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Solvent-membrane-solute interactions in organic solvent nanofiltration (OSN) for Grignard functionalised ceramic membranes: explanation via Spiegler-Kedem theory

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Abstract

Amphiphilic Grignard modified ceramic nanofiltration membranes have been demonstrated to perform well for a wide range of solvents in organic solvent nanofiltration (OSN). The purpose of this study is to obtain a better understanding of the influence of the solvent-membrane-solute interactions governing the OSN membrane performance. This was achieved by performing an extensive retention study on two types of Grignard functionalised membranes, in many different solvents with a wide variety of polarity, and choosing three PEG molecules and polystyrene as solutes, all with almost the same size but different polarities. To unravel the transport mechanism properly, also the pressure effect on flux and retentions was thoroughly investigated.

The retention results showed in general a very different behavior in different ranges of solvent polarity: at low solvent polarity, retentions are relatively low, varying with pressure and solvent polarity; at high solvent polarity, retentions are relatively high, and independent of pressure and solvent polarity. The Spiegler-Kedem theory, taking into account both diffusion and convection transport mechanisms, appears to be a very good basis for a fundamental explanation of all results. This knowledge shows also how membrane-solvent-solute interactions can be manipulated to enhance the membrane performance.

Key words: Grignard grafted membranes; Organic solvent nanofiltration; Solvent-solute-membrane interactions; Spiegler-Kedem theory

1. Introduction

Nanofiltration (NF) was successfully used as an addition to or even an alternative for reverse osmosis for water purification [1-3]. The success of NF in aqueous systems [4-6] has triggered the application of NF for separation and purification in non-aqueous systems. In recent years, much attention has been devoted to organic solvent nanofiltration (OSN) [7]. OSN has a significant potential in chemical-related industries employing non-aqueous media, such as organic solvents and ionic liquids. Application areas can be found in the pharmaceutical industry, the fine chemicals industry, in biorefineries, and in natural product industries [8]. Polymeric [9-15] and inorganic [16-26] materials have been used for preparation of OSN membranes and application in organic solvent filtration. The ideal OSN membrane combines thermal, chemical and mechanical stability, i.e., the non-swelling and non-compaction behavior of inorganic materials combined with the high selectivity of polymeric materials. Therefore, recent new types of organic-inorganic hybrid membranes are expected to combine the best of both worlds. There are two ways of preparing hybrid organic-inorganic membranes: 1/ by grafting organic molecules on the surface of the ceramic material by means of post-modification treatment(s), 2/ by building in organic linkers within the ceramic (inorganic) matrix by modifying the ingredients within the synthesis step of the sol used to form the separation layer (in-situ modification) [27, 28].

Post-modifications have been done in different ways and a variety of grafted membranes was characterized for their performance in OSN. Silanisation of mesoporous zirconium dioxide membranes with an initial pore size of 3 nm has been developed by Dudziak et al. [29], and was successfully used for retention of homogeneous catalysts in non-aqueous solutions [30]. Van Gestel et al. [31] reported surface modification of γ -Al₂O₃/TiO₂ multilayer membranes. The effect of silane treatment ((CH₃)₂SiCl₂ and C₈H₁₇CH₃SiCl₂) on solvent permeabilities was found to depend on the pore size of the membrane (microporous or mesoporous) and on the organosilane reagent used. The hexane permeability indicated that C₈ organosilanes could be successfully introduced in the pore structure of the mesoporous membrane. Mesoporous γ -alumina membranes were also chemically modified with several organochlorosilanes by Sah et al. [32, 33]. They found that the penetration of long chain organochlorosilanes into the mesopores was sterically hindered and that grafting was not as effective as for short chain organosilanes. Verrecht et al. [34] presented contact angles and hexane / water permeability ratios for modified mesoporous γ -Al₂O₃ membranes. Recently, Pinheiro et al. [35, 36] developed a new type of OSN membrane by grafting a PDMS polymer into the pores of 5 nm γ -alumina ceramic membrane using a two-step synthesis; the linking agent, 3-aminopropyltriethoxysilane (APTES), was first applied on a ceramic membrane, followed by grafting of an epoxy-terminated PDMS. The results showed a molecular weight cut-off (MWCO) of 500 Da using a solution of polyisobutylene in toluene, and higher permeabilities for the non-polar solvents toluene and hexane than for the more polar isopropanol(IPA).

Buekenhoudt et al. [37] used organo-metallic compounds for the post-treatment and for the bonding of different functional groups to the membrane surface by a Grignard type reaction. In a previous paper [38], the properties of the Grignard modified membranes were examined by physico-chemical characterisation (contact angle measurements, micro-ATR/FTIR-spectroscopy) in addition to performance characterisation in water and a few organic solvents. All observations are consistent with the assumed partial replacement of the OH-groups on the membrane surface and the consequent amphiphilic character of the modified membrane surface. In a subsequent paper [39], the retentions of Grignard modified and unmodified membranes in five different test solutions composed of one of two solvents (polar acetone or apolar toluene) and one of three solutes (polar polyethylene glycol PEG, apolar polystyrene or catalyst ligand BINAP) clearly show that an increase of hydrophobicity of the membranes leads to an increase in retentions, in accordance with recent findings in OSN [40]. Moreover, clear effects of solvent-membrane and solute-membrane affinity were demonstrated. As already noticed by other researchers [15,41], the Hansen solubility parameters proved to be very efficient to quantify the different affinities and the resulting retentions.

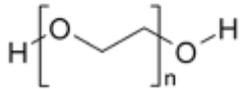
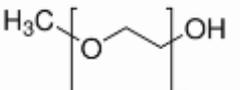
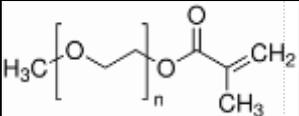
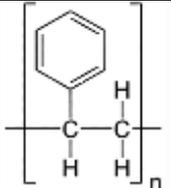
In this new study, Grignard modified membranes were used to obtain a much better understanding of the solvent-membrane-solute interactions influencing the OSN performance, and this in a controlled way, and without the extra complexity of swelling. To achieve this goal we performed an extensive retention investigation on two types of Grignard functionalised membranes, in many different solvents with a wide variety of polarity, and choosing three PEG molecules and polystyrene, all with almost the same size but different polarities, as solutes. Moreover, the effect of solvent switches was also studied using diafiltration from one solvent to another. Additionally, to unravel the transport mechanism properly, also the pressure effect on flux and retentions was thoroughly investigated. The results allowed a satisfactory interpretation using the well-known Spiegler-Kedem theory [42].

2.1. Materials

In order to investigate the solute affinity effects on the separation of Grignard modified membranes, three polyethylene glycol (PEG) molecules with almost the same size but different hydrogen bonding capacities and consequently different polarities were used. These were PEG-600, partially methyl capped PEG and fully methyl capped PEG, acquired from Sigma Aldrich. In addition, polystyrene with molar mass 580 Da, acquired from Agilent Technologies, was used as solute. The molecular weights mentioned are mean molecular weights, as these solutes consist of a mixture of polymers with different molecular weight ranging from about 300 to about 1500 Da. The most important properties of these solutes plus their structures are presented in table 1. The total Hansen

solubility parameter for the solutes, δ_{tot} , was calculated, using a group contribution method as explained elsewhere [39, 43].

