Prediction of single salt rejection in nanofiltration membranes by independent measurements

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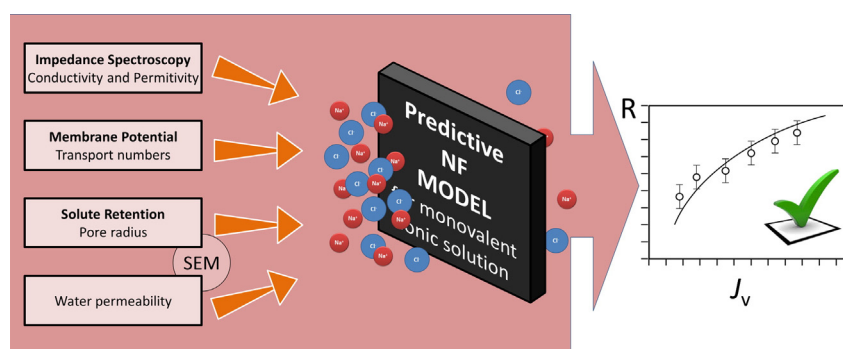
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HIGHLIGHTS

- The proposed model predicts retention of simple salts by nanofiltration,
- Main input parameters are obtained by impedance spectroscopy,
- Predicted retentions deviate less than 5% from the experimental ones.

GRAPHICAL ABSTRACT

ABSTRACT

In this work a method is proposed to predict salt rejection by nanofiltration. The procedure starts from the steric, electric and dielectric exclusion model with charge (and permitivity) depending on the concentration along the pore, SEDE-VCh, for membrane characterization, and substitutes all fitting parameters by values obtained by independent methods. These parameters are the relative permittivity inside the pores and the two constants of the Freundlich isotherm for the volumetric charge density, which can be obtained by impedance spectroscopy techniques. Moreover, the pore size and shape and the active layer thickness are required to complement the model. The pore size was obtained by using a neutral solute rejection test and the active layer thickness was estimated by SEM. Therefore, the model also requires pore shape as input. AFM measurements suggest the assumption of a slit shape for the pores.

A Desal-HL membrane has been structurally, electrically and functionally characterized. These data allowed the testing of the predictive model that was subsequently demonstrated; as far as results are good enough considering the complexity of the mechanisms involved. Consequently, it seems clear that once the model parameters have been obtained by independent methods, it can be used as a predictive tool.

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1. Introduction

Nanofiltration (NF) membranes possess some special characteristics that distinguish them from ultrafiltration (UF) and reverse osmosis (RO) ones. Firstly, they keep relatively high permeate flux at low

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pressure operation compared with conventional RO [1], and secondly, most of them are electrically charged with the subsequent effect on the solute separation mechanism.

Due to the clear interest of NF, it is desirable to have a way to estimate the performance of NF membranes for different solutes and/or combinations of solutes in order to have a predictive understanding of their behavior. As a consequence, there have been many efforts, with this aim in mind, focusing on the development and optimization of mathematical models to predict the separation properties of NF membranes. Firstly based on irreversible thermodynamics (Kedem, Katchalsky and Spiegler works) [2,3], continuing with the hydrodynamic model or pore model introduced by Ferry [4], and the development of hydrodynamic approach models based on the extended Nernst-Planck equation such as the steric hindrance pore, SHP, [5], Teorell-Meyer Sievers, TMS, [6,7], the space charge model, SCPM, by Wang et al. [8] and more recently the Donnan steric partitioning model, DSPM, which combines the steric and Donnan exclusion effects [9].

Nowadays the most complete models include dielectric exclusion effect [10], including steric, Donnan and dielectric partitioning effects in the interfaces and convective, diffusive and electromigrative transport effects in the inner part of the membrane. The mass transfer through the membrane is described using the extended Nernst-Planck equation modified by hydrodynamic coefficients to reflect the influence of the pore constriction on both convection and diffusion. The equilibrium partitioning relation takes into account electric and dielectric effects to describe the distribution of species at the pore inlet and outlet [1]. These effects are the Donnan exclusion and the dielectric exclusion, being the later composed by two terms, the Born effect and the image forces one. The Born effect is connected with the low values of the relative permittivity of a liquid inside a pore of nanometer dimensions. The image forces effect correspond to the interaction between the ions and the polarization charges induced by them at the pore wall.

Bandini in 2001–2002 firstly presented the Donnan steric partitioning model with Dielectric exclusion model, DSPM&DE, [11]. It is a model in which the ionic partitioning at the interfaces between the membrane and the external phase takes into account the three separation mechanisms: steric, Donnan equilibrium and dielectric exclusion. Bandini's model introduced the idea of the dielectric exclusion as an additional cause of partitioning to those of bare Donnan steric pore model (DSPM) initially proposed by Bowen [9,12,13]. We refer to the reading of the work of Bandini for a more extensive explanation of the model [14].

