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Systematic investigation on the influence of solutes on the separation behavior of a PDMS membrane in organic solvent nanofiltration

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ABSTRACT

Organic solvent nanofiltration (OSN) offers a great potential to save energy and increase product quality in chemical production. Although the numbers of publications increased in the last years, the transport mechanism in OSN has not yet been clarified due to the complex interactions among membrane, solvent and solute. To simplify membrane selection and accelerate process development for industrial applications, parameters which affect the separation behavior and help to predict rejection have to be determined. In this work, experimental investigations concerning the interactions among membrane–solvent–solute and the influence of functional groups in the solute molecules on the rejections in OSN are presented. Therefore, the rejection of two, three or four ring-type core substances with different functional groups like fluorination, polar endgroups or different side chain lengths were measured in different solvents. The chosen solvents are ethanol (polar), *n*-heptane (nonpolar) and tetrahydrofuran (polar aprotic), which resemble the solvents used in the various synthesis steps in the production of those specialty chemicals.

The results show that rejections vary widely in the three solvents. Rejection in THF varied between 55% and 95% and in *n*-heptane between 20% and 80% while in ethanol negative values in a range between −10% and −45% were measured. To explain these results a comparison of the solubility parameter of the solute, the membrane and the solvent has been used here, which gives good correlations with the measured data.

Incorporating the functional groups into a Design of Experiments, in particular the groups that influence the polarity of the molecules show a significant influence on the rejection depending on the polarity of the solvent.

1. Introduction

Organic solvent nanofiltration (OSN) is a young, energy efficient separation technology and, therefore, a versatile tool for process intensification. It allows for the separation and purification of compounds in a molecular range between 200 and 1000 g/mol solely driven by a pressure gradient over the membrane. This driving force allows for – depending on the application – large energy savings compared to thermal separations like distillation, a decreased process time and higher product quality.

Applications of OSN have just emerged during the past 15 years with the development of stable solvent resistant nanofiltration membranes. Improvements of the membranes and a couple of publications attracted attention to OSN by the industry. Meanwhile, a lot of applications are reported in the literature: concentration [1], recovery of homogenous catalysts [2–4], solvent exchange [4,5], product purification [6] and solvent recycle [7].

Several researchers have dedicated work on the description and prediction of transport phenomena in organic solvent nanofiltration, mostly by making use of existing transport models originating from aqueous membrane separations as the pore flow model [8], the solution-diffusion model [9] or combinations thereof, e.g. the Spiegler–Kedem model [10] and the solution-diffusion model with imperfections [11,12]. However, most of the experimental verifications just worked with pure solvents [13–18] and/or are limited to a specific material system. Apart from that, there is still no general agreement whether the transport in OSN membranes is caused by diffusion or convection.

Robinson et al. [13] found that the solvent flux through a PDMS membrane can be well fitted by the Hagen–Poiseuille equation, thus indicating that convective flow to may be predominant.

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Machado et al. [16] assume that transport occurs by viscous flow in their transport model development. In contrast, Silva et al. [14] calculated the deviation of the pore flow and solution-diffusion model from their experimental results. They concluded that the solution-diffusion model gives a more accurate prediction of the measured fluxes through a polyimide membrane (Starmem 122™). Dijkstra et al. [15] measured the permeation of alkanes through dense PDMS/PAN membranes and compared their results with the values calculated by the solution diffusion with imperfections model and the Maxwell–Stefan transport equation. The permeation could be successfully modeled with both approaches but Maxwell–Stefan gave more realistic values of the estimated parameters. Both models take diffusive and convective flow into account.

Nevertheless, membrane performance remains unpredictable. The reasons can be found in the complex interactions among membrane, solvent and solute. Therefore, it is very difficult to select an adequate membrane for a given separation problem. Mostly, the only information provided by the membrane manufacturers is the molecular weight cutoff (MWCO). It defines the molecular weight of a molecule that is 90% retained by the membrane. However, there is still no standardized method to determine the MWCO and the determined value depends strongly on the specific solvent [19,20]. Hence this information can only be used to compare membranes of exactly the same material.