Table 1. Solute properties [43-44]

Solute	Formula	MW [g mol ⁻¹]	δ_{tot} (MPa ^{0.5})	Structure
Polyethylene glycol (PEG)	$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$	600	25.21	
Partially methyl-capped PEG	$\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OH}$	550	22.83	
Fully methyl-capped PEG	$\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2$	500	18.56	
Polystyrene	$(\text{C}_8\text{H}_8)_n$	580	16.96	

The following solvents, ordered by polarity in table 2, were used in this work. For the experiments with the three PEGs, water, ethanol (EtOH), dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM) and ethyl acetate (EtAc) were chosen. No lower polarity solvents were used as they solve these solutes insufficiently. For the experiments with polystyrene, all solvents of table 2 except ethanol and water were utilised (again because of solubility issues in these higher polarity solvents). For water, reverse osmosis purified water was used and the organic solvents were of analytical grade (>99%) supplied by VWR, Leuven, Belgium. Relevant properties of the solvents are summarized in table 2.

Table 2. Solvent properties at 25°C (Formula = molecular formula; MW = Molecular weight; ρ = density; μ = viscosity; δ_{tot} = total Hansen solubility parameter) [45-46]

Solvent	Formula	MW [g mol ⁻¹]	ρ [g cm ⁻³]	μ [mPa s]	δ_{tot} (MPa ^{1/2})
Methyl cyclohexane	C_7H_{14}	98.2	0.770	0.67	16
Cyclohexane	C_6H_{12}	84.16	0.779	1.02	16.8
Methyl isobutyl ketone (MIK)	$\text{C}_6\text{H}_{12}\text{O}$	100.16	0.802	0.58	17

Ethyl acetate (EtAc)	C ₄ H ₈ O ₂	88.11	0.897	0.426	18.1
Toluene	C ₇ H ₈	92.14	0.867	0.59	18.2
Methyl ethyl ketone (MEK)	C ₄ H ₈ O	72.11	0.805	0.43	19
Tetrahydrofuran (THF)	C ₄ H ₈ O	72.11	0.889	0.48	19.4
Dichloromethane (DCM)	CH ₂ Cl ₂	84.9	1.326	0.45	20.3
Acetone	C ₃ H ₆ O	58.1	0.791	0.32	20
Isopropanol(IPA)	C ₃ H ₈ O	60.1	0.785	2.30	23.4
Dimethylformamide (DMF)	C ₃ H ₇ NO	73.1	0.944	0.92	24.8
Ethanol (EtOH)	C ₂ H ₆ O	46.1	0.789	1.20	26.5
Water	H ₂ O	18.0	0.9988	0.916	47.8

For the retention experiments, solutions with a concentration of 1 g/L for the chosen solute were prepared in the different solvents. In this work, only one solute was solved in each mixture; no multi-component mixtures were used.

For all experiments in this study, many different membranes (in total 9 membranes) were modified. For all modifications 1 nm TiO₂ single tube membranes with a length of 12 cm and outer and inner diameter of 100 mm and 70 mm from Inopor, Veilsdorf, Germany, were used. All membranes were modified with octyl (C8) or phenyl (Ph) groups by using the appropriate organometallic Grignard reagents [38,39]. We have to remark that some small differences in quality exist for the 9 different 1 nm TiO₂ membranes used as starting material for the modification. This quality difference is visible from small differences in pure water permeabilities of the native membranes (variation from 20 to 30 L/hm²bar). As we noticed in our previous work [26] there is a clear correlation between the water permeabilities and the MWCO values for the Inopor membranes. And consequently, also the MWCO values of the native membranes vary somewhat: in this case, from about 600 Da to about 850 Da.

2.2. Experimental procedures

The experimental set-up for the nanofiltration tests consists of a feed vessel with maximum volume of 4 L, a circulation pump to pump the feed from the feed tank towards the membrane module, a flow meter to measure feed flow which is adjustable via a bypass, two manometers, placed before and after the membrane module to determine the transmembrane pressure, and a thermostatic bath containing a mixture of water and

glycerol to adjust the temperature by circulating through a cooling spiral in the feed tank. Experiments were carried out in cross flow (2 m/s) mode, at room temperature ($25 \pm 3^\circ\text{C}$) and at a transmembrane pressure (TMP) of 5 to 16 bar for all membranes.

In a specific experiment, diafiltration was used. Continuous diafiltration was conducted in the following manner. A total of 1 L solution of PEG in ethyl acetate was subjected to NF filtration at 10 bar. In continuous mode, one diavolume (1 L) of ethanol was pumped into the feed tank to replace the ethyl acetate permeating through the membrane. During this operation the level of the feed tank was kept constant (using a pressure difference measurement). Permeate and retentate samples were collected after the permeation of every 100 ml of feed.

2.3. Analysis

Concentrations of PEG-600, partially capped PEG and polystyrene in the permeate and retentate samples were analysed by Gel Permeation Chromatography (GPC). For PEGs, the GPC was equipped with three columns of Waters in series, i.e., an Ultrahydrogel 120 column 7.8×300 mm, an Ultrahydrogel 500 column 7.8×300 mm and an Ultrahydrogel guard column 6×40 mm. The mobile phase was water, isocratic flow 0.6 ml/min at 40°C , 100 μl injection, 38 min total run time. The calibration curve was created with 12 polyethylene oligomers from 106 to 12000 Da dissolved in water, fitted with 3th order regression. For polystyrene, the GPC was equipped with two Waters columns in series, i.e., Styrogel, HR 1-toluene 7.8×300 mm and HR 2-toluene 7.8×300 mm. The mobile phase was toluene, isocratic flow 1 ml/min at 40°C , 100 μl injection, 30 min total run time. The calibration curve was created with 8 polystyrene oligomers from 162 to 19760 Da dissolved in toluene, fitted with 3th order regression.

To determine the concentration of fully capped PEG in different solvents, samples were analyzed by measuring the amount of non-purgeable organic carbon (NPOC). NPOC is a measure of the non-volatile organic carbon fraction in water. NPOC gives no information about the nature of the organic substance. Prior to the measurement, the TIC (Total Inorganic Carbon) is removed by acidification and purging. Then, the fraction of NPOC is determined by catalytic combustion of the sample at 850°C under oxygen atmosphere. The CO_2 is measured directly using infrared spectrometry. The supplier of the instrument was AnalytikJena, type Multi N/C 3100. It should be noted that all samples were first weighed and then the solvent was evaporated and replaced with the same amount of water and then analysed for the PEG concentration.

The fractions of EtAc and EtOH in the EtAc/EtOH mixtures obtained during diafiltration were determined using Gas Chromatography using Flame Ionization Detection (GC-FID). The GC-FID of InterScience was equipped with the column DB-5 ms, $60 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ from Agilent Technologies. The injection volume was 1 μL , inlet temperature 290°C , flow 1 mL/min He, and FID detector temperature 320°C .

