Journal of Membrane Science 526 (2017) 221–228

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Molecular weight cut-off determination of organic solvent nanofiltration membranes using poly(propylene glycol)

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ARTICLE INFO

Keywords:
Molecular weight cut-off (MWCO)
Organic solvent nanofiltration (OSN)
Solvent Resistant Nanofiltration (SRNF)
Poly(propylene glycol) (PPG)
Poly(propylene oxide) (PPO)
Reverse phase high-performance liquid chromatography (HPLC)
Evaporative light scattering detection (ELSD)
Membranes

ABSTRACT

A new method for determining the molecular weight cut-off (MWCO) of an organic solvent nanofiltration (OSN) membrane has been developed utilising poly(propylene glycol) (PPG) oligomers. This new MWCO method overcomes the limitations of the currently popular methods: namely the high molecule cost in the popular polystyrene method, the Donnan Exclusion effects when using dye molecules and the solvent compatibility and HPLC separation resolution limitations of the lesser used poly(ethylene glycol) (PEG) method. A new reverse phase high-performance liquid chromatography separation with evaporative light scattering detection (ELSD) allows the concentration of each oligomer of PPG to be accurately determined and from this the MWCO curves are constructed. The method has a high resolution (size increment of 58 g mol^{-1} corresponding to the $OCH(CH_3)CH_2$ structural unit) and can be used in polar, polar aprotic, and non-polar solvents. The accuracy of the method has been demonstrated in three different solvents (methanol, acetone, and toluene) and 5 different OSN membranes (DuraMem® 150, 200, 500, PuraMem® 280 and StarMem™ 240). Other advantages include; oligomers of PPG are cheap and widely available, can probe a wide range of MWCO and provide high resolution MWCO curves. Consequently, it is proposed that this method be adopted as a new standard MWCO test for OSN membranes.

1. Introduction

Membrane separation processes are increasingly being adopted throughout industry as they can provide low energy separations for a number of commercially important chemical species [1,2]. Among these, organic solvent nanofiltration (OSN; also known as solvent resistant nanofiltration, SRNF) is an emerging technology for more efficient separations within the chemical and pharmaceutical industries [2–5]. When applying a particular membrane to a separation it is important to understand its general separation ability before conducting feasibility testing; or if a new membrane material has been developed it is important to be able to generally quantify its separation potential. For nanofiltration (NF) membranes, the molecular weight cut-off (MWCO) is an important characteristic for determining their usefulness in a particular separation. Used as a general guide for the separation ability of a membrane it is defined as the molecular weight (MW) for which 90% of a solute is rejected [1,6]. In practice, a range of different MW solutes are filtered in the target solvent and the MWCO value is the real or interpolated MW of the solute molecule that gives a 90% rejection. Although in many circumstances a key factor, it is important to note that MW is not the only property to affect separation [7]. Despite this, the MWCO of a membrane provides an important general description of a membrane's separation ability.

In aqueous solutions, a number of methods have been developed to determine the MWCO of a NF membrane [6,8–10]. However, these methods cannot be directly applied for use in organic solvent systems due to various issues such as solute solubility and compatibility in organic solvents, as well as the numerous and complex solute-solvent-membrane interactions present. Suitable techniques for determining the concentration of the probe molecule in the permeate is also problematic when applied across a range of solvents. Thus, several new methods using different solute molecule types have been developed specifically for OSN systems as summarized in Table 1. Researchers also use a range of different MW dye molecules (including methylene blue and rose bengal) – however these have not been included in Table 1, since the rejection is generally due to both charge (Donnan Exclusion) and MW related factors that make them less comparable (and ultimately less accurate and therefore applicable to MWCO determination) than those listed.

One of the more commonly used solutes and methods for MWCO

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http://dx.doi.org/10.1016/j.memsci.2016.12.038
Received 4 August 2016; Received in revised form 1 December 2016; Accepted 20 December 2016
Available online 21 December 2016
0376-7388/

Table 1
Comparison of important attributes of common methods of MWCO determination in OSN, (✓=advantage, ✗=disadvantage, ~=neutral).

