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Solvent dependent solute solubility governs retention in silicone based organic solvent nanofiltration

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ABSTRACT

The application of silicon-based polymers as membrane material for organic solvent nanofiltration has grown over the last decade. A comprehensive understanding of this polymer as membrane material and its interaction with different solvent and solute systems is necessary to evaluate the transport properties. The solution diffusion mechanism covers solvent and solute transport through PDMS membranes. However, little is known about the solution part of the model. This work investigates swelling behavior of solvent/solute systems in PDMS being a representative for silicon-based polymers used today in industrial membranes. A gravimetric method measures remaining solute inside the polymer after solvent evaporation when equilibrium is reached. Three different solvents are evaluated as pure solvent, binary solvent mixtures and solvent/solute mixtures. Moreover, three different solutes are investigated: linear alkanes, polyethylene glycol and carboxylic acids. Swelling and solute concentration inside the polymer strongly depend on the solvent properties. Earlier observed negative retentions correlate with high solute solubility in the PDMS. It proves the importance of solvent dependent solute solubility in the retention mechanism in polymer based organic solvent nanofiltration.

1. Introduction

In recent years, dense rubbery silicone based polymer membranes with high swelling tendency have gained more attention as solvent resistant nanofiltration-membrane material, due to its stability against most organic solvents. Most of the published work focuses on permeation and rejection properties [1–6]. Different models are used, the most likely to govern transport through silicone-based membranes being the solution diffusion model [7–10]. Actually, very little is known on the solubility of the solute partitioning in the membrane material. In our prior publication [6,10], we have speculated that preferential solute solubility may be responsible for negative solute retentions which only recently have been observed. Here, we aim to proof that swelling measurements are essential to understand transport phenomena using PDMS based membrane materials, in particular when so-called negative retentions are observed. The subsequent described methodology describes a rigorous methodology to quantify the swelling behavior of PDMS based polymers in complex solute/solvent mixtures.

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2. Background

Stafie et al. [11] proposes a method where a liquid solution comprising a single solvent and a single solute is used to immerse a PDMS sample in. Removal of the sample from the liquid, evaporating the volatile solvent and measuring the remaining amount of solute in the polymer allowed a first estimation of solute solubility. These measurements showed an influence of the molar volume of the penetrant, but also points already towards the influence of the solute solubility. A three dimensional relationship (Fig. 1) between solubility parameter of solute, solvent and polymer is presented in this work.

Several papers were published in recent decades discussing the influence of different solvents on the swelling behavior of PDMS using different techniques [12–17]. Favre et al. [12,18–20] extensively analyzed sorption, diffusion and permeation of different solvents and solvent mixtures through dense polydimethylsiloxane membranes. A quasi-ideal behavior following the Flory–Huggins theory was measured using apolar solvents, while highly non-ideal sorption behavior was observed using polar solvents. As an explanation of this non-ideal behavior they supposed at the one hand increased clustering tendency of polar solvents but on the other hand they suggested an application of more refined free volume theories.

Furthermore the influence of temperature on the swelling

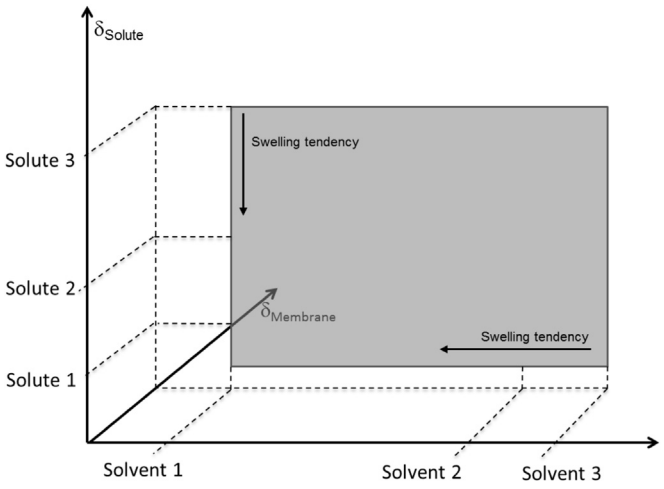

Fig. 1. Correlation between solubility parameter of solute, solvent and membrane adapted and redrawn from Stafie et al. [11].

degree of crosslinked PDMS networks using different solvents was investigated by Favre [21]. In general, a clear relation between solubility parameter and sorption was found: the smaller the difference between solubility parameter of solvent and membrane the higher the sorption due to higher affinity of the solvent to the membrane material. This relationship using PDMS membranes or PDMS based composite membranes and different solvents but also solvent mixtures were verified by several authors [22–27]. They found a clear dependency between affinity, swelling and permeation of the solvents, while also viscosity and temperature has to be taken into account to explain the observed results.