The retention R (%) was calculated with the following equation:

$$R = (1 - C_p / C_f) \times 100 \quad (1)$$

C_p is the solute concentration in the permeate and C_f is the solute concentration in the feed. The flux is determined by weighing the permeate and is calculated automatically by a PC using the following equation:

$$J = m_p / \rho t A \quad (2)$$

where J is the solvent flux [$L h^{-1}m^{-2}$], m_p is the mass of permeate [g], ρ is the solvent density [$g L^{-1}$], t is the filtration time passed when collecting the permeate sample [h], and A is the active membrane area [m^2]. To calculate the permeability, the flux is divided by the applied transmembrane pressure in each experiment.

3. Results

3.1 Retention of three PEGs in different solvents

The first series of experiments determined the retention values of six 1 nm C_8 modified membranes for the three PEGs (PEG-600, partially capped PEG and fully capped PEG) in six solvents: EtAc, DCM, THF, DMF, EtAc and water. The transmembrane pressure used for all experiments was 10 to 12 bar. For every solvent a new, freshly modified membrane was used. For each membrane first the retention of PEG-600 was measured, followed by the measurement of partially capped PEG, and finally fully capped PEG. In between the measurements, no rinsing step was included, and each PEG retention measurement was done directly after the other one. To check the occurrence of any effects of the previous measurements, at the end of the sequence the PEG-600 retention was re-evaluated, and it could be concluded that the history effects are minor.

The retention results for all solvents measured are given in [figure 1](#). The total Hansen solubility parameter of each solvent is also mentioned for every solvent. The statistical error bar of the retentions is +/- 5% (based on multiple repetitions of the same experiments). However, the trends as observed in [figure 1](#) are always the same. As a consequence the data in [figure 1](#) is considered relevant data. Comparing the retentions of the three PEGs in each solvent, [figure 1](#) shows that the retention of PEG-600 is the lowest for the relatively apolar solvents, EtAc and DCM. On the contrary, for the more polar solvents (THF, DMF, EtOH and water) PEG-600 has the highest retention. Moreover, the retention results for these more polar solvents are quite similar. Some small differences are visible; however this might be due to the quality differences of the different membranes.

We want to remark also that the retention value found for the PEG-600 in water (76%) corresponds very well to the retention found for this molecule during a standard MWCO measurement on a 800 Da membrane [26]. For a molecule with a molecular weight of 500 Da, like the fully capped PEG, we expect a retention of about 60 to 65 % for a 800 Da membrane. This is again very similar to the retention values found for this more apolar molecule in the more polar solvents. The values found for the most apolar solvent EtAc, are definitely much smaller than the ones expected on the basis of size exclusion through membranes with a MWCO between 600 and 850 Da.

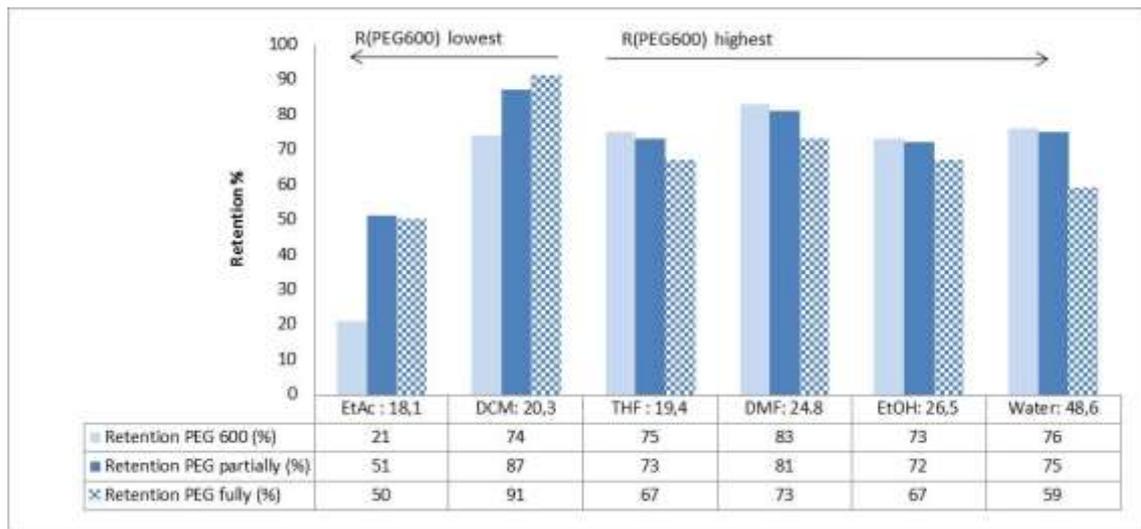


Figure 1. Retention of three PEGs in different solvents for 1nm C₈ modified membrane, determined at a transmembrane pressure of 10 to 12 bar. Numbers next to every solvent present Hansen solubility parameter (in MPa^{0.5}) of each solvent. The error bars are ±5 % for all retentions.

From figure 1 the retentions of one specific PEG in different solvents can be compared. However, as mentioned before, the variation of this retention for different solvents is influenced by possible small differences in the membranes used (for each solvent a new membrane was used). Therefore, to better evaluate the change of retentions as function of the solvent, and to confirm the findings above, a diafiltration experiment was set up for a new 1 nm C₈ grafted membrane. For this membrane, diafiltration was performed from pure EtAc (Hansen parameter of 18.1 MPa^{0.5}) towards EtOH (Hansen parameter of 26.5 MPa^{0.5}). These particular solvents were chosen as during this diafiltration we then change from an apolar to a more polar solvent. In the experiment about one diavolume of EtOH was added, gradually changing the solvent from pure EtAc to a 50/50 EtAc/EtOH mixture with a Hansen parameter of 22.3 MPa^{0.5}. The Hansen solubility parameter of the varying mixture during diafiltration was calculated, using the EtAc and EtOH fractions, x_{EtAc} and x_{EtOH} , with the following equation:

$$\delta_{tot}(\text{mixture}) = x_{EtAc} \cdot \delta_{tot}(\text{EtAc}) + x_{EtOH} \cdot \delta_{tot}(\text{EtOH}) \quad (3)$$

The EtOH and EtAc fractions in the solvent mixture were determined using GC-FID, as mentioned in the analysis section.

In fact, this diafiltration experiment was repeated three times on the same membrane: first using PEG-600 as the solute, subsequently using partially capped PEG, and finally using fully capped PEG. All diafiltrations were done at 10 bar. During each diafiltration, samples were taken after permeation of every 100 ml, allowing to determine the variation of the retention of each solute in the varying EtAc-EtOH mixture.

