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Can the variance in membrane performance influence the design of organic solvent nanofiltration processes?

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Abstract

The development of organic solvent nanofiltration (OSN) membranes has been a continuous effort during the past decade. Several groups generated and published experimental results and simulations with either tailor-made membranes or industrial products. The published data space is diverse, with a single publication often focusing on a certain membrane only, a group of specific solutes only, on the effect of solvent only. A comprehensive comparison of all of these is still lacking. An analysis on the reliability of quantified transport parameters is missing, in particular when different analysis methods and different membrane systems are used. The technology is in its incubation phase with a need for reliable data and measurement standards to ground the process design on reliable membrane transport properties. This

study uses an unprecedented extensive standard experimental procedure to measure separation characteristics of polymer membranes for the separation of organic solutes from organic solvents.

For a variety of different solvents, solutes and membranes, flux and retention measurements are rigorously characterized by round robin tests at different labs using different analytical systems. This extensive collaborative study evaluates for the first time which fluctuations in results occur under comparable conditions of lab-scale experiments at different locations and which influence these have on the design of OSN processes.

Utilizing the variance in the membrane transport data, a process design study and optimization is presented. For the first time ever, we report how variance in membrane transport properties can influence the process design ranging from a simple single stage system for values for the upper transport limits, to a two stage system with a permeate recirculation for mean values, to a complex three stage system for the lower limits.

Keywords: Organic solvent nanofiltration, Solvent resistant nanofiltration, Experimental standardized procedure, Statistical comparison, Functional membrane characterization

1. Introduction

Taking membrane research from its initial phase of concept development, material and membrane design into process development requires substantial resources and time. This is not special but true for many innovations starting with an innovation trigger. This is also known as the Gartner Hype Cycle [1]. Judgment of the quality of the innovation trigger occurs often through

reproducibility and applications studies and generally also creates - after a peak of inflated expectations - a trough of disillusion.

In membrane research, the innovation trigger is assumed to occur through the availability of new materials and membranes made thereof. Yet, it is often not well known how statistically significant the mass transport properties of new membrane materials and new membrane products are. In a recent meta-study for example [2], published in this journal with more than 3000 references, the authors pose the fundamental questions (a) whether there is an average proton conductivity for Nafion membranes, (b) how the proton conductivity due to Nafion modification has evolved over past 10 years, (c) which additives really contribute to a conductivity increase, (d) how temperature or humidity affect conductivity. While such questions are not scientifically inspiring and do not initiate a new hype cycle, such questions are important in order to understand and judge the significance of a new material or membrane type. Here we pose similar questions with respect to the statistical significance and comparability of characterization methods to quantify mass transport properties for membranes used in organic solvent nanofiltration. As opposed to the meta-study, we have chosen to engage different labs and research groups with comparable analytical infrastructure, to use a round robin test evaluating the results of a developed standard experimental procedure. This leads to conclusions on standard deviations in flux and retention values in a complex parameter space for different membrane materials in various solvent/solute systems.

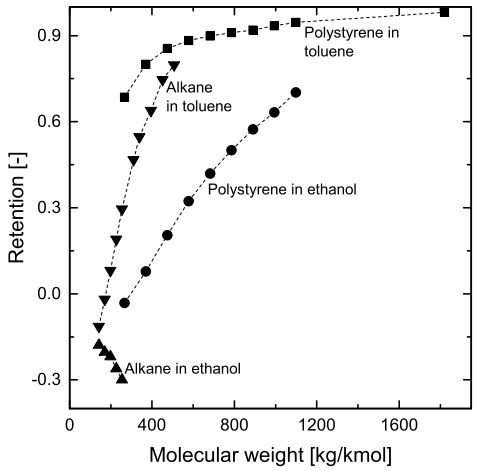


Figure 1: Retention measurements using different solvents and solutes for PuraMem® S600 at 30 bar and 25 °C show different behaviour of the membrane.

2. Background

Organic solvent nanofiltration (OSN) became a new member of the family of pressure-driven membrane processes by the discovery of solvent resistant membranes. Up to now, a great number of various applications were developed since the production and reactions in organic solvents comprises a wide range [3, 4]. Although OSN is still in the focus of industry as an energy-efficient separation process, there are only a few established plants [5–7]. However, the progress in the investigation of this field is still growing, and the challenges include a wide spectrum of different issues. For instance, the community knows that flux and retention depends on the interaction of solutes, solvents, and membranes [8–14]. Stamatialis et al. [15] suggested a three-dimensional space of properties determining the mass transport properties of solvent and solute transport.

Due to this complex interplay, the molecular weight cut off (MWCO),

defined as the molecular weight that is rejected by 90 %, also depends on the system of compounds. Figure 1 shows retention curves for PuraMem® S600 at 30 bar in two different solvents using two different solutes. It demonstrates the strong dependence of the functional membrane characteristic on the used compounds.

Nevertheless, the MWCO is measured and determined for OSN membranes in many different ways, and no standard test system is established [16–19]. See Toh et al. [20] proposed first to standardize the method for a membrane characterization measurement of the MWCO in OSN. The idea was to use a homologous series of polystyrene oligomers which are soluble in many organic solvents to find the MWCO and possibly recognize leak flux. In fact, lot of data can be found in the literature for commercially available and new developed membranes [21]. These data are commonly presented as individual or a few measurements, and often it is not stated if the data are reproducible.

This diversity of methods and lack of information about comparability and reproducibility is delicate for research as well as an industrial application of the technology, since it complicates and delays a possible commercialization of new membranes. In addition, it poses a risk to process design since data for specific products have to be retested and evaluated. Thus, the expansion of OSN plants in real processes slows down and turns out of focus of the process designer. However, Schmidt et al. [22] have offered a process design workflow for general new OSN processes, and there exist manuals to support membrane experiments for process design [23]. These approaches are indeed steps towards a higher acceptance of OSN in industry, though

we still owe a proof of accuracy for results from membrane characterization experiments. Also, Shi et al. [24] conclude that new research in module and process design is necessary besides new membrane materials to achieve for example ultra-high permeance. Marchetti et al. [25] point out the selectivity challenge in OSN and suggest that process engineering solutions lead to a need of standardized procedures for membrane characterization. In their general review of data quality, Keller et al. [26] highlight the importance of data quality and especially accuracy and precision as important elements for a correct interpretation and evaluation of experimental results.

In order to achieve this aim and to follow the recommendations of [24] and [25], a consortium of research groups and industrial partners has been formed, working on a comparison and validation of experimental results. The main objective of this consortium is to define and assess a standard experimental procedure for several chemical systems. The standardized procedure should enable an estimation to determine whether (new) membranes/materials are suitable for process design. For this purpose, results for a membrane must ideally exist for a similar chemical model system. We categorized the solvents and solutes to combine ideal model systems. The results from the experimental plan ought to be comparable and reliable between different institutions. Therefore, we performed extensive round robin testing to show for the first time the comparability and reliability of such measurements by cooperative experiments. Subsequently, we evaluated the results of the standardized procedure with statistical methods. Furthermore, additional bilateral cooperative tests were performed for other chemical systems and evaluated accordingly as well. During the development of the standardized

procedure different sources for occurring errors, caused e.g. by the different analytic methods, were identified and ruled out. For an evaluation of the comparability of the measurements at the different locations, a statistical analysis is indispensable to avoid arbitrary criteria. The error estimation enables end-users to select suitable membranes more quickly. Besides, it allows membrane manufacturers to judge faster whether it is economically viable to bring newly developed membranes to production. The present work is consequently of major importance for the transfer of research results in the field of membrane development to later processes and the evaluation in industry.

