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Pore size analysis from retention of neutral solutes through nanofiltration membranes. The contribution of concentration–polarization

Noemi García-Martín [a], Verónica Silva [a], F.J. Carmona [b], Laura Palacio [a,*], Antonio Hernández [a], Pedro Prádanos [a]

[a] Grupo de Superficies y Materiales Porosos (SMAP, UA-UVA-CSIC), Dpto. de Física Aplicada, Facultad Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain
[b] Dpto. de Física Aplicada. Escuela Politécnica, Universidad de Extremadura, 10004 Cáceres, Spain

HIGHLIGHTS

- We determine pore size distribution of a nanofiltration membrane.
- We study the influence of mass transfer coefficient on pore radius calculation.
- We review the Reynolds number and the application of Sherwood relation.

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ABSTRACT

Pore size distribution is one of the most important characteristics of a membrane. This can be obtained from the fitting of pore radius calculated from retention versus flux measurements for a set of solute solutions. In this work a set of non-charged similar molecules is chosen as solutes to minimize other interactions apart of those related to size. The hydrodynamic model will be used to characterize the behavior of the membrane to uncharged solutes, assuming that membrane pores are straight and cylindrical.

As is known, the phenomenon of concentration polarization must be taken into account because true retention is not experimentally accessible by concentration measurements. Frequently, the film layer model is applied for the dependence of concentration with experimental conditions; but the application of this model requires prior knowledge of the mass transfer coefficient which is evaluated by different dimensionless correlations (Sherwood correlation). Here we show a review of different alternatives in doing it and analyze their consequences when computing the pore size distribution.

Experimental data were obtained from dead-end filtration experiments of a set of four ethylene glycol solutions with a nanofiltration membrane. Obtained results show the importance of the mass transfer model in the pore size value obtained.

1. Introduction

Membranes have found a broad range of application in an endless list of production sectors, such as food, gases, pharmaceuticals, or water. The pressure driven membrane processes are frequently classified in four big groups: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes. The last two are the most important ones when the issue is desalination or purification of water [1]. Taking into account the economic importance of the two most common purposes of such processes, watering and human consumption, one can imagine the amount of resources devoted to improving the characterization and optimization of membranes made for these objectives. This membrane characterization can be focused on the structural or functional aspects. Between those belonging to structural characterization, the pore size distribution plays an important role in determining the membrane retention, especially in the case of uncharged solutes.

There are several methods to determine the pore size distribution of nanofiltration membranes [2]. But, since in these membranes the pore size is extremely small (about 1 nm) the result is strongly influenced

* Corresponding author. Tel.: +34 983 423943.
E-mail address: laurap@termo.uva.es (L. Palacio).

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by the method used. For this purpose various methods can be applied, for example: image analysis in atomic force microscopy, liquid–liquid displacement, or retention–flux models [3]. Though ideally they provide the same information, the final results reveal the peculiarities of each one [3,4]. The method of retention of neutral solutes is one of the most used because with uncharged solutes the interaction solute–membrane is minimized. But solutes of different sizes or molecular weights should be appropriately chosen to assure similar interactions with the membranes, if not, the differences of their interaction with the membrane material can cause differences in their relative retention that could not be attributed to their size exclusively. When using a retention–flux model, pore radius is calculated from permeate flux and retention values for one or more different solutes at different conditions of pressure and stirring speed. Knowing that the flow is "a priori" trivially measured, and retention values could be calculated from concentration at both sides. However, due to the concentration–polarization effect, to measure real concentrations on the membrane surfaces, although possible, would require complex experimental techniques [5–9]. Some of these techniques are, for example: interferometric measurements of the concentration–polarization profile in an unstirred batch cell [10, 11], light deflection techniques (shadowgraphy, refractometry), magnetic resonance imaging, radio isotope labeling, electron diode array microscope or direct pressure measurements as is reviewed in [12]. Moreover, unfortunately, these techniques are at present far from being unambiguous.

To solve this problem, the film layer model is usually applied to describe the dependence of concentration with experimental conditions [13]. In this model, the mass transfer coefficient is related with the Schmidt, Reynolds and Sherwood numbers (named *Sc*, *Re* and *Sh* respectively) through the so called Sherwood correlation [14]. In this work the coefficients of this correlation are reviewed because different values have been used for the same fixed parameter without any clear criteria to do so.

Once the true retentions for each solute have been determined, the pore radius is calculated as the fitting parameter of the "Steric pore flow model" (SPFM) [2,15] from data for each solute filtration; the knowledge of both the solute and the pore sizes allows building the pore size distribution.

