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Characterisation of organic solvent nanofiltration membranes in multi-component mixtures: Membrane rejection maps and membrane selectivity maps for conceptual process design

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ABSTRACT

In organic solvent nanofiltration (OSN), the transfer of results attained during the membrane characterisation and testing to industrial applications plays a crucial role in the development of new processes. Even though industrial applications typically include multi-component mixtures, most permeability and rejection experiments are only conducted with single solvents. Therefore, this paper presents a characterisation of two commercial polyimide-based membranes, Starmem^{TM}122 and Puramem^{TM}280, in multi-component solvent mixtures. The experimental investigation includes solvent flux and rejection measurements of five dissolved compounds in binary and ternary mixtures of toluene, *n*-hexane and 2-propanol. The experimental results demonstrate the existence of permeate flux minima and maxima in binary solvent mixtures. Moreover, a strong dependence of the solute rejections on membrane swelling, solute solubility parameter and solute size is shown. As the solvent choice has a significant impact on membrane performance, membrane rejection maps (MRM) and membrane selectivity maps (MSM) were developed. They can be used as decision tools in the early stages of conceptual process design by selecting either pure solvents or solvent mixtures that enhance the downstream processing in OSN and thus can replace costly and time-consuming membrane screening or OSN membrane modification. To address the relevance towards other solvents, the transferability of these results to classes of similar solvents was demonstrated.

1. Introduction

Organic solvent nanofiltration (OSN) is a pressure-driven membrane process for the separation of dissolved compounds from liquid organic solvents. In the past decade, OSN has received increased attention because it offers a large potential for energy savings in petrochemical, pharmaceutical and catalytic applications [1]. Although OSN has recently become technically feasible with the development of solvent-stable polymeric and ceramic membranes and modules, the choice of a suitable pairing of the membrane with a pure solvent or solvent mixture (dependent on the upstream processing) for a new application presents a challenging task.

In general, OSN membranes can be characterised by two parameters, the permeability and the rejection. The permeability is the overall mass flux per unit time. The rejection represents the capability of retaining a key component or solute, or in other words, the decrease in concentration of one component from feed to permeate, expressed by Eq. 1:

$$R_i = 1 - \frac{c_{i,perm}}{c_{i,feed}} \tag{1}$$

From a process point of view, the separation coefficient or selectivity $\alpha_{i,j}$ (Eq. (2)) is defined in analogy to distillation processes as

$$\alpha_{i,j} = \frac{x_{i,perm}}{x_{i,feed}} \frac{x_{j,feed}}{x_{j,perm}} \tag{2}$$

and can be used to characterise the ability of a membrane to separate two components *i* and *j* from each other [2]. Moreover, the molecular weight cut off (MWCO) is often used as a measure for separation efficiency. It is defined as the molecular weight at which 90% of a component is rejected. The state-of-the-art MWCO determination is conducted using standard solvents, such as toluene, using a homologous series of neutral compounds (e.g. linear alkenes, oligostyrenes or polydispersed PEG) giving a rejection curve in a single experiment [3,4]. In literature, several studies characterising polymeric [5,6] and ceramic membranes [7] were reported.

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However, real applications mostly involve multi-component solvent and solute mixtures with distinct and non-ideal mixture properties. The permeation through polymeric OSN membranes depends strongly on the mutual interactions between solvent, solute and membrane, making an extrapolation from the single solvent results to multi-component mixtures not feasible. Nevertheless, most experimental studies on OSN membrane characterisations focused on the permeation of single solvents and/or single dissolved solutes [8–10]. Vankelecom et al. [11] published one of the first works discussing the physicochemical parameters affecting solvent permeation in OSN. They linked rejection properties of several dyes with SEM images of the active layer of Koch MPF-50 and a PDMS based membrane. Important parameters influencing permeability and rejection include the solute, solvent and membrane solubility parameters [12–14], solute size [15–18], solute and solvent polarity [17,19], surface tension [20] and solvent viscosity [21]. Coupling between the solvent and solute fluxes have also been reported for permeation of dyes dissolved in organic solvents through different reverse osmosis and nanofiltration membranes [22].