3. Experimental standard measurement procedure

3.1. Materials and categorization

An appropriate categorization usable for test systems has to be as simple as possible and as accurate as necessary. Following this maxim, we decided to categorize the solvents in protic and non-protic solvents. In protic solvents, we extended the category with two degrees of polarity and for non-protic solvents with three degrees of polarity. Therefore, the normalized polarity index of Reichardt [32] supplies the values. The same as the polarity, in this way a wide range of the Hansen-Solubility parameter [28] and the relative permittivity [27] is covered. Overall, six solvents were chosen to define the set of ideal test-solvents (Table 1), of which ethanol and toluene were used as solvents in the round robin tests. The purity of all solvents used is ACS grade. The supplier of the solvents could be chosen individually by the contributors.

Table 1: Properties of the selected test solvents for the experimental standardized procedure [27, 28].

	Hansen Solubility Parameter						
	δ_{tot}	δ_d	δ_p	δ_h	ϵ_r	Polarity	
Solvent	$[MPa^{1/2}]$				[−]	E_T^N [%]	Category
Ethanol (EtOH)	26.52	15.8	8.8	19.4	22.4	65.4	protic-polar
Isopropyl alcohol (IPA)	23.58	15.8	6.1	16.4	18.3	54.6	protic-moderate polar
Butanone (MEK)	19.05	16.0	9.0	5.1	18.5	32.7	aprotic-polar
Ethyl acetate (ESTP)	18.15	15.8	5.3	7.2	6.02	23	aprotic-moderate polar
Toluene	18.16	18.0	1.4	2.0	2.38	9.9	aprotic-nonpolar
n-Heptane	15.3	15.3	0.0	0.0	1.92	1.2	aprotic-nonpolar

Table 2: Properties of the selected test solutes for the experimental standardized procedure [16, 29–31].

Solute group (Category)	Selected examples	Mw [kg/kmol]	Structure	Polarity	Branch of industry
n-Alkane	Decane - Hexatriacontane	ca. 140 - 500	Linear	Nonpolar	Petrochemistry
Sugar and Derivative sugar	Sucrose octaacetate (SOA)	677	Branched out widely	Moderate polar	Food- and agricultural chemistry
Polymer	Polystyrene (PS), Poly-(methyl methacrylate) (PMMA)	ca. 200 - 2000	Linear	PS: nonpolar PMMA: moderate polar	Commodity chemicals and polymer chemistry

The categorization of solutes is much more complicated than for the solvents because of the multitude of possible compounds and functional groups. Additional to a classification of the structure, polarity and molecular weight, it is beneficial to give the branch of industry in which the solutes and related solutes are often used. Supplementary, we take solubility, analyzability, and costs into account. Thereby, the solute groups are chosen in such a way that either MWCO curves or individual retention as indicator for estimations on real substances can be measured.

Table 2 shows three solute groups defined with the solute properties for the ideal test systems. All solute substances used are of ACS grade purity. The contributors used as solutes in the round robin tests polystyrene oligomer mixtures containing PSS-ps560 and PSS-ps1.8k (Polymer Standards Service GmbH, Mainz, Germany) with a molar mass distribution from 266 to 1800 kg/kmol. The bilateral cooperative test systems consisted of these polystyrene oligomers in the remaining solvents from Table 1 as well as n-alkanes (Thermo Fisher Scientific Inc.) and sucrose octaacetate (SOA) (Merck KGaA) in each solvent and poly-(methyl methacrylate) (Polymer Standards Service GmbH) in each solvent. We selected the solute combinations concerning solubility and simple analysis assuming that solute/solute interactions have no significant influence on the measurements [33].

The OSN membranes can be distinguished in terms of membrane material and membrane type [3]. For the standard measurement procedure development, we focused on polymeric membranes and tested several integrally skinned asymmetric membranes as well as some thin film composite membranes. Four different membranes were used in the round robin test by

each contributor: DuraMem® 200 and 300 (polyimide-based membranes), PuraMem® S600 and a PDMS membrane (both with silicone-based separation layer). DuraMem® and PuraMem® membranes are products of Evonik Resource Efficiency GmbH and the Helmholtz-Zentrum Geesthacht provided the PDMS membrane. The membranes with a polyimide-based separation layer are suitable for applications in polar solvents (e.g. ethanol) whereas the silicone-based membranes are more appropriate for nonpolar solvents (e.g. toluene). Therefore, the particular membranes selection covers a broad range of possible membrane uses (e.g. solvents and solutes with different physico-chemical properties).

While the different partners were performing the same experiments, there were important differences in the experimental set-ups and the analytical methods. Some set-ups are commercially available (e.g., METcell cross flow set-up from Evonik Resource Efficiency GmbH), some are tailor-made by an equipment manufacturer, and one is self-constructed. Therefore, membrane test cells with different geometry (round cells, rectangle cells) and scale were applied throughout the tests. The active membrane areas used vary between 50 and 100 cm^2 per module. Test system volume, control instruments (pressure, temperature, flow) and analytical devices were various too. This is representative for the diversity that is present not only in the scientific community, but also in industrial laboratories. The diversity brings, naturally, a high number of important factors that can potentially contribute to differences in the experimental results. Such results might even lead to different conclusions. Therefore, it is indispensable to implement a standard measurement procedure, as well as to evaluate the variance in the obtained results,

as has been done in the scope of the current study.

3.2. Experimental standardized procedure

All contributors unified the measurement procedure together. At least two identical membrane coupons were tested at the desired conditions. Usually the testing cells were connected in parallel. The DuraMem® and PuraMem® membranes were pre-washed using the process solvent until $5\,\mathrm{ml\,cm^{-2}}$ permeate was collected or permeate became colorless. This procedure is necessary to prepare the membrane for its use, by removing the conditioning agent from its surface. Furthermore, the solvent treatments of the membranes have to be equal since they have a major impact on the membrane performance [34]. The membrane performance was determined by measuring the pure solvent permeate flux and the retention of different molecules (markers) in different solvents.

Figure 2 illustrates the agreed process conditions of the experimental standardized procedure. The pure solvent flux measurements were carried out at a pressure of 20 bar and 30 bar, a temperature of around 25 °C and a cross-flow velocity of $1\,\mathrm{m\,s^{-1}}$. Flux was measured by collecting 5 ml of permeate sample. The amount of collected permeate was controlled with a mass balance (especially important by low permeate flux and high volatile solvent). Also, measured flux values of electronic flow meters were validated by this method.

For the retention measurements, samples were taken at the same process conditions as in the permeation measurements. The process pressure was sequentially increased (20-30-40 bar) whereby permeate and retentate samples were taken at the end of each pressure step. The solute concentration in the

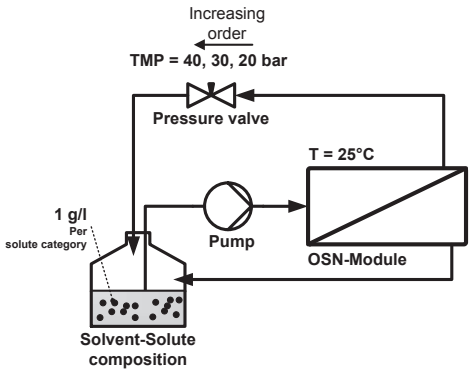


Figure 2: Schematic illustration of the experimental standardized procedure.

feed mixtures was kept constant during the experiments (continues permeate return) at a maximum of $1\,\mathrm{g\,L^{-1}}$ for each used solute group.