In 2005, Szymczyk and Fievet proposed another model, the steric, electric and dielectric exclusion, SEDE, model [15]. The volume charge density of a NF membrane was determined from tangential streaming potential measurements (TSP) and the model was used to assess the rejection rate of the membrane with a single adjustable parameter: the relative permittivity of the solution filling the pores. In a later work [1] Lanteri et al. proved that the SEDE model is able to reproduce both experimental rejection rates and membrane potentials by using several fitting parameters: effective pore size, effective thickness-to-porosity ratio, $\Delta x_a/A_{ka}$, effective volume charge density, X, and relative permittivity inside the pores, ε_p, all them being considered constant through the membrane. Unfortunately, it was observed that there are different couples of values (X, ε_p) that lead to the same membrane potential value, between all of them, true values of X and ε_p are difficult to obtain by any fitting procedure with reasonable physical meaning for both the parameters. In a continuing work [16], Déon et al. assumed the model proposed by Silva et al. [17] that considered that the charge density within the pore varies with concentration. Déon et al. did not included the image force term into the dielectric effect. However they assumed that this effect would be indirectly included in the "effective" estimated value for ε_p that can be obtained by fitting but that sometimes lead to weird values.

This article presents a novel method to predict the salt rejection developed by a NF membrane. The model includes three parameters: the relative permittivity inside the pores, ε_p, and the Υ and Γ parameters of a Freundlich charge isotherm of the volumetric charge density, $X = \Upsilon c^\Gamma$. Unlike the papers presented so far, in the present work these three parameters are obtained by independent methods or experimental techniques.

In this case, an estimation of the thickness of the active membrane layer, Δx_a, is obtained from scanning electron microscopy, SEM, allowing the evaluation of membrane porosity, A_k, from water permeability measurements. The membrane porosity of the active layer is necessary to link the relative permittivity of the wet membrane with the corresponding value for the solution inside the pores and the dry membrane material, as it will be explained later. Transport numbers are obtained from membrane potential measurements. The viscosity inside the pore is calculated by using only the pore radius and the bulk value. In the present work, as it was done previously [17], the volumetric charge density and the relative permittivity inside the pores were considered as variable along the pores and depending on concentration, $\varepsilon_p = f(c)$ $X = f(c)$. These two magnitudes are obtained from Impedance Spectroscopy (IS) measurements using a similar method to that described previously [10]. The model can be called SEDE-VCh model because it uses steric, electric and dielectric exclusion with X (and ε_p) assumed as depending on concentration (an consequently on distance along the pore). The changes of charge along the pore, within this model, can be as large as to span over an order of magnitude, depending on the operation conditions and leads better fitting to the experimental results [17].

The main objective of the present work is to evaluate the predictive capacity of the model to foretell NF performances. The predictive character of the model consists in its ability to obtain retention from independently known morphological and electrical properties of the membrane. This permits securing the proposed model as to get membrane retention by easier and faster procedures tan the simple measurement of observed retention followed by a careful concentration-polarization through mass transfer models. With this aim, the experimental volume flux and intrinsic retention of aqueous NaCl solutions through a flat sheet Desal HL, a polyamide NF membrane made by GE-Osmonics, will be compared with the corresponding predictions obtained from independently measured ε_p and X. It will be shown that fair accordance is found for the concentrations range studied.

Desal HL is a typical composite membrane, it consists of three layers: a thin top selective polyamide layer of a few hundred nanometers in thickness (poly(piperazine-amide)), an asymmetric microporous polysulfone support layer, and a polyester non-woven fabric layer for mechanical strength [18,19]. This membrane has been studied in our previous work [10,20–22] and others authors [18,19,23,24] so there is a good reservoir of knowledge on its characteristics and functionality that can help to assess the models and its predictive capacity.

2. Theory

2.1. Dielectric analysis

Impedance spectroscopy measurements determine the electrical impedance of a system as a function of frequency. When the objective is the electrical characterization of a membrane, the system is formed by five elements or layers: electrode + electrolyte + membrane + electrolyte + electrode. The system corresponds to three phases: electrode, membrane and electrolyte. In such a system it is possible to recognize a scheme of series resistance as shown in Fig. 1. Evidently similar layers can be characterized by a unique set of electrical parameters or elements.

For the dielectric analysis, we follow the same procedure than in our previous work, in order to analyze the Impedance Spectroscopy results [10,21]. A summary of the procedure followed can be found in the Appendix A.