The few experimental reports on solvent mixtures have been mostly restricted to binary systems. Silva et al. [23] investigated the permeation of binary solvent mixtures of ethyl acetate, toluene and methanol through Starmem^{TM}122 and Koch MPF-50 membranes. Modelling the binary permeation using a solution-diffusion and one and two-parameter pore-flow approaches resulted in a good agreement with the experimental data over the entire concentration range of the mixture. Darvishmanesh et al. [21] conducted experiments to characterise multiple types of membranes, ranging from reverse osmosis to ultrafiltration, using binary mixtures of ethanol and *n*-hexane. They highlighted the role of viscosity, surface tension, coupled diffusion and the solubility parameter difference between the membranes and the solvents. Machado et al. [24] investigated the effect of solvent properties on the permeability of silicon-based Koch MPF-50 OSN membranes. They investigated binary mixtures of acetone with different alcohols and alkanes demonstrating the existence of flux minima as function of the acetone weight fraction [24]. They concluded that both surface tension and viscosity play a major role in permeation. Robinson et al. [25] reported on the fluxes of binary mixtures (aromatics/linear alkanes, linear/cyclic alkanes) through dense PDMS-based OSN membranes highlighting the role of solubility parameter and viscosity. Dijkstra et al. [26] analysed the permeation of a homologous series of alkanes, alcohols and ketones through dense PDMS/PAN membranes, concluding that the transport for mixtures of pentane and dodecane is governed by both viscous and diffusive permeation mechanisms. Geens et al. [20] studied the permeation of binary mixtures of water and different alcohols and the rejection of raffinose through different commercial OSN membranes. They concluded that the surface tension of the solvent and the membrane are both important parameters, whereas the permeation is governed by a viscous flow mechanism.

The influence of the molecular properties of the dissolved compounds on the solute rejection has been investigated by several authors. The first important property is molecular size. Van der Bruggen et al. [17] reported a good correlation between molecular weight, the Stokes diameter, the equivalent molar diameter and a size parameter based on molecular modelling with the solute rejection for membranes ranging from nanofiltration to ultrafiltration. Zheng et al. [27] reviewed and compared several molecular size descriptors, including the molecular length, the molecular width, the Stokes diameter and the calculated mean molecular diameter. They found a good correlation between several of the molecular size descriptors and the rejection of the dissolved compounds using Starmem^{TM}122, Starmem^{TM}240 and Koch MPF-44 membranes [27]. Moreover, they suggested a new size descriptor based on molecular modelling and a three-dimensional projection method [15]. The second important property is solute solubility. For solute solubility, Hildebrand and Hansen solubility parameters can be applied [28]. Zeidler et al. [14] highlighted the influence of the solute, solvent and membrane solubility parameters and molecular side groups, such as polar end groups, on rejection. They found good agreement between the theoretic predictions and the experimental data for different solutes and solvents through a dense PDMS-based OSN membrane.

Modelling of permeation in OSN has mostly been performed using semi-empirical solution-diffusion or pore-flow models. In general, the driving force is assumed to be a chemical potential gradient [29]. In a solution diffusion model, the transport mechanism is assumed to consist of sorption on the feed side, diffusion through the membrane active layer and a desorption on the permeate side, resulting in a strong dependence of both flux and rejection on the solubility parameters and diffusivities. In contrast, a pore flow model assumes a sieving-type of transport mechanism where flux and rejection depend strongly on the solvent viscosity and solute size. For binary mixtures, the solution-diffusion model, the pore flow model and a combination of both, the solution-diffusion with imperfections model, have been applied [26]. A phenomenological model for ceramic membranes was developed by Marchetti et al. [30]. Based on physical parameters of the single solvents and mixture viscosities, the model allowed good predictions for permeation of binary aqueous and organic solvent mixtures. Moreover, the model can be used for solvent or solvent mixture selection from minimal data due to its predictive character.

The objective of this work is threefold: (i) characterisation of the membrane transport by solubility parameters and solute sizes; (ii) check of transferability to solvent classes; (iii) facilitate conceptual design by introduction of graphical tools (MRM, MSM). The first goal is to expand the experimental studies available in the literature by using binary and ternary solvent mixtures of *n*-hexane, toluene and 2-propanol as representatives of the solvent classes used in multiple petrochemical, pharmaceutical and catalytic applications (sections 3.1 and 3.2). The solvent fluxes of the binary mixtures were investigated first. Subsequently, the rejections of five dissolved components (*n*-hexadecane, 2,2,4,4,6,8,8-heptamethylnonane, phenyldodecane, 2,6-diisopropylnaphthalene and triphenylphosphine) in binary and ternary solvent mixtures were analysed and interpreted using the solute size and the solubility parameters for the solvent mixture, solute and polymer. Since experiments are resource demanding, the second objective is to check the transferability of these results to solvent classes (Section 3.3). Thus, the effect of substituting one solvent in the ternary mixture with a similar solvent from the same solvent class was investigated (toluene – *o*-xylene, *n*-hexane – *n*-heptane/*n*-decane, 2-propanol – *n*-butanol). The third objective is to facilitate conceptual process design in OSN. This is done by introducing membrane rejection maps (MRM) and membrane selectivity maps (MSM). They can be used as graphical tools to select appropriate solvents for OSN and to identify a particular solvent mixture that achieves a desired solute rejection or selectivity for a given separation task (Section 4). By exploiting the variation of the OSN performance for the solvents and solvent mixtures, the selectivity, rejection and the permeate flux can be changed even beyond/below the performance using pure solvents.

2. Material and methods

2.1. Chemicals

In this study, seven organic solvents and five solutes were used. Three organic solvents, toluene, *n*-hexane and 2-propanol,