Following the membrane manufacturer recommendation, polyimide-based membranes were operated under pressure for 4 h before taking samples for flux and retention measurements. The time is required for the membrane to reach the steady state of its performance and abating representative results accordingly. When silicone-based membranes were applied, the time for compaction was set to 2 h. Permeate and retentate samples were taken simultaneously to determine the membrane retention. The retention was calculated by:

$$R_i = 1 - \frac{c_{i\,(Permeate)}}{c_{i\,(Retentate)}} \tag{1}$$

3.3. Analytic methods

Evonik, Merck and TU Dortmund University applied the high-performance liquid chromatography (HPLC-method) described by See Toh et al. [20] after all round robin tests and for tests with Poly-(methyl methacrylate) (PMMA). The existing facilities of the partners were used. The used HPLC device at

Merck KGaA, for example, is an HPLC Hitachi LaChrom (Hitachi High Technologies America, Illinois, USA) equipped with an UV-vis detector. RWTH Aachen University and the Helmholtz-Zentrum Geesthacht (HZG) used a gel permeation chromatography (GPC) method to determine the concentrations of the polystyrene oligomers and PMMA. The GPC were executed with a UV/vis detector and minimum two columns (SDV, 100 Å pore size, 3 µm particles, 8.0x300mm (IDxlength), Polymer Standards Service GmbH, Mainz, Germany). Tetrahydrofuran (AnalaR) was used as mobile phase, and the UV detector was set at the same wavelength as in the HPLC-method (264 nm). The solvent had to be evaporated from the samples before analysis, and the solutes had to be re-dissolved in the mobile phase. These steps were carried out in a very cautious way (evaporating at low temperature, accurate re-dissolving) to minimize loss of solute. Samples from tests with alkanes and sugar were analyzed by gas chromatography as described by Postel et al. [16]. The used GC device is dependent on the contributor. At RWTH, for example, a GC 6890 system (Agilent, CA, USA) with liquid autosampler and flame ionization detector (FID) was used. An Agilent 19091J-413 HP-5 column was used coated with 5 % phenyl methyl siloxane, 30 m length, 0.32 mm inner diameter and 0.25 mm thickness.

In order to compare the analytical technique used by the partners, they mutually exchange samples (permeate and retentate) during the experimental phase and re-analyze these in their laboratory. The resulting retention curves were compared and an analytical error was calculated.

4. Statistical analysis and evaluation

While it is often stated that comparable results have been obtained in different studies, these statements are qualitative and therefore subjective. To avoid such subjectivity and allow for a meaningful quantitative reference, we considered a statistical evaluation of the results. Thus, we defined a degree of congruence. The difference between a random sample and a reference or confidence intervals compared to each other are typically used. Confidence intervals should give the precision of an estimated value. However, real values for flux or solute retention cannot be determined because of the limited influenceable structure of membranes.

We considered confidence intervals, stated at the 95 % confidence level, as a measure of precision. The arithmetic mean values for flux and retention measurements were determined based on the taken samples, and the related confidence intervals were calculated. As result there is a 95 % probability that such an estimated interval contains the real value. Furthermore, intervals with a breadth of one (estimated) standard deviation (1σ) are reported to relate the obtained data points to the probabilistic distribution of measured values. The smaller the interval, the more narrow is the expected distribution.

Obvious single outliers and failed tests had to be identified and removed from the database prior to the statistical evaluation. Failed tests were recognized by an overall visible lower retention or a significantly higher flux value compared to the parallel tested module. They could occur by sealing problems (leak flux) inside the membrane module, membrane defects or contamination of the samples before analyzing. These tests were repeated to get

a reliable database with minimum 18 raw data points for every single pure solvent flux and nine raw data points for retention of each molecular weight. The amount of samples arose from the number of parallel tested membranes and contributors with the assumption of one failed test. For flux measurements this number were doubled since higher deviations were expected. In total, this approach generated at least 81 data points for retention curves measured in ethanol and 90 data points for retention curves measured in toluene.

The calculation of the standard deviation and the confidence intervals was based on the assumption that the given samples (data points) are unbiased, independent and statistically normally distributed [35]. Further we had to notice that the original variance is unknown. Hence, the variance s^2 with the unbiased sample variance arise from:

$$s^2 = \frac{1}{n-1} \sum (x_i - \bar{x})^2 \tag{2}$$

n is the number of measurements, x_i, and $\bar{x}$ are the individual measured values and the related mean value, respectively. The standard deviation σ is accordingly the square root of the variance s^2. Due to the limited sample size, the confidence interval calculation uses the student's t-distribution, considering the $(1 - \alpha/2)$ quantile of t. The quantile is tabled in the literature [36]. Thus, the confidence intervals result from:

$$\left[\bar{x} - t_{(1-\alpha/2)} \frac{s}{\sqrt{n}}; \bar{x} + t_{(1-\alpha/2)} \frac{s}{\sqrt{n}} \right] \tag{3}$$

With this way of calculation, the range of reliable mean values is determined. Confidence intervals from future experiments can overlap and

therefore narrow the range in regard to a real value. However, the primary objective of this study is to define a standard experimental procedure and perform a statistical analysis of the obtained results, allowing for a representative retrospective on reported data in literature. The effort of the contributors to generate comparable results become apparent in the standard deviations of the data points. Assuming an exact normal distribution of the measurement data, reflecting random differences of the membrane material (e.g. thickness of the active layer) it is expected that 95 % of all measurements will be located in the vicinity of the interval with 2σ range around the real mean. Thus, almost all of the measurements should be located within a range of two (estimated) standard deviation, around a value within the confidence interval of the mean.

In addition, tests of normality evidenced the assumption of statistic normally distributed data. The gathered results were tested on normal distribution with the methods of Anderson-Darling (a Goodness-of-Fit-Test) [37, 38] and Shapiro-Wilk (an omnibus test) [39–41]. The Shapiro-Wilk-Test analyzes the variance. Data are normally distributed if the estimated variance is near the hypothetical variance of the normal distribution. With the Anderson-Darling-Test data are sorted and transformed into a uniform distribution. The distance to the hypothetical normal distribution is, in this case, the critical value. Normal distribution was granted if the results passed both sensitive tests.

The bilateral cooperative test systems cannot be compared in this way, since only two contributors measured the data. In these cases, minimum four data points are available, which is too few for a reasonable calculation

of confidence intervals. The results comply with our claims if the deviation of each data point to the related ones is less or equal than the deviation between the data points in the round robin tests.

4.1. Superstructure optimization

In order to evaluate the effect of the extent of uncertainty related to the experimentally determined performance metrics, different scenarios are evaluated within a superstructure optimization approach considering a sampling within the ranges of the determined confidence intervals around the estimated mean values. The superstructure represents a so-called state-space approach [42] and builds on a previous implementation for the optimization of reverse osmosis processes for seawater desalination [43]. Similar superstructures have been used for the optimization of gas permeation processes for natural gas upgrading [44] and nitrogen removal from natural gas [45].

An illustration of the superstructure, which consists of a generic distribution network and three OSN membrane stages is provided in Figure 3. The distribution network allows distribution of the entering streams, which are the overall feed stream and all product streams from the membrane stages, to all outgoing streams that are the feed streams of the OSN stages and the final permeate and retentate product streams. Thereby any kind of combination between the different membrane stages is possible. The performance of each membrane stage is modeled based on the available performance metrics from the experimental data, which are an overall flux as well as solute-specific retention. Furthermore, a concretization of the membrane stage concerning 100 finite elements is performed to account for the composition changes along the membrane length.

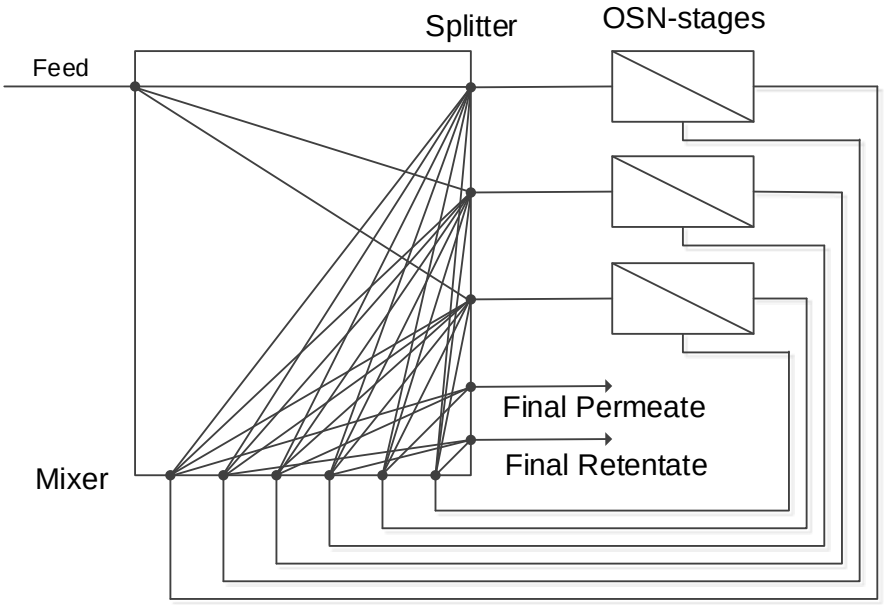


Figure 3: Superstructure for membrane network optimization.