Many studies were done to identify parameters like polarity, crosslinking of the membranes or molar volume [21–23], which influence the separation behavior of polymeric nanofiltration membranes. Apart from these, the Hildebrand solubility parameter was pointed out by several authors to be a suitable approach to explain differences in solvent fluxes [13,24] or rejections [25,26].

The Hildebrand solubility parameter is a numerical estimate of the degree of interaction between nonpolar materials. This means that materials with similar values of solubility parameters are likely to be miscible. If the solubility parameters of a solvent and a polymer are equal, the polymer tends to swell [27]. The Hildebrand solubility parameter δ is derived from the square root of the cohesive energy density:

$$\delta = \sqrt{\left(\frac{\sum E_{coh_i}}{\sum V_{m_i}}\right)}$$

It can be readily obtained for many materials from literature or it can be easily estimated by the group contribution method.

Another solubility parameter is provided by Hansen. This value was developed for predicting if a material will dissolve in another and form a solution [28]. The three-dimensional parameter is also suitable for polar, hydrogen-bonding molecules due to consideration of the energy from dispersion forces, dipolar intermolecular forces and hydrogen bonds.

To implement OSN successfully in industrial applications, it is indispensable to simplify and accelerate the membrane selection. Thus, to minimize the effort of process development, influencing factors of the solutes have to be identified and parameters that enable a pre-estimation of the performance of a membrane have to be found.

A systematical experimental investigation of the separation behavior concerning the interactions between membrane and solvent and the influence of functional groups to identify parameters significantly influencing membrane performance was carried out. For this purpose a typical material class produced at Merck KGaA (Darmstadt, Germany) with different molecular weights and sizes and diverse functional groups by keeping an unchanged core structure was chosen.

The rejection of these substances by a PDMS membrane was measured in different solvents. The solutes were integrated into a Design of Experiments (DoE) according to their functional groups to identify the most important impacts.

2. Experimental

2.1. Membrane

The membrane used for the study was the commercial available OSN composite membrane GMT-oNF-2 (GMT Membrantechnik GmbH, Rheinfelden, Germany) with an active layer of PDMS (Polydimethylsiloxane) on a PAN (Polyacrylonitrile) support. The manufacturer declares a rejection of 75% for tetracosane (338 g/mol) in toluene.

For each experiment a new membrane sheet was used. The membrane was prepared by storing it at least 12 h in the respective solvent previous to the rejection measurement.

2.2. Solvents

For the solvent flux determination, ethanol, methanol, ethyl acetate, isopropyl alcohol, *n*-heptane, toluene, tetrahydrofuran and distilled water were used.

The solvents used for the rejection experiments were ethanol, *n*-heptane and tetrahydrofuran (THF) which represent the most common solvents in the production of specialty chemicals. All solvents were supplied by Merck (Merck KGaA, Darmstadt, Germany) and were of analytical grade ($\geq$99%). Ethanol was of absolute, undenatured quality to exclude interactions of the membrane or the solute with the denaturant. Relevant properties of the solvents are listed in Table 1.

Table 1
Solvent properties [29].

Solvent Unit	Molecular weight [g/mol]	Density [g/ml]	Molar volume [m^3/mol]	Viscosity [mPas]	Surface tension [dyn/cm]	Dielectric constant [As/Vm]	Dipole moment [D]	Polarity	Solubility [30] [(J/cm^3)$^{1/2}$]
T [°C]		20		25	20	20	25		
THF	72	0.888	81.08	0.55	28	7.6	1.75	21	18.5
n-heptane	100	0.664	147.5	0.41	19.3	1.924	0	1.2	15.3
Ethanol	46	0.789	58.68	1.08	22.3	22.4	1.7	65.4	26.2
Methanol	32	0.792	40.4	0.6	22.6	32.6	1.7	76.2	29.7
Ethyl acetate	88	0.895	98.5	0.46	24	6.02	1.7	23	18.2
Toluene	92	0.867	106.85	0.59	28.5	2.38	0.4	9.9	18.3
i-Propanol	60	0.786	76.92	2	21.7	18.3	1.66	54.6	23.8
Acetone	58	0.79	73.4	0.33	23.3	20.6	2.9	35.5	19.7
Water	18	0.998	18.02	0.89	72.75	79.7	1.87	100	48