Parameters determining transport mechanisms through unfilled and silicalite filled PDMS-based membranes and dense PI membranes in solvent resistant nanofiltration: Comparison with pervaporation

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ABSTRACT

Solvent parameters and solvent–membrane interaction parameters that determine the permeation of pure solvents through silicalite-filled and unfilled PDMS-based membranes in solvent resistant nanofiltration (SRNF) were investigated and compared to pervaporation (PV) data. Transport mechanisms were investigated for dense PDMS and PI membranes, using a wide range of solvents and pressures.

It was found that in SRNF, the affinity of the solvent for the membrane polymer determines the flux primarily, but viscosity could not be neglected. It was shown that the relation between flux and molar volume/solvent viscosity reported in the literature was not followed, so that also other parameters are to be taken into account to describe transport. This was valid for all investigated membranes. In PV, no influence of selected parameters on solvent transport was observed.

PDMS membranes showed a good performance in both SRNF and PV. Retentions mostly above 90% were obtained for all dye/solvent mixtures at 20 bar. Incorporation of 15 wt% silicalite fillers reduced swelling significantly and improved retention for measured dye/propanol systems. This was however not seen for isopropanol. In PV, all membranes used showed similar selectivities (~4), except for the commercial Pervap 1060 membrane (~2.8), which was related to the higher hydrophilicity of PDMS.

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1. Introduction

One of the main challenges of SRNF is to develop membranes with a high and stable performance on the long term, and with a high stability in a wide range of organic solvents. On the other hand, a mathematical description of the transport mechanism through the membrane is essential for a wider implementation in industrial applications [1]. In order to predict fluxes for a given membrane, the transport mechanism of solvents through SRNF-membranes should be thoroughly understood. This knowledge should be integrated in readily applicable mathematical models, or alternatively be translated into clearly understood physico-chemically mechanisms, or a combination of both [2]. However, the wide range of hydrophobic/hydrophilic balances, viscosities and surface tensions among the different solvents and solvent mixtures, and the enormous variety of membrane materials available, complicates a unified approach [3]. As stated in the literature, the mutual inter-actions between solute and solvent, solvent and membrane, as well as between solute and membrane, play an important role in SRNF in addition to mere molecular size [4–8]. Unfortunately, the physico-chemical properties of commercially available membranes are often unknown, while their composition is not disclosed by the manufacturers of commercial membranes. This makes the selection of the membrane materials for a given separation difficult, and additionally, detailed understanding of their transport mechanism impossible.

Several authors have already highlighted that nanofiltration (NF) and pervaporation (PV) are both membrane processes in which diffusion contributes significantly to the transport of components from the feed side to the permeate side [9–11]. It is generally accepted that transport through dense PV membranes takes place by a mechanism of preferential sorption into the membrane polymer, followed by diffusive transport through the membrane phase. Therefore separation occurs as a result of differences in sorption/diffusion behavior between components in the feed mixture. The transport mechanism can be described by readily available solution–diffusion models originating from the description of transport through reverse osmosis membranes [9,12–14]. According to White [15], the solution–diffusion model suggests that SRNF and PV are directly related, in the sense that

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both are dependent on permeate interaction with the polymer matrix, with the separation driven by differences in partial pressure for feed and permeate components. A detailed description of the transport mechanism through SRNF membranes is, however, still under development. Any new transport model should incorporate the interactions between solvents, solutes, and the membrane [15]. Swelling of the polymeric matrix in contact with organic solvents is thought to play an important role in SRNF, since it promotes the faster convective transport over the slower, but more selective, diffusive transport. Thus, diffusion and sorption in the membrane strongly depends on the composition of the feed [1].

Regarding the membrane structure required for processes such as NF and PV, Van der Bruggen et al. [16] and Sekulic et al. [17] stated that these are similar, and that membranes are sometimes even interchangeable. Membrane materials used for PV and NF can be the same, although the structure and the thickness of the active layer possibly differ as a function of the envisaged process, which is related to the fundamental principles of both processes.

In this study, PDMS (polydimethylsiloxane) was chosen as the membrane material, as it is the most commonly used hydrophobic material, which has been successfully applied in various membrane techniques such as pervaporation, gas separation, vapour permeation and dialysis [18–21]. This elastomer contains a siloxane (Si–O) backbone substituted with methyl groups and is reported to be chemically stable in all organic solvents when cross-linked. One of the main drawbacks of PDMS is its extensive swelling in organic solvents, possibly inducing release of the top layer from the support [2,22,23]. Limitations resulting from swelling can be partially overcome by either the use of halogen-substituted silicone rubber, or by applying additional cross-linking via, e.g. incorporation of reactive porous fillers, i.e., zeolites [24–28]. Several patents have already been granted in the field of PDMS composite membrane preparation for chosen applications [2].

