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Solvent permeation behavior of PDMS grafted γ-alumina membranes

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ABSTRACT

Solvent permeability in polymer grafted ceramic membranes was described by incorporating solvent sorption terms into the Hagen–Poiseuille equation. Two types of ceramic membranes grafted with a relative short or long PDMS chain ($n=10$ and $n=39$), which differed in pore size, were examined. Sorption was measured “ex situ” using a pure PDMS phase. The results show that curves of flux versus transmembrane pressure were identical for all solvents studied if flux values are corrected for viscosity as well as sorption of the solvent. It is suggested that the permeable volume of the membrane reduces by swelling of the grafted organic moiety by the solvent used. This model provides a way to predict the performance of grafted porous membranes for solvent filtration.

1. Introduction

Solvent resistant nanofiltration (SRNF) or organic solvent nanofiltration (OSN) is a potential separation technology for e.g. the recycling of solvents and the recovery of products from reaction solvents [1]. For SRNF, a chemically stable membrane is required to endure the rather aggressive operation environment. Modification of mesoporous ceramic membranes by means of grafting is an interesting way to prepare a chemically stable nanofiltration membrane. In the grafting process, the macromolecules are linked to the membrane surface by a covalent bond, resulting in a chemically stable modified ceramic membrane. The surface wettability of the membrane can be tuned by grafting a suitable polymer with the desired hydrophobicity. In the same time, pore size tuning can be realized by grafting macromolecules inside the ceramic pores.

In literature several examples are given on modification of porous inorganic membranes by grafting for various applications. Leger et al. [2] used silicone oil (viscosity 545 mPa) to graft the surface of alumina membranes with a pore size of 5 nm for gas permeation and pervaporation. Faibish and Cohen [3] grafted polyvinylpyrrolidone on zirconia membranes for oil-in-water emulsion treatment. Free-radical graft polymerization was performed by using a vinyl silane as linker to the zirconia membranes. A reduction in pore size of around 25% after grafting was claimed. Yoshida and Cohen [4] grafted γ-alumina membranes (pore size 5 nm) by using vinyl acetate or vinyl pyrrolidone monomers. Yoshida and Cohen [5] grafted vinyl acetate or vinyl pyrrolidone to silica membranes (pore size of 20 nm) by free radical graft polymerization for pervaporation of methyl-tertiary-butyl ether from water. Popat et al. [6] grafted polyethylene glycol to straight pore alumina membranes (“anodisc”) using a silane coupling agent. Sang Won et al. [7] grafted polyethylene glycol to render straight pore alumina membranes for anti-fouling properties. The pore sizes of the bare alumina, used in [6] and [7], are in the order of 25–80 nm, while the grafted membranes are still in the ultrafiltration range.

Pinheiro et al. [8] developed nanofiltration membranes by grafting PDMS in the pores of γ-alumina membranes (pore size 5 nm) using aminopropylethoxysilane as the linker and (mono (2,3-epoxy) polyetherterminated polydimethylsiloxane with an average number of repeating monomers (n) of 10 and a viscosity of 10–50 mPa. Tanardi et al. [9] grafted PDMS with an average number of repeating monomers (n) of 39 on the same type of mesoporous (pore size 5 nm) γ-alumina layer, supported on macro porous α-alumina, with 3-mercaptopropyltriethoxysilane as linker.

Detailed knowledge of major parameters influencing the solvent transport of grafted ceramic membranes is very important in

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order to predict their permeation behavior for various solvents. Castro et al. [10] studied the effect of different types of solvents on the permeability of an ultrafiltration membrane, prepared by grafting of PVP inside the pores of a macroporous silica support with a native pore diameter of 410 nm. It was found that the permeability of nonpolar solvents, like cyclohexane and toluene, was higher than the permeability of polar solvents, like propanol, water, and ethanol, for the hydrophilic PVP grafted membranes, as opposite to what was expected.

An interesting behavior of modified ceramic membranes prepared via grafting of macromolecules inside the pores is their response towards the applied pressure. Castro et al. [11] observed a shear-rate flow induced behavior of the PVP grafted macroporous ceramic substrate with d_{avg} of 410 nm due to the mobility of the grafted polymeric chain. The effect of shear rate on the permeability of the grafted membrane was described as a condition in which the membrane is experiencing a more open membrane structure due to the movement of the grafted moieties in the direction of the feed flow, resulting in an exponential increase in the membrane permeability towards the trans-membrane pressure.

In this study, the effect of viscosity as well as sorption of the solvent on the transport behavior were investigated for two types of PDMS-grafted membranes with respectively a relative short and long chain length ($n=10$ and $n=39$). PDMS was selected as it has been proven to be an excellent material for SRNF applications [8,9,12–14]. The permeability was studied by means of permeation tests at operating pressures between 1 and 20 bar to investigate the effect of trans-membrane pressure on the membrane permeability. Various solvents were used to study the effect of different solvent types on the membrane permeation behavior. Permeation tests at elevated temperature were conducted to study the effect of temperature on the membrane permeability. A model is proposed to describe the permeation of pure solvents through these membranes.

