.5–1.5 nm and consisting of three layers: (1) a nonwoven polymeric support, usually polyethylene terephthalate (PET), (2) a microporous polymeric support, made of polysulfone, and (3) a thin separation layer consisting of cross-linked polyamide, produced by interfacial polymerization [5,6]. Other polymeric materials have been investigated for the preparation of asymmetric NF membranes by phase inversion, as polyethersulfone (PES) with pore sizes in the range of 1–200 nm, in order to increase the thermal stability [7]. Accurate characterization of NF membranes surface charge and hydrophilicity is vital for understanding water and solute permeation, essential in applications with specific requirements, for example, desalination of seawater for oil reservoir injection [8,9].

Several studies have been concluded that NF membranes have a porous active layer in nanoscale [2,10,11]. This results in complex mechanisms for solute transport, a combination of both steric and

non-steric effects, including: (1) sieving mechanisms, (2) solution-diffusion mechanism and (3) additional effects due to the surface characteristics of the NF membranes, including Donnan (charge balance) and dielectric effects [12–15].

Surface charge in polymeric membranes is commonly described through zeta potentials, determined from electrokinetic measurements [16]. The membrane charge originates from the dissociation of ionic groups at the membrane surface, including pores wall, which strongly depends on the pH and ionic strength [13,17,18]. In addition, ions from the contacting solution may adsorb on the membrane surface modifying the membrane surface charge [19]. Several studies are dedicated to experimental evaluation and modeling of the membrane charge influence on permeation through NF membranes. Childress and Elimelech [16] evaluated the performance of a commercial NF membrane with solutions containing divalent ions (CaCl₂, Na₂SO₄ and MgSO₄), relating with the membrane surface charge. Teixeira et al. [8] determined zeta potential measurements of a commercial NF membranes and concluded that the surface charge of the membrane, pH and salt kind have influence on monovalent and divalent ions separation. Tanninen et al. [20] analyzed the selectivity of commercial NF membranes using single and mixed salts solutions, showing that Donnan and sieve effects have significant impact on salt permeation. Some studies revealed that dielectric exclusion is an additional mechanism for ions exclusion, appearing when the solvent is confined in nanopores [14,21–23].

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The hydrophilicity of NF membranes, which is determined by the nature of the ionic groups such as $-\text{OH}$, $-\text{NH}_2$, SO_3^- , has important influence on its performance, especially on permeate flux [6]. Different researchers have evaluated the use of contact angle measurements for characterizing the material wettability and surface energy [6,24–26]. Bhattacharjee and Sharma [27] characterized UF membranes with organic solutes and Brant and Childress [28] characterized RO/NF membranes interactions with colloidal particles. These studies found that interaction with the membranes was primarily dictated by the surface energy. More recent, Hurwitz et al. [29] reported that commercial polyamide RO and NF membranes changed its contact angle as a function of pH, salinity and ion kind, pointing out that additional study could improve the comprehension about transport mechanisms and the membrane performance.

In our work, contact angle, surface free energy and zeta potential of three commercial NF membranes (NP010, NP030 and NF90) were determined. The combination of these characterization techniques represents a novelty on nanofiltration studies and allows a better comprehension of the membrane performance and about the phenomena involved in ions permeation. To investigate the ion selectivity, single and mixed salt solutions with monovalent and divalent ions (NaCl , Na_2SO_4 , MgSO_4 , K_2SO_4 , and CaSO_4), were also used in permeation experiments.

2. Material and methods

2.1. NF membranes and chemicals

Nanofiltration membranes were acquired from Microdyn-Nadir, NP010 and NP030, and from Dow FilmTec, NF90, whose main characteristics are shown in Table 1.

Synthetic aqueous solutions of different salts were used as feed solutions. Certified analytical grade potassium chloride (KCl), calcium chloride (CaCl_2), magnesium sulfate (MgSO_4), sodium sulfate (Na_2SO_4), sodium chloride (NaCl) and potassium sulfate (K_2SO_4) salts were purchased from VETEC. Ultra-pure water (conductivity below $1 \mu\text{S}/\text{cm}$) was used in all experiments.