In [figure 2](#), all retentions are plotted as function of the Hansen solubility parameter of the EtAc/EtOH mixture. From this figure it can be clearly seen that, for all PEGs, retentions are low for the apolar mixtures, increase when the solvent polarity rises, and become constant at sufficiently high polarity of the solvent. In other words, there are again two distinctive regions as previously observed in [figure 1](#): one region at low solvent polarity where the retention increases with solvent polarity and the PEG-600 retention is the lowest, and another region at high solvent polarity where the retention is almost constant and PEG-600 retention is the highest. We note also that, for fully capped PEG, the retentions decrease again at high solvent polarity. This effect is also seen for the partially capped PEG in [figure 2](#), however, to a much lesser extent.

Furthermore, it can be noticed that the retention plateau is different for the three PEGs, and that the more apolar fully capped PEG already reaches its plateau at much lower solvent polarities as compared to the other PEGs. The retention values at the three plateau's are: about 72% for the PEG-600 (600Da), about 67% for the partially PEG (550 Da), and about 57% for the fully capped PEG (500 Da). These values are pretty close to what one expects for size exclusion of these molecules through a 800 Da membrane (MWCO of the membrane used in this diafiltration test) [[26](#)].

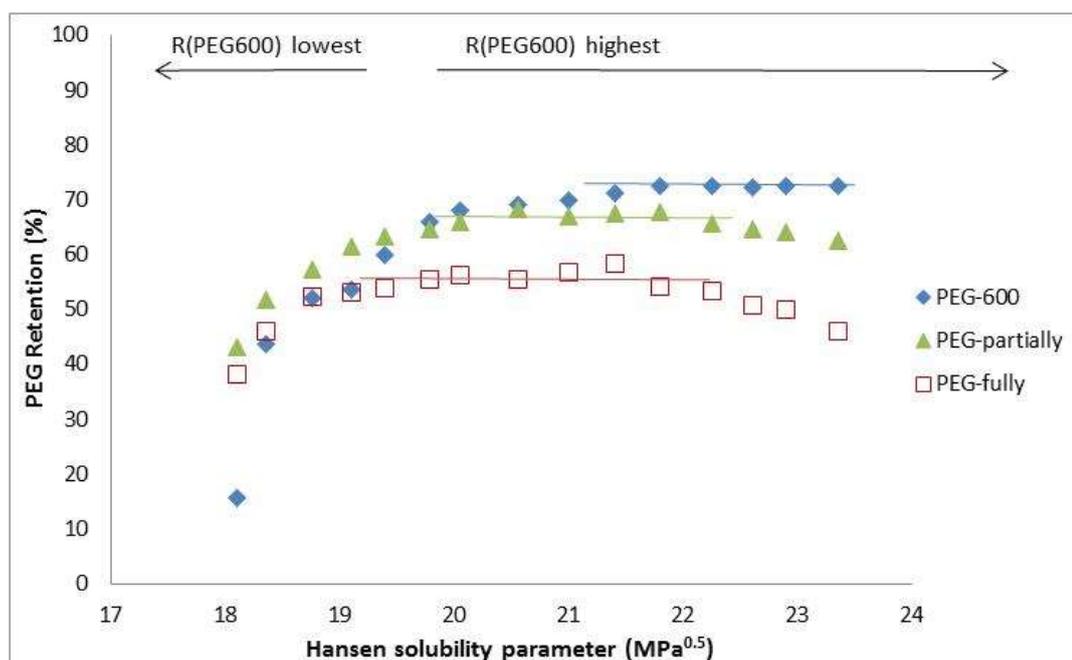


Figure 2. Variation of the retention of three PEGs as function of the total Hansen solubility parameter of the EtAc/EtOH mixture during diafiltration from EtAc to EtOH for a 1nm C₈ Grignard modified membrane. The experiments were performed at a transmembrane pressure of 10 bar. The lines are a guide for the eyes.

Finally, comparing the EtAc and EtOH fractions measured in the retentate and permeate samples taken at the same moment in the diafiltration, revealed that the solvent mixture is not changed during transport through the membrane. In other words, no solvent separation is observed, as expected for nanofiltration.

3.2. Retention of polystyrene in different solvents

For extra confirmation, experiments were also performed with another solute of similar size namely, polystyrene with a MW of 580 Da. These experiments were performed with two new, freshly grafted 1 nm TiO₂ membranes: one grafted with C₈ groups, and one grafted with phenyl groups. Polystyrene retentions were determined again in a range of solvents from non-polar methyl cyclohexane ($\delta_{\text{tot}}=16 \text{ MPa}^{0.5}$) to more polar ones. Due to the limitation in dissolving polystyrene in solvents with high Hansen solubility parameter such as methanol, ethanol or water, DMF ($\delta_{\text{tot}}=24.8 \text{ MPa}^{0.5}$) was selected as the most polar solvent. As it was not possible to find a pure solvent still solving polystyrene and having a Hansen solubility parameter between 20.3 MPa^{0.5} for DCM and 24.8 MPa^{0.5} for DMF, a mixture of 50/50 vol% of DCM and DMF was used as well ($\delta_{\text{tot}}=22.55 \text{ MPa}^{0.5}$).

For all polystyrene retention measurements in different solvents, the same two modified membranes were used. However, the experiments were not performed in the order of solvent polarity, but the sequence of solvents was such that each new solvent was miscible with the previous solvent to avoid any multiphase creation. In particular, for the phenyl modified membrane, first toluene ($\delta_{\text{tot}}=18.2 \text{ MPa}^{0.5}$), than EtAc ($\delta_{\text{tot}}=18.1 \text{ MPa}^{0.5}$), methyl cyclohexane ($\delta_{\text{tot}}=16.1 \text{ MPa}^{0.5}$), MEK ($\delta_{\text{tot}}=19 \text{ MPa}^{0.5}$), THF ($\delta_{\text{tot}}=19.4 \text{ MPa}^{0.5}$), DCM ($\delta_{\text{tot}}=20.3 \text{ MPa}^{0.5}$) and DMF ($\delta_{\text{tot}}=24.8 \text{ MPa}^{0.5}$) were used. For each of these solvents, three experiments were performed at three transmembrane pressures: first at 11 bar, than at 5 bar, and finally at 16 bar. There was no rinsing step in between the different experiments. Afterwards, in order to fill the polarity gaps in the solvent series, filtrations in three other solvents with Hansen solubility parameters around 17 and 22 MPa^{0.5} were performed. The following sequence was used: MIK ($\delta_{\text{tot}}=17 \text{ MPa}^{0.5}$), cyclohexane ($\delta_{\text{tot}}=16.8 \text{ MPa}^{0.5}$) and the 50/50 mixture of DCM/DMF ($\delta_{\text{tot}}=22.55 \text{ MPa}^{0.5}$). These measurements were only performed at 11 bar. For the 1 nm C₈ modified membrane, all polystyrene retention experiments were performed at 11 bar in the following order of solvents: methyl cyclohexane, cyclohexane, EtAc, toluene, MEK, THF, DCM, DMF, MIK and the 50/50 mixture of DCM/DMF.