However, a constant performance regarding the experimentally determined values is assumed, and concentration polarization and pressure drop are neglected since no information on module geometry and hydrodynamics is considered. Operating temperature and pressure are also fixed to the experimental conditions, such that only the membrane area remains as a degree of freedom for every membrane stage. For the current study a maximum membrane area of $50\,\mathrm{m}^2$ per stage and a total of three possible stages was considered. The objective of the optimization is to perform a specific separation, concerning purity and recovery constraints, with a minimum number of membrane stages and membrane area.

The superstructure optimization model is implemented in the general modeling framework GAMS as a mixed integer nonlinear programming problem (MINLP). The discrete decisions account for the existence of the different membrane stages, for which additional Big-M constraints enforce a minimum feed flowrate for existing membranes, while further constraints introduce additional cuts to eliminate topologically equivalent solutions by enforcing a specific order on the available membrane stages [43]. This is important to avoid multiplicity of equivalent optima in the solution space, which severely complicates global deterministic optimization. The resulting MINLP is solved using the global deterministic solver ANTIGONE to determine the best possible solution.

5. Results and Discussion

Considering the spent effort devoted to the standardized experimental procedure and the validation of the analytic methods, it can be concluded that the obtained results of the round robin test are a best case representative for the diversity of measurements in diverse laboratories. Differences are quite normal since locations, set-ups, measurement devices, analytic methods, time of measurements and experimenter vary from each other. The contributors endeavored to operate as equal as possible to ensure that the experimental procedure became a standard in functional membrane characterization.

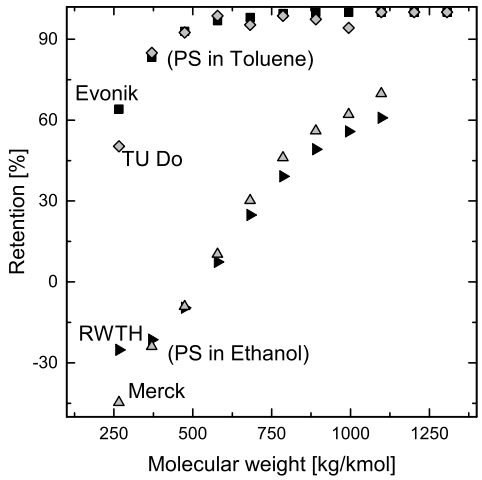
5.1. Comparison of analytic methods

Testing identical samples in different laboratories resulted in a minimal data points variation. Figure 4 shows two diagrams with four exemplary re-

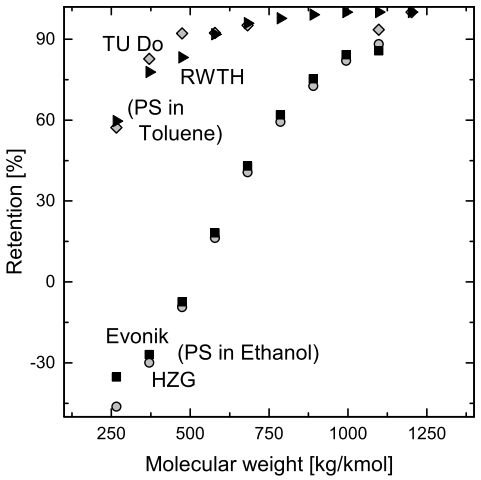
tention curves for the comparison of the analytical methods at different laboratories. The retention of the different styrene oligomers is plotted versus their molecular weight. Single occasional outliers could be identified by comparing the curves. The reason for the apparent deviations at $266\,\mathrm{kg\,kmol^{-1}}$ was the more sensitive evaluation of the small peaks obtained by analyzing the retentate and permeate samples. The biggest differences between the measured retention values, excluding outliers are only about 6 %, proving the comparability of the analytic methods.

5.2. Pure solvent flux

Figure 5a shows the results plotted in a box plot (left part for toluene fluxes, right part for ethanol fluxes) for each membrane to display the distribution and differences of the data. Toluene fluxes could be measured only with PuraMem® S600 and PDMS membranes. DuraMem® series membranes showed very low or no permeation with toluene. Ethanol fluxes, however, were measured with all selected membranes. One point worthy of note, is the different scales on the flux axes. Figure 5b illustrates the meaning of the boxplots, in which the dots represent the measured fluxes while the white boxes indicate the standard deviation as 1σ interval of the measured data. The accompanying percentage gives the difference from the arithmetic average to the upper or lower value of the range. Inside the boxes the line and the dot are the median and the arithmetic average of the data respectively. Above and below, the whiskers show the 2σ interval. The grey colored boxes represent the calculated confidence intervals (Eq. 3). The horizontal spread of the data dots is plotted this way to avoid overlap of too many points for the same membrane. It is randomized and has no physical meaning.



(a) Retention measurements with the PDMS membrane.
Evonik ■ and TU Do ◊ used samples with toluene as solvent (sampling at 30 bar).
Merck △ and RWTH ► used samples with ethanol as solvent (sampling at 30 bar).



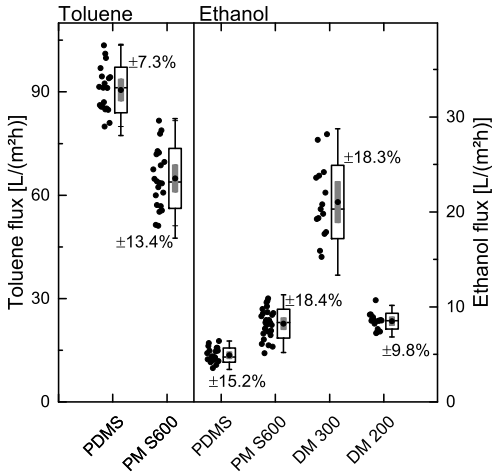
(b) Retention measurements with the PuraMem® S600.
TU Do ◊ and RWTH ► used samples with toluene as solvent (sampling at 20 bar).
Evonik ■ and HZG ◯ used samples with ethanol as solvent (sampling at 40 bar).

Figure 4: Comparison of analytic results from retention measurements with the PDMS membrane and PuraMem® S600

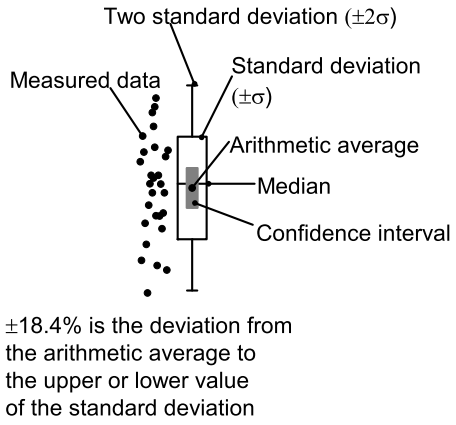
The fluxes (Figure 5a) for toluene are much higher than for the polar solvent ethanol. Highest fluxes with few scattering were measured for the PDMS membrane. The mean could be found at $90.5\,\mathrm{L\,m^{-2}\,h^{-1}}$ and the corresponding confidence interval is close to this value with $\pm 3.1\,\mathrm{L\,m^{-2}\,h^{-1}}$. The standard deviation has limits at $\pm 7.3\,\%$ of the mean. The results from the flux measurements with the PuraMem® S600 membrane show wider scattering with an arithmetic average of $64.9\,\mathrm{L\,m^{-2}\,h^{-1}}$. However, the breadth of

the 1σ interval is $\pm 13.4\,\%$ of the mean and the measured data shows that only single higher and lower values lead to the comparative high deviation. The precision around the estimated mean value amounts to $\pm 3.8\,\mathrm{L\,m^{-2}\,h^{-1}}$.