2.2. Membrane characterization

2.2.1. Scanning electron microscopy (SEM)

Scanning electron microscopy (FEI Company Quanta 200) was used to observe NF membrane morphology. Membrane samples were gently removed from the nonwoven support and cryofractured in liquid nitrogen and then coated with gold to make them conductive.

2.2.2. Contact angle and surface free energy

Static advancing contact angle was assessed by the sessile drop method using a goniometer (Dataphysics OCA 15) at room

temperature. For surface energy analysis, ultra-pure water deionized water and diiodomethane were used. A droplet of each liquid ($1 \mu\text{L}$) was delivered onto the membrane surface and a static image of the droplet was taken. SCA software (Dataphysics) was used to calculate the contact angle. Surface free energy of NF membranes was obtained by the Owens, Wendt, Rabel and Kaelble method (OWRK), taking the average value of three contact angle measurements [32].

2.2.3. Zeta potential of the membrane surface

Zeta potential of NF membranes was determined by streaming potential measurements with an electrokinetic analyzer (SurPASS, Anton Paar) with a clamping cell (Fig. 1). According to Fig. 1, two membrane samples of $55 \text{ mm} \times 25 \text{ mm}$ were mounted opposite each other and separated by a spacer, forming a thin slit channel. The streaming potential is resulted from the pressure-driven flow of an electrolyte solution that passes through this channel. Then the zeta potential was calculated using the Fairbrother-Mastin equation, Eq. (1) [28]:

$$\left(\frac{\Delta\phi}{\Delta P}\right) = \zeta \frac{\varepsilon_0 \varepsilon_r}{\eta \lambda_0} \left(\frac{\lambda_h R_h}{R}\right) \quad (1)$$

where ζ is the zeta potential (mV), $\Delta\phi$ is the measured streaming potential in the flow cell (mV), ΔP is the applied pressure (mbar), ε_0 is the vacuum permittivity (F m^{-1}), ε_r is the relative dielectric constant of the electrolyte solution, λ_0 is the bulk conductivity of the circulating electrolyte (mS m^{-1}), R_h and R are the measured electrical resistances (mV A^{-1}) across the flow channel filled with the saline reference solution and with the electrolyte solution, respectively. Prior to the sample mounting, the membranes were soaked in the electrolyte solution for 24 h.

2.3. Nanofiltration experiments

The performance of the nanofiltration membranes was evaluated using a membrane filtration set up. The system is equipped with a feed tank (10 L) where the feed solution is kept at constant

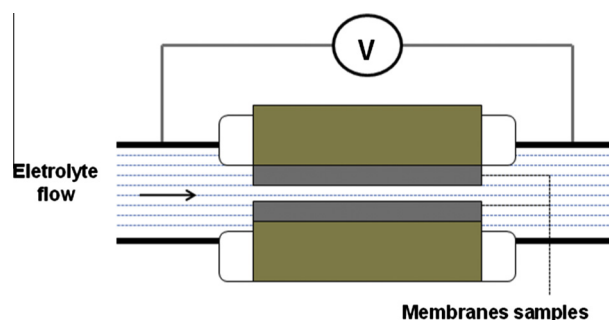


Fig. 1. Schematic draw of the clamping cell used in the zeta potential measurement.

Table 1
Characteristics of NF membranes.

	NP010	NP030	NF90
Supplier	Microdyn-Nadir	Microdyn-Nadir	Dow FilmTec
Material of skin layer ^a	Polyethersulfone	Polyethersulfone	Full aromatic polyamide
Max. temp., °C ^a	95	95	45
Average pore radius (nm)	1.29 ^b	0.93 ^b	0.68 ^c
pH range ^a	0–14	0–14	3–9

^a According to membranes supplier.

^b [30].

^c [31].

Table 2
Permeation conditions for NF membranes.

Salts	Feed concentration (mol L^{-1})	pH	Osmotic pressure (bar)
NaCl	0.025	5.83	1
Na_2SO_4	0.025	6.22	1.5
MgSO_4	0.025	7.52	1
K_2SO_4	0.025	5.75	1.5
CaSO_4^1	0.025	5.83	1
$\text{NaCl} + \text{Na}_2\text{SO}_4^2$	0.050	6.55	2.5
$\text{NaCl} + \text{MgSO}_4^2$	0.050	7.02	2

Obs: ¹ supersaturated solution; ² solutes mol ratio of 1:1.

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