2. Existing transport models for porous and dense membranes

Two models are generally used to describe solvent transport through membranes [15]. The first one is the pore-flow model, in which the membrane is regarded to have defined open pores from the feed side to the permeate side. Darcy's Law, often referred to as the pore-flow or viscous-flow model, describes liquid permeation through porous media as a function of the trans-membrane pressure (TMP)

$$J = \frac{k}{\mu}\frac{\Delta P}{l} \tag{1}$$

where J is the solvent flux, k the permeability constant, μ the fluid viscosity, ΔP the trans-membrane pressure, and l the membrane thickness.

For viscous flow, the Darcy's law can be combined with the Hagen–Poiseuille equation

$$J = k\frac{\Delta P}{\mu} \tag{2}$$

with

$$k = \frac{\varepsilon r_p^2}{8\tau l} \tag{3}$$

where J is the solvent flux, ΔP the trans-membrane pressure, μ the solvent viscosity, and k the membrane permeability constant representing the structural properties of the membrane with ε the membrane porosity, r_p the membrane average pore diameter, τ the membrane tortuosity, and l the membrane thickness.

If there are no pores identified in the membrane, the solution–diffusion model is generally used [15]. This means that the transport of liquids occurs via free volume elements between polymeric chains which can appear and disappear as a function of time and place according to the movement of the solvent [16]. The model assumes that pressure is constant through the membrane and the driving force of solvent transport is the chemical activity difference between the feed and permeate side of the dense membrane. The solution–diffusion equation is as follows:

$$J_i = \frac{D_i K_i}{l}\left[a_{if} - a_{ip}\exp\left(\frac{-v_i(P_f - P_p)}{R_g T}\right)\right] \tag{4}$$

where J_i represents the solvent flux, l the membrane thickness, D_i the diffusion coefficient of solvent or solute i through the membrane, K_i the partition coefficient, a_{if} and a_{ip} are the activities of species i in respectively feed and permeate, υ_i the partial molar volume of specimen i, P_f and P_p the pressures at feed and permeate side, R_g the gas constant and T the temperature. If a pure solvent is used, then the a_{if} is 1 and υ_i is 1, while the a_{ip} is 0. Thus, the equation becomes

$$J_i = \frac{D_i K_i}{l}\left[1 - \exp\left(\frac{-(\Delta P - \Delta\pi)}{R_g T}\right)\right] \tag{5}$$

where $\Delta\pi$ stands for the osmotic pressure [17].

When the difference between the applied and osmotic pressure is small, the equation can be written as

$$J_i = \frac{D_i K_i}{R_g l T}(\Delta P - \Delta\pi) = S_i(\Delta P - \Delta\pi) \tag{6}$$

where S_i is a solvent permeability constant of solvent or solute i.

The pore-flow and the solution–diffusion models are commonly used for aqueous applications [15,18,19]. For SRNF membranes, both pore-flow and solution–diffusion models have been used in literature to describe the transport behavior for PDMS membranes. Vankelecom et al. [16] found that a viscous flow model can be used to describe the permeation of pure solvents through PDMS membranes by taking into account membrane swelling. This finding was later confirmed by Robinson et al. [20], who successfully used a pore-flow model to describe the transport behavior of PDMS membranes for nonpolar solvents based on the reasoning that the swollen PDMS layer may form a pore-like structure in the presence of nonpolar solvents. Meanwhile, Zeidler et al. [21] found that a viscous flow behavior was observed for PDMS membranes in the presence of swelling solvents like n-heptane and THF. On the other hand, in the presence of non-swelling solvents, like ethanol, it was proposed that the rejection of PDMS might be closer to that of the solution–diffusion mechanism. Postel et al. [22] used the solution–diffusion model to describe the negative rejections of dye solutes in ethanol through dense PDMS membranes. No prior study is found in the literature to investigate the use of these models for modeling of the transport behavior of grafted ceramic membranes.

3. Experimental procedures

Three types of membranes were investigated. All membranes were in the form of flat discs with a diameter of 20 mm and a total thickness of 2.5 mm. The first series of membranes (M1) consisted of a mesoporous γ-Al_2O_3 layer with a pore diameter of 5 nm and 3 μm thickness, supported on macroporous α-Al_2O_3 supports [23,24]. The second series (M2) consisted of macroporous α-Al_2O_3 supports, coated with a 3 μm thick mesoporous (5 nm) γ-Al_2O_3 layer, which is modified with 3-aminopropyltriethoxysilane