In this work, experimental data are obtained from a set of four filtrations of a small lineal ethylene glycol solution by a typical NF membrane. This set of noncharged solutes was chosen to minimize the differences in the interaction pore–solute apart from volume (or size).

The hydrodynamic model will be used to characterize the behavior of the membrane to uncharged solutes; assuming that the membrane pores are straight cylinders where diffusion and concentration gradients are the forces acting for the solute transport.

2. Theory

The transport through the membrane, and the transfer control of a solute can be studied from different points of view: hydrodynamics, electrostatic and thermodynamics [16]. In our case, the hydrodynamic model will be used to characterize the behavior of the membrane to uncharged solutes, assuming that membrane pores are straight and cylindrical in shape and the molecules of solute are substantially spherical. Diffusion and concentration gradients act through the pores as the forces for solute transport.

The separation selectivity of a nanofiltration membrane is governed by three processes: transport along the pores, partitioning through the membrane–solution interfaces and transport through the polarization layer [17].

The first two of these phenomena depend essentially on the behavior of the chemical potential. The first one is governed by the first Ficks' law or by the extended Nernst–Planck equation if convection is included. The second one is based on the equality of chemical potentials at both sides of each interface. Meanwhile, the third phenomenon is governed by the hydrodynamics of the filtration set, essentially given by the mass transfer coefficient, which depends on the set-up configuration and experimental conditions.

2.1. Chemical potential

Chemical potential of a species s under isothermal conditions is given by [17]:

$$\mu_s = \mu^0_{s\,(T,p_0)} + \int_{p_0}^{p} \overline{V}(p')\mathrm{d}p' + kT\ln\left(\frac{a_s}{a_0}\right) + W_s \tag{1}$$

where $\mu^0_{s\,(T,p_0)}$ is the standard chemical potential, p_0 the reference pressure, and $\overline{V}$ the partial molar volume in the standard state. a_s is the solute activity, being a_0 the activity for the standard state. And W_s quantifies the interaction free energy including all interactions of the solute with the medium not included into activity; for neutral molecules, only the purely steric interaction must be considered.

2.2. Membrane partition coefficient

Each side of the membrane defines an interface. Assuming that there is equilibrium between both phases (bulk phase, and membrane phase), both chemical potentials must be equal:

$$\mu_{s,b} = \mu_{s,m}. \tag{2}$$

When expressions for both chemical potentials, at bulk and membrane phases, as Eq. (1) indicates, are introduced in identity (2), this leads to a ratio between activities inside and outside the pore, the membrane partition coefficient. In the case of unity activity coefficients and assuming that the molar volume difference is negligible, i.e. for low concentrations, this fraction is the ratio between concentrations [18]. This is supposed identical at both sides of the membrane. For the case of uncharged solutes, only purely steric effects determine this ratio, which coincides with the steric partitioning coefficient. Assuming that flow through a membrane takes place along the *x*-axis direction, being $x = 0$ and $x = \Delta x$ the coordinates for the interfaces, and denoting $-$ and $+$ the left and right sides of each interface, the membrane partition coefficient [19,20] is:

$$K_s \equiv \frac{c_{s,m}}{c_{s,b}} = \frac{c_s(0^+)}{c_s(0^-)} = \frac{c_s(\Delta x^-)}{c_s(\Delta x^+)} = \phi. \tag{3}$$

Different expressions for ϕ, the steric partitioning factor, can be obtained depending on the geometry of the pore, cylindrical, slit, etc. In terms of λ, the ratio between solute and porous radius, $\lambda = r_s/r_p$, for cylindrical pores $\phi = (1-\lambda)^2$ [20–22].

2.3. Transport equation

The membrane pores, supposedly oriented along the *x*-direction, have a length Δx, and a radius r_p. The transport of a species through them is described by the Nernst–Planck equation:

$$j_s = -\frac{D_{s,p}c_s}{RT}\frac{d\mu_s}{dx} + c_s v_s. \tag{4}$$

The flux of species s, j_s, is given by the sum of a diffusion term and a convective one. In the diffusion term, c_s is the solute concentration, $D_{s,p}$ is the diffusivity inside the pore and μ is the chemical potential. The hindering effect introduced by pore walls on solute transport is taken into account by means of the hindrance factors. The hindrance factor for diffusion, K_d, relates the diffusion coefficients inside ($D_{s,p}$) and outside ($D_{s,b}$) the pore $D_{s,p} = K_d D_{s,b}$. The hindrance factor for convection relates the solute (v_s) and the solvent (v_w) speeds into the pore: $v_s = K_c v_w$.