The aim of this research was to study the importance of solvent parameters (viscosity, molar volume) and solvent–membrane interaction parameters (swelling, difference in surface tension) in both nanofiltration and pervaporation, starting from state-of-the-art models.

2. Materials and methods

Unfilled PDMS (General Electrics, USA) membranes were cast from 10 wt% polymer solutions. Filled PDMS membranes were also prepared from 10 wt% polymer solutions but with addition of 15 wt% of silicalite zeolites (CBV3002, PQ-Corporation, USA). The zeolites had a particle size ranging from 1 to 1.5 μm, pores with a diameter of 5.4–5.8 Å and a Si/Al ratio of 240 rendering it hydrophobic.

2.1. Membranes

2.1.1. Support preparation

The polyimide (PI) support layer was prepared by casting a Matrimid 5218 (Huntsman, Switzerland) solution on a polypropylene non-woven (FO 2471), kindly provided by Freudenberg (Germany). A PI-solution, consisting of 15 wt% PI, 2 wt% H_2O, 62.25 wt% NMP and 20.75 wt% THF was cast on the non-woven support with a knife blade, set at a gap of 250 μm. After casting, the solvent was allowed to evaporate for 30 s, which resulted in the formation of a skin layer with elevated polymer concentration. Due to the presence of this ultrathin and denser skin-layer, the intrusion of PDMS into the support pores is prevented [2,21,29]. The resulting film was then immersed in water at room temperature to form the membrane. Fig. 1A presents schematically the preparation of the PI

supports. After immersion precipitation, membranes were placed for 24 h in a para-xylenediamine/methanol (1:10, w/v) mixture in order to cross-link the PI [30,31], and then rinsed with methanol to remove all traces of reactant. Membranes were further treated by a solvent-exchange procedure, involving immersion in IPA for 3 h and subsequently for 3 days in a mixture of toluene/4-methyl-2-pentanon/mineral oil (volume ratio of 40:40:20) [21]. Supports obtained in this way were gently wiped with tissue and dried in the oven at 60 °C for at least 1 h.

2.1.2. Unfilled PDMS

Fig. 1B presents the preparation of PDMS-based membranes. A 10 wt% solution of PDMS (RTV 615A and B, pre-polymer and cross-linker in a 10:1 ratio) in hexane was pre-polymerized at 60 °C for 0.5 h, followed by mixing for 0.5 h at room temperature. To coat the solution on the PI support, the support was taped onto a stainless steel plate, which was placed under an angle of 60° to allow the polymer solution to flow down over the support. After the solvent had partially evaporated, the plate was turned upside down and the coating procedure was repeated. After evaporation of most of the solvent, the membrane was placed in an oven for at least 1 h at 110 °C to complete cross-linking and to evaporate all traces of solvent.

Prior to the measurements the CO_2/N_2 selectivity was measured, proving good quality of the synthesized membranes ($\alpha = 3.5$).

2.1.3. Zeolite filled PDMS (Sil-PDMS)

Silicalite filled PDMS membranes were prepared by following the procedure described by Gevers et al. [28]. The filler fraction was calculated in weight percent:

$$\text{Filler fraction} = \frac{\text{weight of filler}}{\text{weight of filler} + \text{weight of polymer}} \times 100 \quad (1)$$

The filler content in the membrane was 15 wt%. The PDMS/filler solutions were coated on the PI support by following the procedure described above.

Prior to the measurements the CO_2/N_2 selectivity was measured, proving good quality of the synthesized membranes ($\alpha = 4.6$).

2.1.4. PI SRNF-membranes

Polyimide membranes were prepared and post-treated as described in 2.1.1. Polymer solution consisted of 18 wt% of Matrimid 5218 (Huntsman, Germany), 48.54 wt% of NMP and 33.46 wt% of THF.

2.2. Membrane characterization

2.2.1. Swelling experiments

PDMS solutions were prepared as described above and poured in a Petri dish. The solvent was allowed to evaporate and the resulting film was cured at 110 °C. Thus obtained dried pieces of PDMS slabs were weighed and then immersed in the solvent. After equilibrium (~5 days), the membranes were quickly wiped with a tissue to remove the solvent from the external surface before weighing. The swelling degree (S) was then expressed as the additional weight of the membrane recalculated to the amount of the solvent sorbed (ml) per gram membrane:

$$S \ (\text{cm}^3/\text{g}) = \frac{(m_{eq} - m_0)/m_0}{\rho_s} \quad (2)$$

where m_{eq} is the mass of PDMS at equilibrium [g], m_0 is the mass of the dried PDMS [g] and ρ_s is the solvent density [g/cm³]. The percentage standard deviation on an averaged measurement was found to be less than 12%.

Swelling of PI slabs was measured for films obtained from 15 wt% PI in chloroform. After complete polymer dissolution, mix-