



Influence of solute concentration and dipole moment on the retention of uncharged molecules with nanofiltration



Jason Shirley, Stephen Mandale*, Victor Kochkodan

Centre for complex fluid processing, University of Wales Swansea, SA2 8PP, UK

HIGHLIGHTS

- Molecular weight cut-off (MWCO) is a value used to quantify membrane rejection.
- MWCO of the NTR 7450 membrane has been investigated.
- The effect of concentration on MWCO has been investigated.
- Increased concentration of solute decreases the apparent MWCO.
- Solutes with large dipole moments gave an increase rejection with concentration.

ARTICLE INFO

Article history:

Received 25 July 2013

Received in revised form 14 March 2014

Accepted 17 March 2014

Available online xxxx

Keywords:

Nanofiltration

Molecular weight cut-off

Dipole moment

ABSTRACT

The molecular weight cut-off (MWCO) is an important parameter used in the selection of membranes for specific filtration tasks. The MWCO is also used as a parameter in various membrane models. In this study the MWCO of an NTR 7450 nanofiltration membrane was investigated by filtration experiment and calculation of the rejection of neutral molecules as a function of solute molecular weight. The results were compared to a reflection coefficient model and it was shown that increasing the solute concentration decreased the MWCO value, indicating that MWCO was not a constant parameter but was dependent on concentration. The dipole moment of a solute molecule was also found to have an effect on the membrane's MWCO. The results showed that molecules with a large dipole moment caused rejection to increase with an increase in solute concentration.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nanofiltration is a pressure driven, membrane separation technique that is situated between reverse osmosis and ultrafiltration [1]. The definition of nanofiltration is not clear cut, but typically it concerns the filtration and rejection, at an artificial polymer membrane, of solutes whose size are in the region of 200–1000 Da and are either charged or neutral. Transfer through the polymeric membrane may either be by diffusion through the polymer lattice or by pore flow. Either way charge and size effects are considered to be central to the process. As such it offers more selectivity than reverse osmosis which typically provides a >99% rejection of all solutes [2].

For a successful implementation of a membrane separation process to be possible, it is useful to have a defining value of the membrane's separation capability and as such it is necessary to obtain rejection information for the membrane–solute system. This information is typically reported as the molecular weight cut-off (MWCO) for a membrane. MWCO is a correlation of rejection against solute molecular weight.

Molecules with a molecular weight above the MWCO have a rejection of >90%, smaller molecules have a rejection of <90%.

MWCO is an important parameter that is widely used and modelled [3–5], but a standard approach has not been agreed for its evaluation [6]. Some published studies have mostly focused on modelling the MWCO, determined experimentally, for different types of nanofiltration membranes without emphasis on the effect of experimental conditions [3–5] and only a few have considered factors influencing MWCO [7]. To this end, this 'fixed' membrane property was shown to be dependent on not only the membrane itself but significant properties of the solutions used, the study of which is the purpose of the investigation detailed here.

The effect of dipole moments along with size and other molecular properties, has also been investigated and found to be strongly influential on membrane rejection [4,8,9]. In these studies, materials with a higher dipole moment exhibited lower rejection when treated with nanofiltration membranes. Clearly these particular properties are not specifically related to molecular weight but still influence the apparent MWCO.

In this paper, the rejection of several organic molecules by a NTR 7450 nanofiltration membrane has been investigated. The molecules

* Corresponding author. Tel.: +44 1792 295216; fax: +44 1792 295676.
E-mail address: s.j.mandale@swansea.ac.uk (S. Mandale).

were chosen for their range in molecular weight and dipole moment with the aim of assessing the techniques previously used to determine MWCO for a NTR 7450 membrane and consideration of the physico-chemical parameters and experimental conditions that affect the MWCO results.

1.1. Theory

Transport models for membrane filtration can be reduced to those drawn from the Nernst–Planck equation which is a phenomenological approach to transport modelling at and through the membrane as proposed and expanded upon by several authors [10–19], and the black box approach based upon irreversible thermodynamics.

In general, the transport equation for a nanofiltration membrane consisted of two components: a diffusion component and a convection component [3]. This is reflected by the transport equation of Spiegler and Kedem [18]:

$$j_s = -P_s \Delta x \frac{dc_s}{dx} + (1-\sigma)j_v c_s \quad (1)$$

where P_s was the solute permeability, x was the distance perpendicular to the surface of the membrane, σ was the reflection coefficient and c_s was the solute concentration at the membrane.

On the basis of Hagen–Poiseuille's law solvent flux, j_v , was represented by:

$$j_v = \frac{A_k r \Delta P}{8 \eta \tau \Delta x} \quad (2)$$

where A_k represents the porosity, r the pore radius, η the viscosity, τ the tortuosity, ΔP the trans-membrane pressure and Δx the membrane thickness. It should be noted that, within the context of this paper at least, the concept of pore is at most a theoretical one since unique pores have not been directly observed at this scale (nanofiltration). To this end pore sizes are not real but 'effective'.