Figure 3 compiles all the polystyrene retentions obtained at 11 bar for the two different Grignard modified membranes. The lines drawn are just guides for the eye. From the results in figure 3 it is obvious that no clear effects of the measurements history can be

noticed (so most probably the solvent of the previous measurement is replaced by the solvent of the next measurement). Some of the measurements were also repeated afterwards. From these extra measurements a tendency to a small reduction of the retentions (3 to 10 %) was noticed.

Figure 3 shows the same retention trends for both modified membranes. The trends are also very similar to the PEG retention results in the EtAc/EtOH mixtures (figure 2). Again two regions are found: in the first region at low solvent polarity, the polystyrene retention increases with solvent polarity, while in the second region at higher solvent polarity, the retention remains constant. The inflection point in between the two regions is observed to be similar for the two membranes tested.

Moreover, the values of the retention plateaus correspond well to the retention values we expect for size exclusion of the 580 Da polystyrene molecule by the two membranes (the MWCO of the 1 nm TiO₂ membrane used for phenyl modification was about 600 Da, while the MWCO of the 1 nm TiO₂ membranes used for C₈ modification was about 750 Da) [26]. Remarkable is also the systematic deviation from the general trend (guide lines) for specific solvents, and this very similar for both membranes. E.g. the retention values of MIK and of the DCM/DMF mixture were systematically lower than the trend line, for both modified membranes.

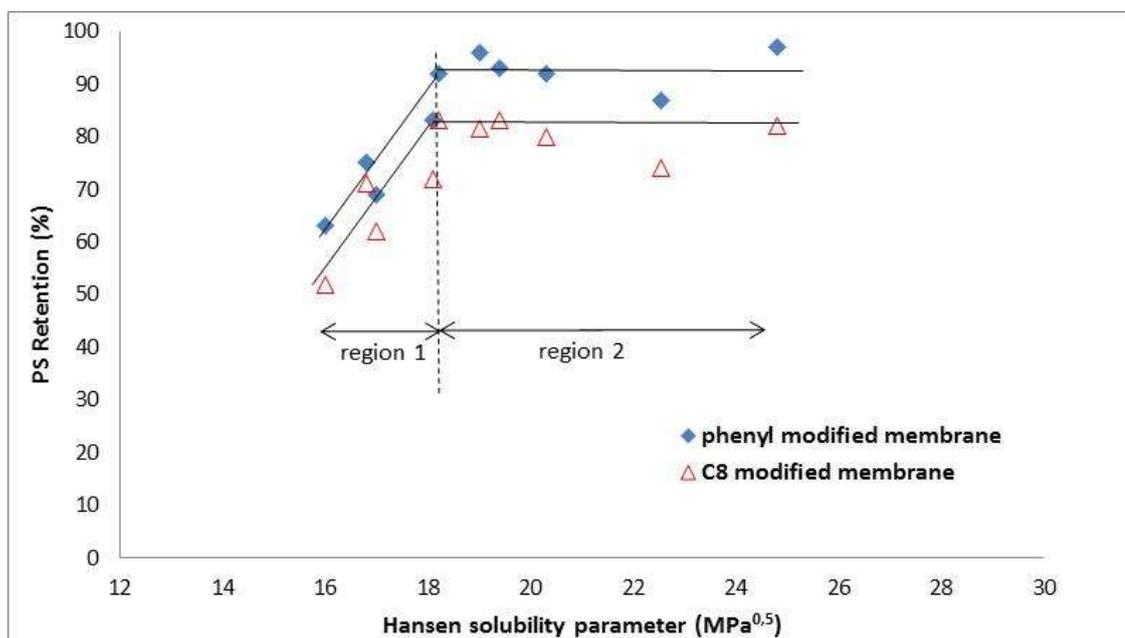


Figure 3. Polystyrene retentions in different solvents for 1 nm C₈ and 1 nm phenyl modified membranes, all determined at a transmembrane pressure of 11 bar. The retention values are plotted as function of the Hansen solubility parameter values of the different solvents. The lines are a guide for the eyes.

3.3. Pressure effect

To obtain further insight in the transport mechanism, also the pressure dependence of the measured membrane performance was investigated. Figure 4 shows the observed permeate flux for the polystyrene solutions in methyl cyclohexane, EtAc, toluene, MEK, THF, DCM and DMF, as a function of the transmembrane pressure for the phenyl modified membrane. It is clear that the permeate flux J , increases linearly with the applied pressure, for every solvent. This confirms that the pressure difference is the only driving force for solvent permeation [21], with a negligible osmotic pressure due to the very low feed concentration [19].

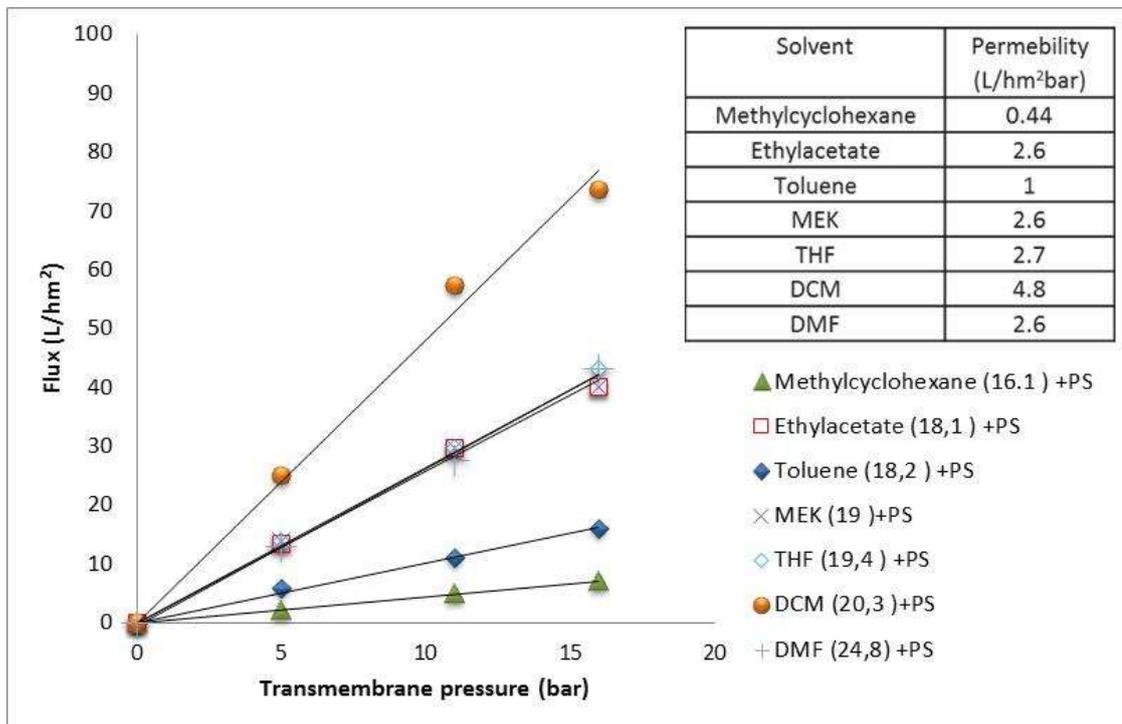


Figure 4. Permeate flux for polystyrene in methyl cyclohexane, EtAc, toluene, MEK, THF, DCM and DMF as a function of the transmembrane pressure for a phenyl modified membrane. The lines are linear fits through zero.