The toluene fluxes correspond to the expectations of the manufacturers. The higher fluxes through the PDMS membrane compared to those through the PuraMem® S600 membrane can be attributed to the structure and material of the membranes. The selective layer of the PDMS membrane consists of radiationally crosslinked PDMS with a thickness of $2\,\mu\mathrm{m}$ [46]. The high toluene fluxes were expected due to the small distance of the total Hansen Solubility Parameters (HSP) according to [16] ($|\delta_{Membrane} - \delta_{Solvent}| = 2.73\ MPa^{0.5}$ with $\delta_{Membrane} = 15.57\ MPa^{0.5}$ for PDMS). The coated silicone-based layer of the PuraMem® S600 membrane



(a) Box plot and data points of pure solvent fluxes of toluene (left) and ethanol (right) at 30 bar transmembrane pressure and 25 °C.



(b) Meaning behind the symbols, boxes, whiskers and numbers of the box plots.

Figure 5: Results of pure solvent flux measurements illustrated as box plot.

is thin and supported by a polyimide structure. This supporting structure is much more polar than PDMS and seems to have an inhibitory effect on the nonpolar solvent. Accordingly, no flux measurement through the cross-linked polyimide-based membranes DuraMem® 300 or DuraMem® 200 with toluene was possible.

Fluxes of ethanol are mostly around or below $10\,\mathrm{L\,m^{-2}\,h^{-1}}$. The lowest fluxes were measured with the PDMS membrane and the PuraMem® S600 membrane with mean values at $4.9\,\mathrm{L\,m^{-2}\,h^{-1}}$ and $8.2\,\mathrm{L\,m^{-2}\,h^{-1}}$, respectively. The limits of their 1σ intervals are around $\pm 15.2\,\%$ and $\pm 18.4\,\%$. Results from the confidence interval calculation show a difference from the mean value of $\pm 0.3\,\mathrm{L\,m^{-2}\,h^{-1}}$ for PDMS membrane and $\pm 0.6\,\mathrm{L\,m^{-2}\,h^{-1}}$ for PuraMem® S600 membrane. There is a remarkable deviation in the flux values of the DuraMem® 300 membrane. The reason for it is most likely the higher porosity of the membrane and its natural deviation from the production process. The standard deviation interval is $\pm 18.3\,\%$ of the mean which is $21.1\,\mathrm{L\,m^{-2}\,h^{-1}}$. For this case, the confidence interval was determined at $\pm 2.1\,\mathrm{L\,m^{-2}\,h^{-1}}$. The measurements with the DuraMem® 200 membrane resulted in a mean value of $8.5\,\mathrm{L\,m^{-2}\,h^{-1}}$ and a confidence interval of $\pm 0.4\,\mathrm{L\,m^{-2}\,h^{-1}}$. The standard deviation has limits at $\pm 9.8\,\%$ of the mean. For all membranes the median is close to the mean. The highest differences are $-1.1\,\mathrm{L\,m^{-2}\,h^{-1}}$ for toluene flux through the PuraMem® S600 membrane and $-0.7\,\mathrm{L\,m^{-2}\,h^{-1}}$ for ethanol flux through the DuraMem® 300 membrane.

Furthermore, Figure 5a shows referring to the measurements in ethanol with the PuraMem® S600 membrane more data points than for the other measurements. The reason is testings about a reasonable size of the database.

For the membrane were additional measurements conducted, so the number of data points rises from 19 to 28. The arithmetic mean value changed slightly (from $8.3\,\mathrm{L\,m^{-2}\,h^{-1}}$ to $8.2\,\mathrm{L\,m^{-2}\,h^{-1}}$). The initial 1σ interval decreased as expected from ca. $\pm 18.6\,\%$ to $\pm 15.2\,\%$. The additional measurements show the dependency of the data gathered on the number of samples. It is evident that the chosen number of samples is sufficient. On the one hand it is high enough to calculate reasonable standard deviations and confidence intervals. On the other hand it is small enough to avoid inefficiency and insignificant interval ranges.

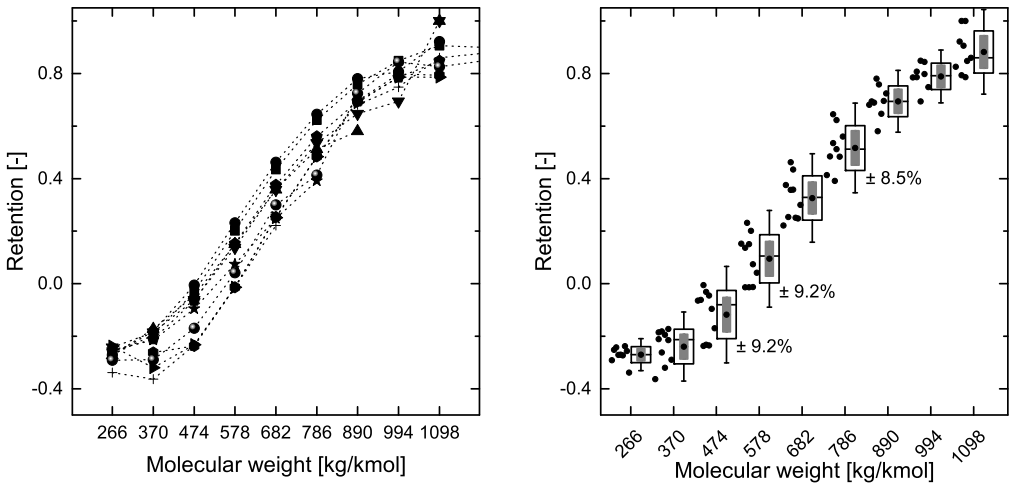
The fluxes of ethanol through the membranes match the expectations of the manufacturers. The fluxes are significantly lower, depending on the material of the active membrane layer. As a second factor, the degree of cross-linking and thus the tightness of the membrane is essential. It is challenging for polar substances, such as ethanol, to permeate through the two nonpolar silicone-based membranes. This low permeation results in the lowest fluxes for the PDMS membrane and only slightly higher values for the coated PuraMem® S600 membrane. In contrast to the flux measurements with toluene, the polyimide substructure of the PuraMem® S600 membrane allows a higher liquid flux for ethanol.

Besides, it is interesting to note that the flux through the PuraMem® S600 membrane corresponds approximately to that through the DuraMem® 200 membrane. According to the manufacturer, the DuraMem® 200 membrane has a lower MWCO than the PuraMem® S600. It is evident that the silicone-based coating (active membrane layer) appropriately hinders the permeation of the polar solvent, since the supporting structure of the PuraMem® S600

membrane (produced of the same material as the DuraMem® 200) is less cross-linked and, therefore, consists of a more open structure.

The observed standard deviations of the measured flux values show that distinct differences can occur in the measurements, despite the standardized procedure. These differences can be observed especially for pure solvent fluxes. However, the differences also confirm the experience of the membrane manufacturers. As already mentioned for the DuraMem® 300, one possible origin of the deviations are the production tolerances that occur within a batch. It should also be remembered that the membranes in laboratory plants have a much smaller surface area. The membrane sample can only show an average value corresponding to the large production batches or modules if they either represent precisely the average of the batch or are measured in sufficient numbers. The low confidence intervals in combination with the close range of median and arithmetic mean demonstrate that the results provide highly precise information on flux averages. This study is unique in that the measurements were carried out at different times in different institutions. The comparison between measurements of laboratory size membranes and industrial membrane modules is an interesting topic for future work.

