



Prediction of physical properties of nanofiltration membranes for neutral and charged solutes

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ABSTRACT

Two commercial nanofiltration (NF) membranes viz., NF 300 MWCO and NF 250 MWCO were used for neutral and charged solute species viz., glucose, sodium chloride and magnesium chloride to investigate their rejection rates using Donnan steric pore model (DSPM) and DSPM-dielectric exclusion (DSPM-DE) model. The estimated pore radii are 0.62 nm and 0.56 nm, respectively for the above models, while permeabilities of both the membranes are almost identical. Charge densities were computed using Stokes–Einstein, Born effective and Pauling radii, while dielectric exclusion was assessed for NF 250 membrane. The effect of pH for sodium chloride was studied to evaluate isoelectric point of NF membrane, which was around pH 5. Correlations were attempted between charge density, concentration and pH for each radius. Charge density decreased drastically for sodium chloride when dielectric exclusion was included in the calculations, thus showing real physical characteristics of the membranes, whereas divalent magnesium chloride showed a shift from positive to negative charge density. The importance of charge density and pore radius in understanding fouling propensity of NF membranes was discussed.

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1. Introduction

Nanofiltration (NF) is a pressure-driven novel membrane-based separation technique developed in the 1980s based on reverse osmosis (RO) that is used in separating dissolved components having a molecular weight cutoff (MWCO) of about 200–1000 and a molecular size of about 1 nm. NF can also be used to separate inorganic salts with much smaller sizes than pore size according to electrostatic repulsion [1–4]. The separation in RO (dense membrane) and ultrafiltration (UF) (porous membrane) is based on solution-diffusion and sieving mechanism, but NF takes into account both solution-diffusion, sieving effect and Donnan dielectric exclusion parameters in addition to electro-migration, all of which makes the process useful in separating both charged and organic solutes [5].

The electric charge of a NF membrane plays an important role in the charge separation during a filtration process due to the formation of electrical double-layers that are comparable or bigger than the pore

size. The presently used NF membranes are generally neutral or negatively charged, whether on a commercial or a laboratory scale [6], but studies on positively charged NF membrane are rare. It is therefore, necessary to evaluate physical properties of the positively charged NF membranes. NF membranes have been widely used in various fields, particularly in production of drinking water to remove undesirable compounds such as pesticides or monovalent anions [7,8] with a special attention to defluoridation in rural areas of many countries [9]. NF can also be an interesting solution to selectively demineralize salted water to produce isotonic waters [10] and for the treatment of food ingredients such as seafood aroma concentration [11] or peptides solution concentration [12].

Besides desalination, NF is also used for organic separation [13], recovery of high value organometallic catalysts from the reaction mixtures for recycling and reuse [14], and to separate inorganic salts with much smaller size than the pore size due to electrostatic repulsions. Pharmaceutical applications of NF include the isolation of industrially important antiviral drug precursor, *N*-acetyl-*D*-neuraminic acid [15], clindamycin from the fermentation waste water [16], sodium cefuroxime from cephalosporin-C [17] and cephalixin [18]. In view of such important applications, NF plays an important role in many industries. However, prediction of separation performance of NF membranes is an important way of improvement and a predictive

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model could be a very useful tool for process development and optimization, or for membranes characterization to assist the end-users for the selection of commercial NF membranes. Many authors have studied the mass transfer through membranes in the recent past on the evaluation of the steric, electric, and dielectric exclusion model on the basis of salt rejection rate and membrane potential measurements [19,20].

In our previous studies [21,22], transport properties of NF membranes have been investigated using a transport model, which includes dielectric exclusion in terms of both Born dielectric effect and image force contribution. It was shown that dielectric exclusion cannot be neglected in the analysis of filtration properties of NF membrane [22,23]. However, average charge of the skin that determines selectivity towards ions of different charge can be quite low and, on the average, membrane skin layer behaves as a dielectric medium. In earlier studies [21–24], it was found that Stokes–Einstein, Born and Pauling ionic radii have a profound effect in predicting charge density at the surface of the membrane. Donnan steric pore model (DSPM) as well as DSPM-dielectric exclusion pore (DSPM-DE) models were useful for solutes like sodium chloride, sodium sulfate, magnesium chloride and magnesium sulfate [25]. However, differences in predictions were observed when membrane is positively or negatively charged. The effect of pore size distribution was also investigated, which gave a different prediction for various radii [26,27].