Important attributes of the MWCO method	Solute used in MWCO method			
	Alkanes Ref. [11]:	*Polystyrene* Ref. [12]:	*Poly(ethylene glycols)* Ref. [13]:	*Poly (propylene glycols)* Ref: this work
Detection method	~ Gas chromatography	✓ Simple detection *via* UV	~ Use of ELSD	~ Use of ELSD
MWCO attributes	✓ Can investigate influence of MW and structure on rejection	MW of solute only	MW of solute only	MW of solute only
MW of solute repeating unit	Not constant	104 g mol^{-1}	44 g mol^{-1}	58 g mol^{-1}
Solvent applicability	✗ Limited solubility in more polar organic solvents	✗ Solvent swap required for solvents that obscure chromatogram (e.g. toluene, hexane, ethyl acetate)	✗ Insoluble in most non-polar solvents ✗ Poor rejection by commercial membranes in organic solvents	✓/✗ Soluble in non-polar solvents however a solvent swap required for non-polar solvents that obscure the chromatogram
Quantitative solute concentration determination	✓ Can determine exact concentrations of each MW	✗ Difficult to determine absolute concentrations of each oligomer	✗ Difficult to determine absolute concentrations of each oligomer	✗ Difficult to determine absolute concentrations of each oligomer
Solutes cost and availability	✗ Lack of pure commercially available alkanes > 400 g mol^{-1}	✗ Expensive Oligomers	✓ Cheap range of available oligomers	✓ Cheap range of available oligomers

determination of OSN membranes is through the use of oligomers of polystyrene [12,14–16]. Polystyrene oligomers having MWs between 200 and 1000 g mol^{-1} allow a sufficient MW range to be covered to produce suitable MWCO curves for OSN membranes in various polar and non-polar solvents. Polystyrene oligomers have been used since they have four of the five essential properties of MWCO probe molecules (related to the important attributes of a MWCO method in Table 1):

A. *Availability:* polystyrenes are available in a wide range of MWs, unlike proposed alternative probe molecules such as alkanes [11] (which lack commercially available pure species of MW > 400 g mol^{-1});
B. *Molecular similarity:* polystyrenes are available in a homologous series, enabling a range of similar molecules to be used for MWCO determination. Systems which use a selection of different compounds as probes which could vary in structure and functionalities (e.g. dyes [17] or alkanes [11]) could have differing and varied interactions with a membrane leading to a skewed increase in rejection with MW [18].
C. *Robust analysis method for mixtures in different solvents:* The various MW polystyrenes when dissolved in the different solvents used in OSN can be separated by HPLC analysis and therefore a MWCO can be determined in a single filtration, instead of a series of filtrations, each with a single solute (which is often the case for MWCO methods that use different compounds).
D. *Good resolution:* The MWCO curve must be obtained in a reasonable resolution – i.e. a small gap between the MW of molecules in the series to enable the MWCO to be determined with good accuracy. The polystyrene method is not ideal with a 104 g mol^{-1} resolution, which may not as accurately discriminate the differences between some membranes which can have differences in MWCO less than this (such as for the DuraMem® series from Evonik which comes in close MWCOs of 150, 200 and 300) as methods with closer gaps in the molecular series.
E. *Affordability/low cost:* The polystyrene method however fails in the last key requirement – low cost. Pure polystyrene oligomers of low MW and polydispersity are very expensive (Polystyrene 500 £153/g; Polystyrene 1000 £85.9/g; Sigma Aldrich 2016) which can mean that the use of the polystyrene MWCO method is prohibitively expensive if it is to be applied as a routine measurement and/or at large scale. The material costs can in part be ameliorated by synthesising the oligomers prior to testing if the test is to be applied at laboratory scale. However, the synthesis can be time-consuming (accruing potentially prohibitively expensive person-time costs) and may produce oligomers with varying quality and purity (e.g. mixtures of oligomers/oligomers with high polydispersity that may not be able to be properly resolved using the HPLC-UV method commonly applied) [12].

A more cost effective and higher resolution alternative to the polystyrene MWCO method is therefore needed.

Polyether-based molecular probes such as poly(ethylene glycols) (PEGs) have been proposed for determining the MWCO in both aqueous systems [6] and in polar solvents [13,19,20]. The analysis of polyethers (such as PEGs) is commonly done by means of reverse phase high-performance liquid chromatography (HPLC) with evaporative light scattering detection (ELSD) which gives suitable separation and detection of the individual polyether oligomers (such as PEGs, poly(propylene glycols) (PPGs) and poly(butylene glycols) (PBGs) [21,22]. However, the insolubility of PEGs in some non-polar solvents as well as the wide range of conformations that PEG adopts in different organic solvents [23] can sometimes limit the reliability and cross-comparability of this method in OSN. This means PEGs can sometimes give quite different results for MWCO determination when compared to other methods [19] (also see further results and discussion demon-