The summary is based on 136 measurement data points, whereby 12 outliers were excluded. The breadths of all 1σ intervals are lower than $\pm 20\,\%$. Also, the mean values were estimated with a high precision. The results verify the reliability of the proposed standard experimental procedure for flux measurements.



(a) Array of all measured retention curves from the round robin test with polystyrene oligomers in ethanol with the PDMS membrane. A different symbol is used for each measurement series. Obvious outliers are removed.

(b) Box plot and measured data points from the round robin test with polystyrene oligomers in ethanol with the PDMS membrane.

Figure 6: Results from the round robin test with the PDMS membrane and polystyrene in ethanol at 30 bar transmembrane pressure and 25 °C.

5.3. Retention measurement

To visualize the retention measurements, we depict the results of the round robin tests in two ways (Figure 6). Figure 6a shows the array of retention curves for this test system, whereby the outliers are already excluded. The outliers were identified only with the help of the regular retention curves (the points were laying clearly outside of the curve). These outliers could also have an analytical background as previously shown in Figure 4. Only six outliers out of 90 data points were identified for the system PDMS membrane-ethanol-polystyrene. The results can therefore be seen as representative. The

curves are forming a belt, starting with a negative retention for the smaller molecules and ending with a retention of above 90 % for the bigger styrene oligomers, as expected. The experimental data points for the retention of each styrene (different molecular weight) adhere to a normal distribution, with the exception of the high retention values of large oligomers (R>97 %), due to the upper limit of 100 % retention. Consequently, outliers for such molecular weights are irrelevant for the results evaluation too.

The second depiction (Figure 6b) displays the relevant retention of the different oligomers (different molecular weight) in box plots similar to Figure 5b. In such diagrams, it is easier to visualize the distribution of the results. Figure 6b shows exemplary the box plots for the PDMS-membrane in ethanol, Figure 7 shows the plots for the DuraMem® 300 membrane also in ethanol and Figure 8 shows the plots for the PuraMem® S600 membrane in toluene.

The values on the horizontal axis are the molecular weights from the single styrene oligomers. They could be identified analytically with $266\,\mathrm{kg\,kmol^{-1}} + \mathrm{n} \cdot 104\,\mathrm{kg\,kmol^{-1}}$. The boxes positions are following the retention curves. While the boxes from the system PDMS membrane-ethanol-polystyrene show the described increase of retention with increasing molecular weight of the oligomers, the boxes of the system DuraMem® 300 membrane-ethanol-polystyrene form a horizontal line above 90 % retention (Figure 7). Fewer oligomers could be considered in this system because of the proximity to the retention limit and the smaller MWCO in this solvent-solute combination. The system PuraMem® S600 membrane-ethanol-polystyrene (not depicted) behaved similarly as the system PDMS membrane-ethanol-polystyrene. The results

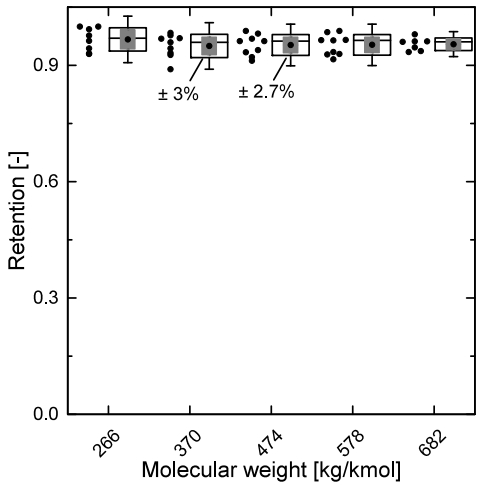


Figure 7: Box plot and data points of retention values from the round robin test with the DuraMem® 300 and polystyrene in ethanol at 30 bar transmembrane pressure and 25 °C.

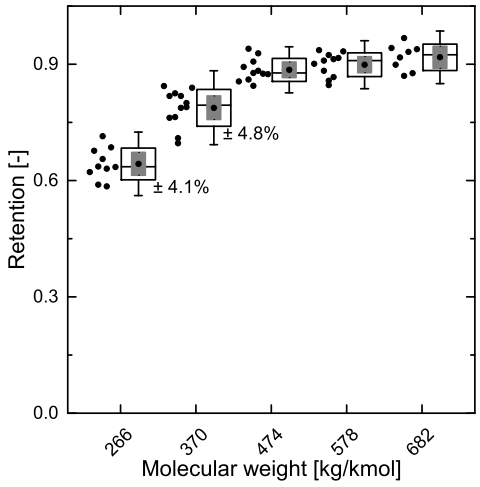


Figure 8: Box plot and data points of retention values from the round robin test with the PuraMem® S600 and polystyrene in toluene at 30 bar transmembrane pressure and 25 °C.

from the PuraMem® S600 membrane-toluene-polystyrene experiments (Figure 8) shows boxes positions from characteristic retention curves as well. The increase of the retention values for the different styrene oligomers is more gradual as 60 % retention was already achieved for the smallest styrene oligomer. In this case, the system PDMS membrane-toluene-polystyrene (not depicted) behaved similarly. The retention values in all these systems were affected by the different pressure level only slightly. Changes primary occurred for the lower retention values. Positive retention values increased by increasing pressure while negative retention values decreased by increasing pressure. Regarding the scattering of the data points, no tendency could be mentioned. At first glance, the measurements seem to be comparable.

The results prove the good applicability of the developed standard testing procedure. All 1σ intervals have a low absolute range. The highest breadth is $\pm 9.2\,\%$ of the mean value at the test system PDMS membrane-ethanol. Even with Figure 9 it becomes apparent that all measured curves are within or close to the calculated confidence intervals. The intervals are drawn as retention curves and superimposed on the array of measured data. Thus, it shows in another way the precision of the results and the quality of a standardized experimental procedure.

The measured retentions are in line with the expectations of the membrane manufacturers. The results show that the gradient of the retention curves is dependent on the membrane for low molecular weight solutes. Oligomers with a higher molecular weight can only permeate to a small extent because of their high diffusion coefficients. The gradient at low molecular weights is highest in both toluene and ethanol for the PDMS membrane and

lowest for DuraMem® 300 membrane in ethanol. Here the interactions between membrane, solute and solvent are the major factors.

The nonpolar polystyrenes dissolve and permeate preferably through nonpolar membranes. However, increasing numbers of polar groups in a membrane, such as the DuraMem® 300 membrane, lead to a stronger permeation barrier. Concurrently, the nonpolar solutes can interact less with the polar ethanol than with the nonpolar toluene. These effects result in very high retentions even for low molecular weight oligomers using the DuraMem® 300 membrane. The high retentions are also supported by the dense membrane structure indicated in the manufacturers' MWCO specification.

The PDMS membrane, on the other hand, impedes permeation of the solvent ethanol rather than of the polystyrene. This preferential permeation leads to negative retentions for the low molecular weights. With increasing molecular weight, the steric effect of the molecules increases and leads to an increase in retention. Since a gradual increase can also be observed in toluene, it can be assumed that the steric factors of the molecules are dominant. This conclusion also corresponds to the statement from Thiermeyer et al. [46].

The polystyrenes have a high affinity to the PuraMem® S600 membrane due to the nonpolar coating. However, the affinity is weakened by the supporting structure. The same applies for the solvent toluene as described for the pure solvent fluxes. Therefore, toluene also provides higher retention for polystyrene oligomers with a lower molecular weight using the PuraMem® S600 membrane compared to the PDMS membrane. Similar to this membrane, the importance of steric effects increases with increasing

molecule size. In ethanol, it is contrary for the solvent, and the nonpolar silicone-based layer hinders the flux through the membrane. These measurements showed negative retentions which were also observed for the PDMS membrane.