Figure 5 shows the evolution of the polystyrene retentions as a function of the transmembrane pressure for the phenyl modified membrane. It can be observed in figure 5 that by changing the solvent from the less polar one (methyl cyclohexane) to the most polar one (DMF), the variation of retention vs. applied pressure evolves from linearly increasing with increasing pressure, towards being independent of the pressure. More specifically, the solvents with relatively low polarity belonging to region one (figure 3), show retentions that clearly increase with pressure, whereas the solvents with relatively high polarity belonging to region two (figure 3), show retentions that are almost independent of pressure.

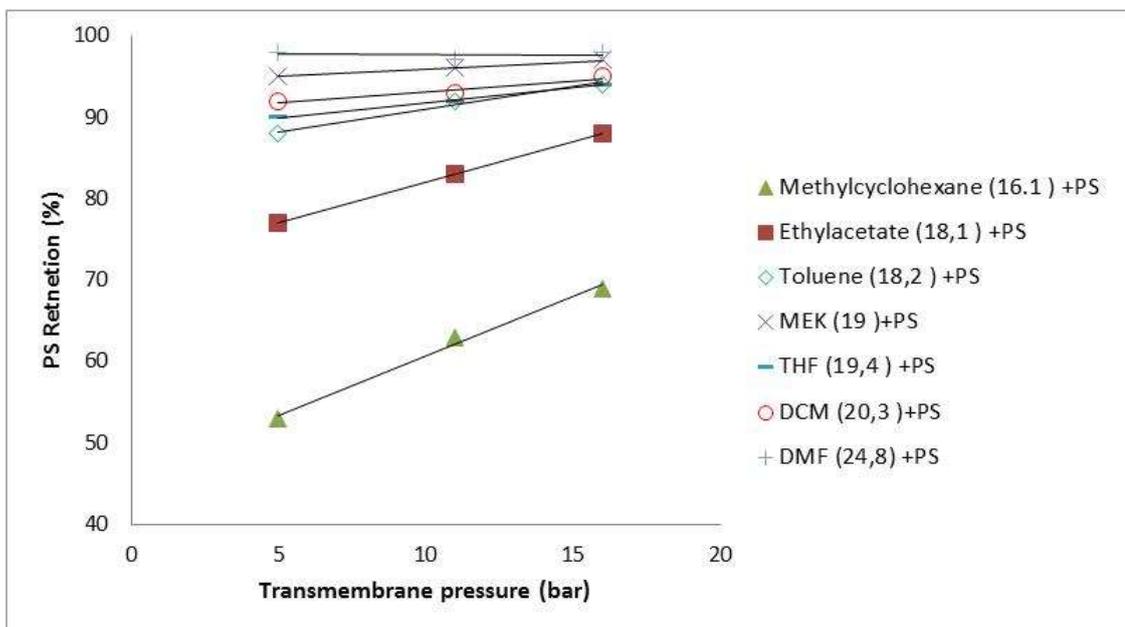


Figure 5. The evolution of the polystyrene retention in different solvents as function of the transmembrane pressure for a phenyl modified membrane.

Furthermore, also the effect of transmembrane pressure on the retentions of the three PEGs was tested for two different solvents: DCM and DMF. These solvents were chosen as they belong to different regions in [figure 1](#): DCM belongs to region one, while DMF belongs to region two. The order of the pressures was as follows: 5, 11 and 16 bar. [Figure 6 \(a\)](#) and [\(b\)](#) show the results. Similar effects as in [figure 5](#) are observed: for DCM of region one a clear linear pressure effect on the retentions is noticed, while for DMF of region two retentions are almost pressure independent.

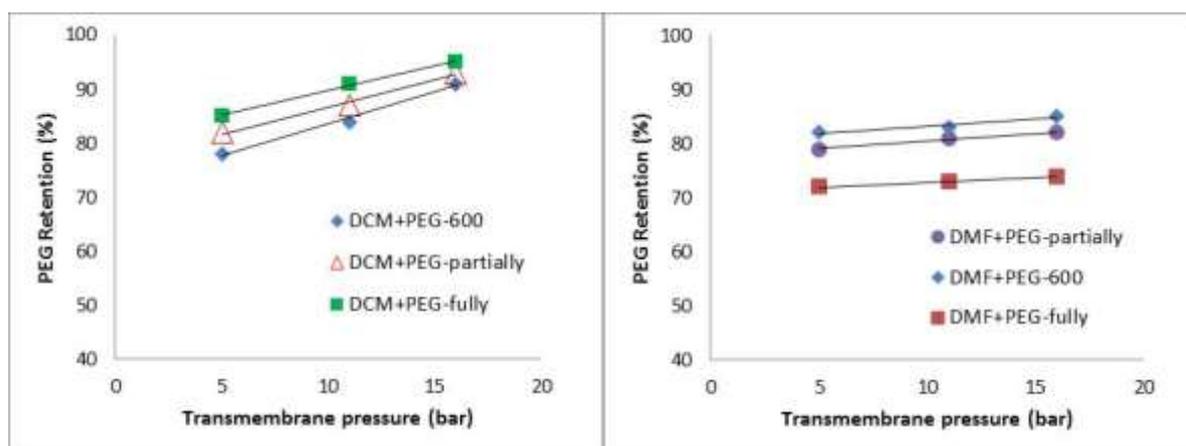


Figure 6. Retention vs. transmembrane pressure for PEG-600, partially capped PEG and fully capped PEG in (left) Dichloromethane (DCM) and (right) Dimethylformamide (DMF).

4. Interpretation of the results by using Spiegler–Kedem theory

Many different aspects of the described results, show similarities of the diffusion and convection transport known for aqueous nanofiltration [1,47]. For instance, in aqueous nanofiltration it is common knowledge that at low flux, or alternatively at low transmembrane pressure, the retentions increase with flux/pressure, while at high flux/pressure the retentions reach a plateau value determined by size exclusion. In the low flux/pressure region, the solute transport is mainly driven by diffusion, while in the high flux/pressure region, the solute transport is dominated by convection (solute dragged with the solvent). In aqueous nanofiltration, this transport is efficiently described by the well-known Spiegler-Kedem theory.

The Spiegler–Kedem equation [48, 49] describes the solute flux J_s , as a result of a diffusion mechanism (first term in the equation) and of a convection mechanism (second term in the equation), as follows:

$$J_s = P_s \Delta x \frac{dC}{dx} + C (1 - \sigma) J \quad (4)$$

where P_s and σ are solute permeability and reflection coefficients, C is the solute concentration and Δx the membrane thickness. The reflection coefficient σ is dependent on the ratio of the solute size and the membrane pore size (size exclusion) and can be expressed in more detail following different theories [50].