In order to further contribute in this area and to investigate the influence of ionic radii using Stokes–Einstein, Born and Pauling equations to predict DSPM and DSPM-DE parameters, we present here experimental data on two commercial NF membranes viz., NF 250 MWCO and NF 300 MWCO (Permionics, Vadodara, India) and prediction of their physical properties. Sodium chloride and magnesium chloride were used as simple salts to study the effect of pH on rejection as well as to determine NF isoelectric point of the membrane. The effect of radii on hindrance factor was also investigated and physical properties like radius of pore and charge densities were calculated using the theoretical models.

1.1. Theoretical background

In our previous paper [21], mathematical equations were developed based on transport models used in the analysis of experimental data on salt rejections using the assumptions: (i) ideal solution is assumed and transport inside the pore is considered due to convection, diffusion and electro-migration, (ii) transport effects with convection and diffusion are corrected with hindrance factors and the NF membrane has a porous structure, such that Hagen–Poiseuille type relationship can be used for solvent velocity and flow inside the pore is assumed to be laminar, (iii) chemical potential of the solute depends on operating pressure and solvent within the pores consists of one layer of oriented water molecules, (iv) variations in solvent viscosity and dielectric constant inside the pore are considered, but concentration polarization across the surface of membrane is neglected, (v) partial molar volume and diffusion coefficient inside the pore are independent of concentration; the separation at pore interface was considered to be due to steric, Donnan effect and dielectric exclusion, and (vi) electro-viscous term was neglected for velocity of ions in the solvent, while concentration and potential gradient can be varied axially, but radial variation and lateral solute concentration distribution at the pore entrances can be neglected.

3. Experimental

3.1. Membranes

Two NF flat sheet thin film composite membranes, TFC (NF 250 and NF 300) prepared by interfacial polymerization of polysulfone

base under pH range of 3–9 having different molecular weight cutoff were procured from Permionics, Vadodara, India. Experimental rig modified as per our requirement was procured from GE of E2 series. Thin active layer of TFC is the proprietary polyamide with a total area of 2.4 m².

3.2. Solvents

Glucose was used as the neutral solute, while sodium chloride and magnesium chloride were chosen as charged solutes for performing NF experiments. Concentration and pH of electrolyte solutions were measured using an electrical conductivity meter coupled with a pH meter (Oakton Inc). Permeation experiments were performed under the applied pressure of 0.2–1.1 MPa. The retentate and permeate samples were recycled back to the feed tank in order to hold the concentration of the feed solution constant. The concentration of glucose was determined by phenol-sulfuric acid method, while that of sodium chloride was varied from 1 to 100 mol/m³. Viscosity of the solution was considered to be the same as that of pure water. All solutes were nanofiltered and their pH was adjusted between 3 and 9 using sodium hydroxide and sulfuric acid, respectively. Schematic of the NF system is shown in Fig. 1.

Various ionic radii such as Stokes–Einstein, Born effective and Pauling radii were considered. Stokes–Einstein radius was derived from the Stokes–Einstein equation [27] to give:

$$r_i = \frac{kT}{6\pi\eta_0 D_{i0}} \quad (1)$$

The calculated Stokes–Einstein radii at 298.15 K are given in Table 1. For calculations, dynamic viscosity of water (η_0) at 25°C was taken as 0.89×10^{-3} Pa s and Born effective radius was derived from Born theory. Fig. 2 illustrates the structure of solutes, which consists of bare ion radius interacting with the solvent. The cation is surrounded by water molecules with oxygen atoms approaching them, while anion is surrounded by water molecules with hydrogen atoms approaching them; R_{ion} is the ionic radius, which is purely a property of the ion. The R_{gmax} is defined as the position of the first peak in the ion–solvent radial distribution function, which depends on both ion and molecular nature of the solvent. Born model was used to treat the solvation free energy of the ion even though use of ionic radius (R_{ion}) overestimates the magnitude of solvation energy. Based on molecular dynamics simulation of ions of varying charges [28], Born effective radius can be calculated as:

$$r_i = (R_{ion} + R_{gmax}) / 2.0 \quad (2)$$

3.3. Description of different ion radii

Recent rejection measurements for ion mixtures using artificial nanofilters have shown that Pauling radius is the best choice [19] and it is defined as the bare ion crystal radius. The Pauling radii for hydrated ions (Na^+ , Mg^{2+} , Cl^- , and SO_4^{2-}) are given in Table 1.

3.4. Computations

Double precision was used in all the simulations, based on Runge–Kutta Gear method and Newton–Raphson technique using FORTRAN subroutines namely, DGEAR and ZSPOW as per details given in our earlier paper [21].

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