From the statistical evaluation, it can be seen that the results show less deviations compared to the pure solvent fluxes. The standard deviation is low and the distance between median and arithmetic mean is small. The low confidence intervals demonstrate that the standardized procedure produces precise estimates of the mean value. Accordingly, it can be assumed that similar results will be achieved with retention measurements using the standardized procedure. Meaning that a few measurements per solute are sufficient for the characterization of a new membrane.

The retention results from the bilateral cooperative tests (performed parallel by two contributors) were compared directly for each molecular weight. Since there were only four data points for the retention of each solute, confidence intervals were not considered and no standard deviations were calculated. Figure 10 shows the retention of alkanes and SOA as well as PMMA in different solvents.

The depicted retention curves of alkanes and SOA were results from measurements with the PDMS membrane. In isopropyl alcohol (IPA) and ethyl acetate (ESTP) negative retention occur. With increasing molecular weight, the retention values decrease in the polar solvent IPA, whereas increase in the moderate polar solvent ESTP. As mentioned above, such negative retentions were also observed in some measurements with styrene oligomers. In the nonpolar solvent n-heptane, the measurements with alkanes resulted in

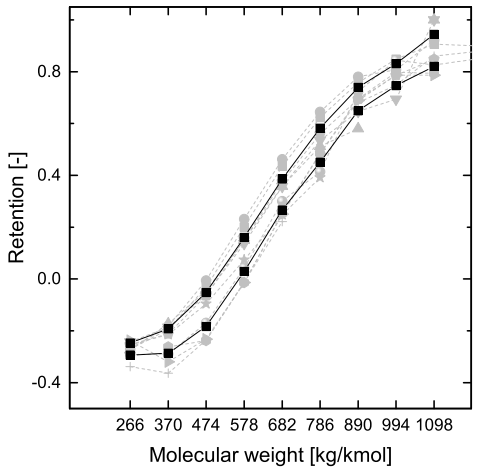
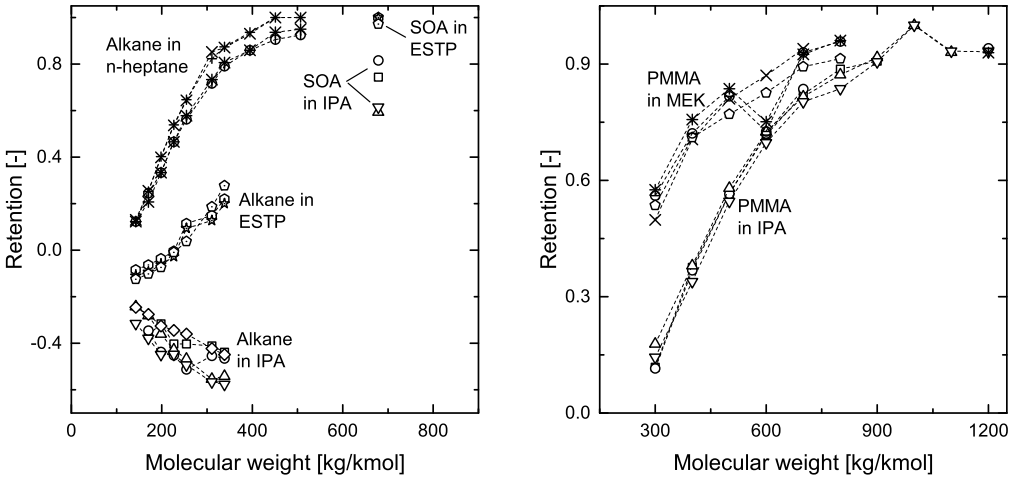


Figure 9: Calculated confidence intervals (■) drawn as retention curves. They are superimposed on the array of measured retention curves from the round robin test with the PDMS membrane and polystyrene in ethanol at 30 bar transmembrane pressure and 25 °C. A different symbol is used for each measurement series.

only positive values as common retention curves. Affinity effects established with solubility parameter could give an explanation about this behaviour. Similar measurements and results were presented in Postel et al. [16]. SOA is a more complex branched molecule with a higher molecular weight than the alkanes. Consequently, it can be argued that the diffusion coefficient is high compared to that of the alkanes. Furthermore, SOA is a moderately polar solute with a high acceptance for hydrogen bonds due to its excellent water solubility and the bounded oxygen. This polarity leads to the assumption of a high Hansen Solubility Parameter. For that reason a low affinity to the nonpolar PDMS membrane is expected. In this combination, similar to the polyethylene glycol retention in Postel et al. [16], the size exclusion is dominant for retention in IPA and ESTP (SOA is not soluble in n-heptane).

The retention measurements of PMMA oligomers with PuraMem® S600 membranes (Figure 10b) results in common retention curves. The measurements with the combination butanone (MEK) and PMMA results in higher retention values than the measurements with the combination IPA and PMMA. Such lower retention values in IPA could also lead back to affinity effects, since the active layer of the PuraMem® S600 membrane is silicon based as the PDMS membrane.

The curves in both diagrams are not corrected and the plausible outliers are easily recognizable (retention curves of PMMA in butanone (MEK) or SOA in IPA). The total deviation in retention for each solute is, however, as



(a) Retention curves of alkane and SOA in various solvents at 30 bar transmembrane pressure and 25 °C for the PDMS membrane.

(b) Retention curves of PMMA in IPA and MEK at 30 bar transmembrane pressure and 25 °C for the PuraMem® S600 membrane.

Figure 10: Results from additional tests distributed to two contributors each. A different symbol is used for each measurement series.

low as the one in the round robin test. Most of the data points deviate by less than 10 % in total, and every deviation is in total less than ±15 % of the arithmetic average.

5.4. Case studies

Two different case studies were investigated using the superstructure optimization approach to elucidate the effect of uncertainties of flux and retention measurement on subsequent process design. In Case Study 1 a concentration of one component with a molecular weight of 474 kg kmol^{-1} solved in ethanol is assessed, considering the experimentally determined performance metrics of the DuraMem® 300 membrane and the mixture of ethanol with styrene oligomers. The flux across the membrane at 30 bar was determined to 21.052 L m^{-2} h^{-1} while the confidence interval was ±2.136 L m^{-2} h^{-1}. The retention for the styrene oligomer with a molecular weight of 474 kg kmol^{-1} was determined to 95.2 % ±2.1 %.

For the optimization a feed flowrate of 100 kg h^{-1}, a concentration from 0.05 g g^{-1} in the feed to 0.1 g g^{-1} in the final retentate and a solute recovery of at least 98 % was assumed.

Figure 11 shows three of the resulting optimal process structures, for exemplary samples within the experimentally determined confidence intervals. Depending on the selected case, significant differences in the necessary membrane area and the complexity of the process arise. While the high flux and retention values lead to a simple process in a single step, the process with the low values is much more complicated and not intuitive. The total feed is divided between a parallel module and a two-stage cascade. The permeate flow of the first stage is only partially used for the second cascade stage.