At non-infinite pressures, equation (4) can be solved to calculate the retention. The result shows that the retention is a function of the reflection coefficient σ , and the ratio of the solvent and solute permeabilities J / P_s :

$$R = (1 - F) \sigma / (1 - \sigma F) \quad (5)$$

where

$$F = \exp (- (1 - \sigma) J / P_s) \quad (6)$$

Following the Spiegler-Kedem theory, the permeation of solutes is always a function of diffusion as well as convection [49]. The contribution of convection increases with applied pressure, and consequently, the retention approaches a limiting value, which is the reflection coefficient. This maximum retention is constant, independent of pressure, and determined by size exclusion (ratio of solute size to pore size). Indeed:

$$\text{If convection} \gg \text{diffusion} : J / P_s \gg 1 \rightarrow F \approx 0 \rightarrow R \approx (1 - F) \sigma \rightarrow R \approx \sigma$$

On the other hand, when solute diffusion dominates the transport mechanism rather than convection, the retention is lower than the reflection coefficient, and is a function of the transmembrane pressure (TMP):

If convection \ll diffusion : $J / P_s \ll 1 \rightarrow F \approx 1 \rightarrow R \approx \sigma J / P_s \ll \sigma \rightarrow R \approx f(\text{TMP})$

The experimental observations shown in this work can be elegantly interpreted using the Spiegler-Kedem theory. In region two of [figures 1, 2 and 3](#), the retention reaches a plateau value, independent of pressure as proven in [figures 5 and 6](#). In this region, convection and size exclusion prevails. In region one of [figures 1, 2 and 3](#), the retentions are lower than the size exclusion value, and dependent on pressure as proven in [figures 5 and 6](#). In this region, diffusion plays a major role in the transport mechanism. Which transport mechanism is the dominant one, seems to depend on the nature of the solvent (influencing J) and on the nature of the solute (influencing P_s). Moreover, the type of membrane plays a role too, as it influences solvent flux (J), solute permeability (P_s) and reflection coefficient (σ).

Using different characterization methods, it has already been clarified [38] that, due to partial surface coverage, Grignard grafted membranes are amphiphilic membranes showing higher affinity, and thus higher fluxes (J), for solvents with medium to high polarity, than for solvents with low polarity. This is also visible from the results of [figure 4](#). As a consequence, in general, solvents with high polarity and thus high Hansen solubility parameter, belong to region two where convection dominates ($J / P_s \gg 1$), while solvents with low polarity and thus low Hansen solubility parameter ($J / P_s \ll 1$), belong to region one where diffusion is non-negligible. This is again consistent with the results shown in [figures 1, 2 and 3](#).

The strength of the Spiegler-Kedem theory to explain our results can also be shown in a quantitative way. As an example, in [figure 7](#) all measured polystyrene retentions for the phenyl modified membrane were evaluated with the Spiegler-Kedem theory (equation 5 and 6). To this purpose, all retentions were plotted as function of the solvent flux (J) measured during the retention experiments. The phenyl modified membrane was chosen, as for this membrane three retentions were determined for three transmembrane pressures for most solvents, and thus the most retention values are available. In [figure 7](#) the curve shows the Spiegler-Kedem equation (5) using the following parameters: reflection coefficient $\sigma = 0.95$, solute permeability $P_s = 1.5$. These parameters were determined as being the ones needed for the best fit of the data. Although some scatter can be noticed, the Spiegler Kedem theory fits rather well to the experimental points (green, blue and red points ; different colours show the results obtained at different pressures). To further check the validity of the Spiegler-Kedem theory, we measured also the retention of polystyrene in IPA for this membrane: 42.3 % (orange point, determined at a transmembrane pressure of 11 bar). This solvent has a high viscosity, and therefore

typically shows relative low solvent fluxes (i.e., low J). The Spiegler-Kedem theory naturally explains the relative low retention observed for polystyrene in this solvent.

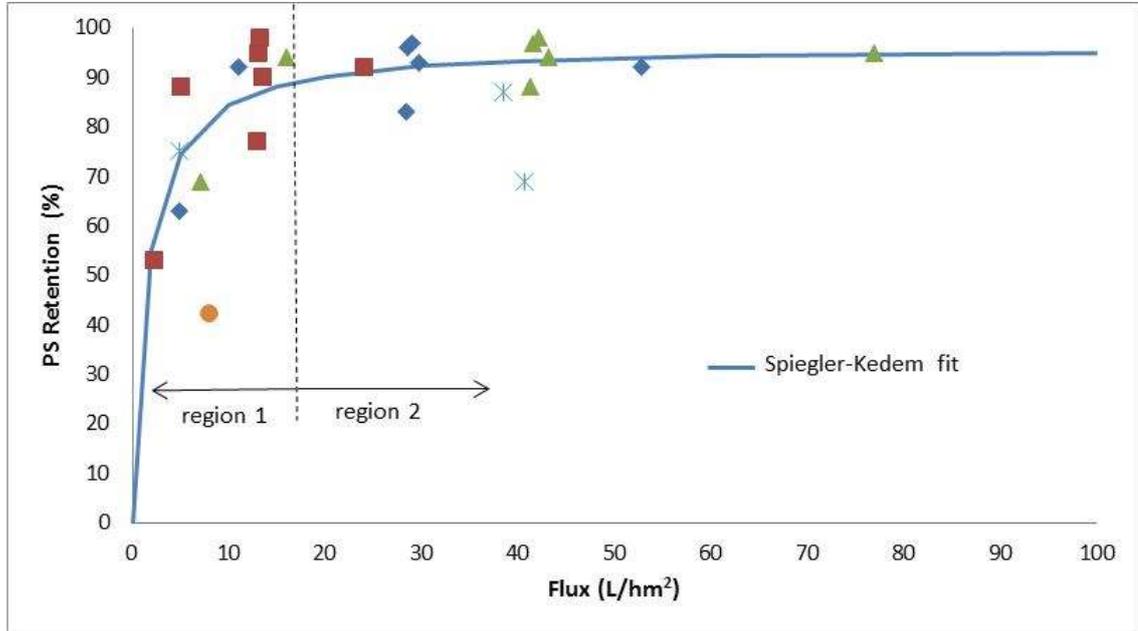


Figure 7. Compilation of all measured polystyrene retentions on the phenyl modified membrane, plotted as function of the flux during the measurement. The retentions for solvents methyl cyclohexane, EtAc, toluene, MEK, THF, DCM and DMF at 16 bar are shown by the green triangles, at 11 bar by the blue diamonds, at 5 bar by the red squares. The crosses are the retentions for solvents cyclohexane, MIK and DCM-DMF(50-50) determined only at 11 bar. The orange point is the retention for solvent IPA. The line is a fit of the Spiegler-Kedem theory to the data.