At non-infinite pressures, Eq. (1) can be solved to calculate rejection as a function of reflection coefficient, σ , and the solute permeability P_s . The result of this calculation is:

$$R = \frac{(1-F)\sigma}{1-\sigma F} \quad (3)$$

where

$$F = \exp\left(-\frac{1-\sigma}{P_s} J_v\right). \quad (4)$$

The diffusion parameter described a general property of the membrane and allowed prediction of the solute permeability on the basis of solute size, hence Eq. (5)

$$P_s = \frac{\rho}{d_s} \quad (5)$$

where ρ is the specific diffusion parameter. In this work $\rho = 2.07 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ [3], and d_s is the diameter of the solute.

Historically these two equations, Eqs. (3) and (4), were fitted to experimental data to obtain values for the solute permeability, P_s , and the reflection coefficient, σ .

Van der Bruggen and Vandecasteele [3], conducted an extensive review of the theoretical "black-box" models that utilise the Spiegler and Kedem parameters, namely reflection coefficient and solute permeability. The models considered were: the steric hindrance pore model (SHP model); the Zeman and Wales model [20]; the log-normal model and the adapted log-normal model. Van der Bruggen et al. [21] concluded that the reflection coefficient was best represented by the log-normal model. This log-normal model considered the reflection coefficient to

be controlled by a logarithmic function of the pore radius and standard deviation, and the size of the solute molecules. The log-normal model can be manipulated to express the size characteristics as both molecular weight (MW) (Eq. (6)) and effective molecular diameter (Eq. (7)). The log-normal model as a function of MW and $MWCO$ was given by:

$$\sigma(MW_s) = \int_0^{MW_s} \frac{1}{S_{MW} \sqrt{2\pi}} \frac{1}{MW} \exp\left[-\frac{(\ln(MW) - \ln(MWCO) + 0.56s_{MW})^2}{2S_{MW}^2}\right] dMW. \quad (6)$$

Log-normal model as a function of effective molecular diameter (r) and molecular diameter cut-off (\bar{r}) was given by:

$$\sigma(r^*) = \int_0^{r^*} \frac{1}{S_p \sqrt{2\pi}} \frac{1}{r} \exp\left(-\frac{[\ln(r) - \ln(\bar{r})]^2}{2S_p^2}\right) dr \quad (7)$$

where S_{MW} and S_p are the standard deviation for molecular weight and effective diameter, respectively. The relationship between molecular weight and effective diameter was stated to be [21]:

$$d_s = 0.065(MW)^{0.438}. \quad (8)$$

The pressure dependency of the retention, implicated through inclusion of the solvent flux in the transport model (Eq. (4)), was evaluated and denoted as a coefficient of water permeability, K . Although Eq. (2) indicated that water permeability was a function of the membrane porosity, pore radius, and tortuosity as well as the membrane thickness and the solution viscosity, this coefficient was determined from an experimental investigation of the variation of pure solvent flux with trans-membrane pressure and was given as flux per unit of applied pressure. In the present study, a value of $K = 4.72 \times 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ bar}^{-1}$ was used as previously calculated [3] for NTR 7450 nanofiltration membrane.

The reflection coefficient represented a maximal condition of the membrane system: the rejection at infinite pressure. However, infinite pressure is an idealised condition and as such is impossible to achieve. Van der Bruggen and Vandecasteele [3] conducted experiments in which the effect of pressure on the rejection for maltose was investigated. They found that for system pressures over 10 bar, there was a minimal pressure effect on rejection. Therefore, the filtrations in this work conducted at 16.5 bar were suitable for fitting with the reflection coefficient.

2. Materials and methods

2.1. Filtration equipment and operation

A stirred SEPA® ST cell supplied by Osmonics (Minnesota, USA) was used for the experimentation in this study. The cell had a capacity of 300 ml and supported a membrane disc of $4.9 \times 10^{-2} \text{ m}$ diameter. The effective area of the membrane was $1.69 \times 10^{-3} \text{ m}^2$. The cell consisted of a cylindrical body with a magnetic stirrer assembly that was mounted inside the body, which allowed the stirrer to be positioned as close to the membrane surface as possible. The stirring speed was set at 200 rev min^{-1} , the maximum permissible by this equipment.

Prior to the filtrations, the cell was flushed at $1690 \pm 10 \text{ kPa}$ ($16.5 \pm 0.1 \text{ bar}$) with deionised water until 20 ml of water had permeated the membrane. This was carried out in order to avoid any compression effects of the membrane and ensures that operation was always under constant conditions.

A solution volume of 250 ml was used for all experiments. The cell was pressurised using compressed nitrogen gas from a freestanding cylinder. A pressure of $1690 \pm 10 \text{ kPa}$ ($16.5 \pm 0.1 \text{ bar}$) was used for all experiments. Permeate flux was measured by recording the mass of

Download English Version:

<https://daneshyari.com/en/article/7008458>

Download Persian Version:

<https://daneshyari.com/article/7008458>

[Daneshyari.com](https://daneshyari.com)