A new technique based on spectroscopic ellipsometry allowing high pressure measurements of solvent induced swelling was recently presented by Ogieglo et al. [15]. n-Hexane sorption in PDMS was investigated in this study by applying different pressure (0.1–10 MPa). In this pressure range no influence of the pressure on the swelling of PDMS layer was found.

Only a few papers were published regarding sorption and swelling behavior of solutes in polymer membranes. However, Michaels et al. [28] used the solubility theories of Hildebrand and Flory–Huggins and demonstrated a predictive correlation between steroid permeability in polymers and their melting temperature using thermodynamic parameters. With respect to solubility and partitioning effects, they generally observed that a drug will be more soluble in the polymer phase as the difference in the solubility parameters of the drug-polymer becomes smaller [28].

In addition to flux and retention measurements published in our first paper [6,10] this study presents, swelling and sorption measurements, in order to complete a systematic investigation of negative retention in organic solvent nanofiltration using a dense PDMS-based membrane. Toluene, isopropanol and methanol as pure solvent and solvent mixtures as well as a selection of solutes are used in order to investigate swelling behavior and solute partition. Additionally the obtained results are interpreted using the Flory–Huggins theory.

3. Experimental

3.1. Materials

Swelling behavior was measured in order to investigate the influence of solvents and solvent mixtures on the swelling degree of the used membrane. For this measurement three different solvents were used as pure solvents but also as binary mixtures. These solvents and the most important properties are summarized in Table 1.

In addition sorption measurements using different solutes dissolved in pure solvents were carry out to verify the before described retention behavior. The selected solutes and important properties are summarized in Table 2.

In order to represent the PDMS-based membrane, a Sylgard 184 Silicone Elastomer Kit delivered by Dow Corning Corporation was used. As PDMS solubility parameter a value of 15.5 $MPa^{0.5}$ is assumed [36].

3.2. Experimental procedure

First the PDMS samples were prepared using the Sylgard 184 Silicon Elastomer Kit and the crosslinking agent (10:1). After the polymer was fully dissolved, the solution was cast into petri dishes and placed into vacuum oven. It takes a time of 48 h to completely harden the PDMS plates. After 48 h the initial weight of the dry polymer was measured before it was immersed either into toluene, isopropanol, methanol, three different binary mixtures of them (25/75%, 50/50%, 75/25%) or in solutions of 1 wt% of each solute in every pure solvent.

After defined time intervals, the immersed PDMS plates were removed, dried with filter paper and weighted. This procedure was repeated until the mass of PDMS remained constant. The swelling was calculated using the mass uptake $\Delta m(t)$ related to the initial weight of the PDMS plate m_0.

$$\text{Swelling degree (SD)} = \frac{\Delta m(t)}{m_0} \quad [\text{g g}^{-1}] \tag{1}$$

To compare the results among themselves, the swelling degree at the equilibrium state (SD(∞)) was used.

Once the equilibrium state was reached the PDMS plate was dried again and weighted in order to measure the sorption of different solutes. The weighing was repeated until the weight remains constant. Using that procedure the amount of solute in the membrane (w_{solute}(Membrane) [g/g]) was determined and solute partition coefficient K_{solute} was calculated using the following equation and the initial concentration of solute in the immersed solution (w_{Solute}(Feed) [g/g]).

$$K_{Solute} = \frac{w_{solute}(\text{Membrane})}{w_{solute}(\text{Feed})} \tag{2}$$

Table 1
Physicochemical properties of the used solvents at 20 °C [29,30].

Solvent	Formula	Molecular weight (kg $kmol^{-1}$)	Viscosity (mPa s)	Molar volume (m^3 mol^{-1})	Dielectric constant (dimensionless)	Solubility parameter ($MPa^{0.5}$)
Isopropanol	C_3H_7OH	60.10	2.04	76.92	18.30	23.7
Methanol	CH_3OH	32.04	0.60	40.40	32.60	29.7
Toluene	C_7H_8	92.14	0.59	106.85	2.38	18.3