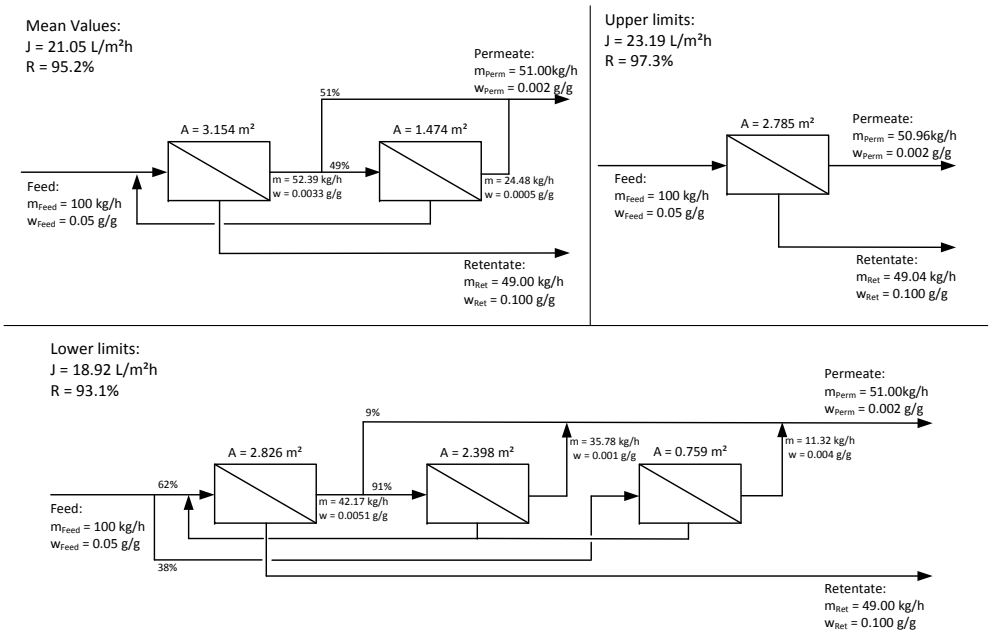


Figure 11: Case study 1: Three optimized process structures for different flux and retention combinations from the test system DuraMem® 300-ethanol-polystyrene (Mw = 474 kg kmol^{-1}) at 30 bar and 25 °C.

The retentate streams from the module operated in parallel and the second cascade stage are fed back to the feed of the cascade, before the first stage. Output streams from the process are the retentate stream from the first cascade stage and the combined permeate streams from all membrane modules. Overall nine different scenarios were evaluated, for which the supplemental file provides the performance metrics and the key structural results, regarding the number of required stages and overall membrane area.

As a second case study, a separation step of two solutes solved in ethanol was chosen. The solute size equals 474 kg kmol^{-1} and 1098 kg kmol^{-1}. The

smaller solute is assumed to be the product while the bigger solute represents an impurity. The feed contains $0.05\,\mathrm{g\,g^{-1}}$ of the product and $0.003\,\mathrm{g\,g^{-1}}$ of the impurity while the flow rate is set to $100\,\mathrm{kg\,h^{-1}}$. The final permeate needs to contain at least 98 % of the product, and the concentration of the impurity in the permeate needs to be lower than $0.001\,\mathrm{g\,g^{-1}}$. For this case study, the experimental values determined with the PDMS membrane and the mixture of ethanol with styrene oligomers are used. The flux was experimentally determined to be $4.925\,\mathrm{L\,m^{-2}\,h^{-1}}$ $\pm 0.331\,\mathrm{L\,m^{-2}\,h^{-1}}$ at 30 bar. The retention of the styrene oligomer with a molecular weight of $474\,\mathrm{kg\,kmol^{-1}}$ equals -11.8 % ± 6.6 % and the retention of the styrene oligomer with a molecular weight of $1098\,\mathrm{kg\,kmol^{-1}}$ equals 88.2 % ± 6.2 %.

Compared to the first case study the flux is much smaller, and additionally, the experimentally determined confidence intervals are broader. Overall 27 different combinations of flux and retentions were evaluated, all of which represent samples within the ranges of the experimentally determined confidence intervals. Three of the determined optimal process structures for the second case study are depict in Figure 12. This case study also shows clear differences in the necessary membrane area and the interconnection concepts. The value combination of high flux and retentions far from each other lead to a simple single-stage membrane process with a small membrane area. On the other hand, lower flux values and a narrower retention range between the individual solutes result in a substantially more complex two-stage process. In this process, the main feed is divided between the two stages, with part of the permeate from the first stage supplementing the feed of the second stage. The feed of the first stage is also fed with the retentate of the second stage.

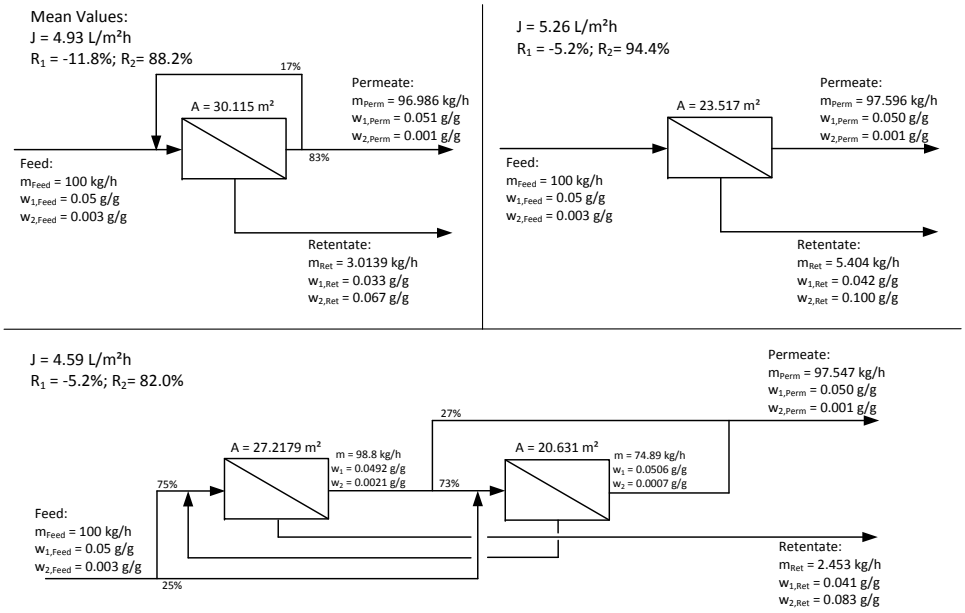


Figure 12: Case study 2: Three optimized process structures for different flux and retention combinations from the test system PDMS membrane-ethanol-polystyrene (Mw = 474 kg kmol^{-1} as product and 1098 kg kmol^{-1} as impurity) at 30 bar and 25 °C.

The output streams are the retentate of the first stage and a mixture of the permeates of the two stages. A summary of the results for the second case study is listed in the supplemental data.

Both case studies demonstrate the dependency of a subsequent process design on accurate information of the membrane performance. A consistent determination and reporting of the data quality, as indicated in the current study, is, therefore, an essential component for the further development and dissemination of OSN processes.

6. Conclusion

The data quality of results from membrane characterizations has never been stated as a basis for the OSN users. This uncertainty hinders the progress in finding one or more reasonable standard systems for OSN membrane characterization. Such standardized procedure can simplify the assessment of membrane performance and their applicability in real separation processes. As a result, the process design of a OSN plant in industrial scale would be less difficult and troublesome.

In this study, we demonstrate the reliability and reproducibility of a standardized experimental procedure to improve and accelerate process design for OSN applications. The procedure was applied with different test and analytical equipment, for several solvents, membranes, and solutes.

The results from the round robin test were statistically evaluated. The calculations for pure solvent flux and retention measurements demonstrate that the precision of the determined mean values from the experiments are high and the standard deviations reasonable. Therefore, the deviation of the data is low enough to permit the assumption of comparable results in future tests by using the standardized experimental procedure.

Using the statistically quantified information on the accuracy of the determined experimental flux and retention values, we further demonstrated the effect of these uncertainties on subsequent process design. The two investigated case studies confirmed the importance of an accurate assessment of data quality and accuracy. The standardized procedure for membrane characterization experiments should help to assess future results better and apply statistical methods. Then data from different sources and their relia-

bility can be used in optimal process design.

Further results with other test systems confirm the reliability of the method and emphasize the comparability of the obtained results.

Considering all results, we showed that the proposed standard experimental procedure, used in a conjunction with the categorized test systems, enable generating comparable and reliable membrane performance data. Prospectively, this procedure can become a standard to characterize OSN membranes and give credible performance information. Nevertheless, further investigation on this field is desirable. A development of heuristic method for membrane selection could promote and strengthen the method. Furthermore, it can help with its reliable results to reveal correlations in the complex solvent-solute-membrane system in future work.

Acknowledgment

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