In region one, at low solvent polarity, where the diffusion transport mechanism dominates, the nature of the solute has a strong influence on the observed retentions. This can be clearly seen in Figures 1 and 2. In this region, the highest retention appears for the most apolar of the PEG solutes, i.e., the fully capped PEG (with the lowest solubility parameter $\delta_{\text{tot}} = 18.56 \text{ MPa}^{0.5}$, compared to $\delta_{\text{tot}} = 25.2 \text{ MPa}^{0.5}$ for PEG-600 and $\delta_{\text{tot}} = 22.83 \text{ MPa}^{0.5}$ for partially capped PEG). This is again naturally consistent with the Spiegler-Kedem theory. Indeed, the fully capped PEG has the lowest affinity for the amphiphilic surface of Grignard modified membranes [39], and thus the lowest P_s , leading to the highest retention R ($R \approx \sigma J / P_s$). In this region, solute-membrane affinity clearly influences the performance and in fact, affinity type of separations are possible.

In region two, at high solvent polarity, where the transport mechanism shifts to size exclusion, the nature/polarity of the solute does not seem to influence the maximum retention value. Indeed, the retention values of the different solutes (different plateau's) correspond very well with the values one would expect from size exclusion for the

different membranes, as already explained when describing the results of figures 1 and 2. Here, also the pore size of the membrane plays a role, as it determines the MWCO and thus the size exclusion potential of the membrane. This was also already explained in conjunction to figures 1 and 2.

Fully capped PEG has a relatively low amount of hydrophilic functional groups (compared to the other PEGs) and is consequently less soluble in water or in other high polarity solvents [51]. This is a possible reason why the retention of this PEG in figure 2 decreases at sufficiently high water content. It is less obvious to explain this behavior using the Spiegler-Kedem theory. A tentative explanation, takes into account an enhanced transport of the solute via diffusion, i.e., extra high P_s , specifically enhanced by the low solute-solvent affinity. One would expect here again retentions low compared to the reflection coefficient, and dependent on transmembrane pressure ($R \approx \sigma J / P_s$).

From figures 2 and 4 it is clear that the inflection point in between region one and two, where the transport mechanism changes from diffusion (affinity based) to convection (size exclusion based), changes for each solute. Figure 8 shows that there is a correlation between the Hansen solubility parameter of the solvent at this inflection point, and the Hansen solubility parameter of the solute. The increase of the inflection point with the solute polarity can be again simply explained by the Spiegler-Kedem theory. The higher the polarity of the solute, the higher the solute-membrane affinity, i.e., the higher solute permeability P_s through the amphiphilic Grignard membranes. Consequently, the solvent flux, or solvent polarity needs to be higher in order to reach the size exclusion regime. From figure 4 it is also clear that the inflection point for polystyrene is the same for both the C_8 grafted membrane, as for the phenyl grafted membranes. This is not illogical, as the polarity (as determined by their water contact angles) of both membranes is quite similar [38, 52].

From figures 4 and 7 it is however clear that there are some systematic deviations from the general Spiegler-Kedem trend for specific solvents. This can be due e.g. to the fact that we use the total Hansen solubility parameter of the solvents, ignoring hereby the details of the interaction possibilities of the solvents (ignoring relative strengths of dispersion, dipolar and hydrogen bonding interactions).

Finally we want to stress that the relative simplicity of the interpretation by the Spiegler-Kedem theory described above, is most probably due to the absence of swelling in the ceramic membranes used for this study.

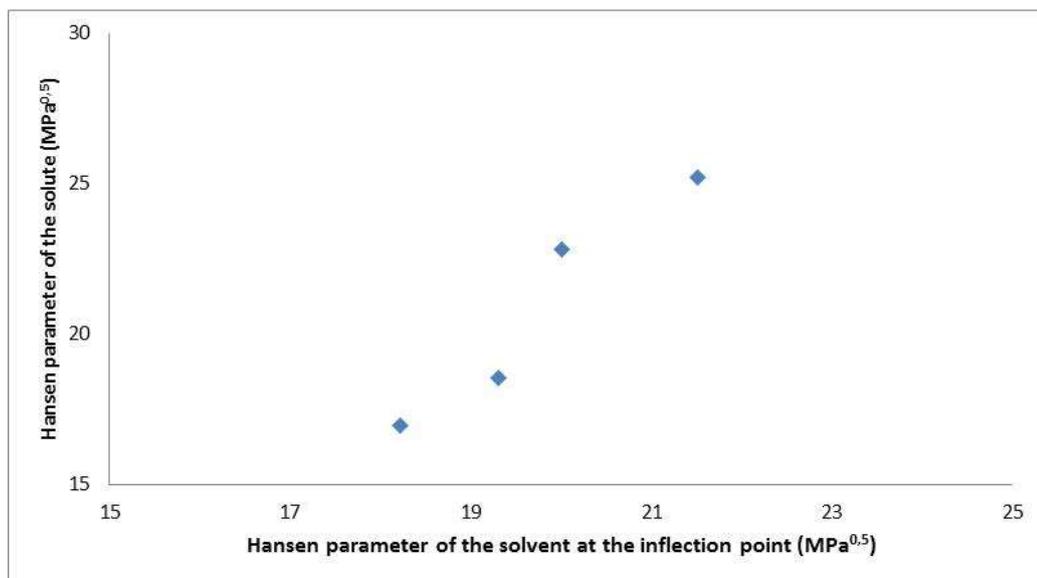


Figure 8. Correlation between the Hansen solubility parameter of the solvent at the inflection point between size exclusion and affinity region, and the Hansen solubility parameter of the solute.

4. Conclusion

This paper reports a new systematic investigation of the OSN transport through Grignard modified ceramic membranes. In this study, the permeation and retention of four solutes, PEG-600, partially capped PEG, fully capped PEG and polystyrene 580 Da, all with similar size but different polarity, was determined in a wide range of different organic solvents or solvent mixtures, through two types of 1 nm titania membranes functionalised with C₈ groups or phenyl groups. For the three PEGs, two different types of experiments, normal filtration with different solvents and diafiltration from pure EtAc to EtOH were done on different 1 nm C₈ modified membranes. For polystyrene, filtration of an extensive range of solvents from apolar to polar ones, was investigated for both 1 nm C₈ and phenyl modified membranes. To further unravel the transport mechanism properly, also the pressure effect on flux and retentions was thoroughly investigated.

The retention results showed in general two regions: one region at low solvent polarity, with relative low retentions, varying with pressure and solvent polarity; and one region at high solvent polarity, with relative high retentions, independent of pressure and solvent polarity. The Spiegler-Kedem theory taking into account both diffusion and convection transport mechanisms, was used to interpret the results. Using this theory, region two naturally corresponds to a region with high solvent flux, and thus dominating convection. In this region the retentions are mainly determined by size exclusion and equal to the reflection coefficient σ . Region one naturally corresponds to a region with low solvent flux, and thus non-negligible influence of diffusion in the solute transport. In this region, also a strong influence of the solute polarity is observed: the solute with the highest solute-

membrane affinity, shows the lowest retentions. In the size exclusion region, not the nature (polarity) of the solute but the size of the solute compared to the pore size of the membrane, influences the retention plateau. The relative simplicity of this interpretation is most probably due to the absence of swelling in the ceramic membranes used for this study.

This study demonstrates again the importance of all solvent-membrane-solute interactions in the OSN transport, but also shows how they can be manipulated to enhance the membrane performance.

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