

NEW EXPERIMENTAL MEASUREMENTS OF SOLVENT INDUCED SWELLING IN NANOFILTRATION MEMBRANES

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ABSTRACT

The paper describes developmental apparatus for *in-situ* determinations of membrane swelling and shows representative examples of the data that can be acquired. The apparatus principally comprises a linear inductive probe and electronic column gauge with an overall resolution of 0.1 μm which was used in two configurations to assess the swelling propensity of polyacrylonitrile (PAN)/polydimethylsiloxane (PDMS) nanofiltration membranes in a range of alkane, aromatic and alcohol solvents.

In the absence of an applied pressure on the membrane, experiments showed a maximum expansion for the PDMS layer of 169% using an n-heptane solvent whose solubility parameter (δ) was close to that of PDMS. With more polar solvents falling in the range $\delta = 23.6\text{-}29.2 \text{ MPa}^{0.5}$, swelling of the PDMS was much reduced (<14%) and comparable shrinkage of the PAN support layer was also observed. If a mechanical pressure was applied to the membrane then swelling was reduced. For example with a xylene solvent, over the pressure range 0-10 bar a progressive decline in membrane swelling from 118% to 50% was observed. At 20 bar swelling was further reduced to 33%. When xylene or heptane solvent was mixed with methanol, ethanol or propanol, reduced swelling of the PDMS layer occurred as the concentration of alcohol increased. The extent of swelling was closely related to the value of the mixture solubility parameter (δ_{mixture}) where a higher value of δ_{mixture} led to less swelling. The results of the swelling experiments are compared to some of the authors previously published results for crossflow nanofiltration and shown to support the salient features.

KEYWORDS

Membrane swelling; Nanofiltration; PDMS; Organic solvents

INTRODUCTION

Detailed knowledge of membrane properties is becoming increasingly important as nanofiltration matures into new areas of technology and researchers attempt to better understand the fundamentals. For example, the development of polymeric solvent resistant nanofiltration (SRNF) membranes has attracted much attention and enabled several potential applications in the processing of organic solvent streams [1-4]. Although precise transport mechanisms across the convection-diffusion spectrum are an ongoing topic of debate, it is generally accepted that polymer swelling plays a significant role in determining levels of flux and rejection [2,5,6].

Most previous efforts to quantify the swelling of nanofiltration membranes have followed the approach of Ho and Sirkar [7] whereby the weight difference between a dry and solvent impregnated polymer sample is determined. Stafie *et al.* [8] used the method with specially prepared 'thick films' of polydimethylsiloxane (PDMS) and measured swelling approaching 205% for hexane-solute (oil or PIB) systems. Vankelecom *et al.* [9] used 'slabs' of PDMS with t-butanol solvent to demonstrate 70% swelling in the unrestrained state, but only 29% swelling when a

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sample was clamped. The same authors also report that tetradecane solvent previously sorbed within PDMS could be removed using an applied 10 bar pressure and then restored in a reversible manner upon release of the pressure and re-immersion in the solvent. Yoo *et al.* [10] used four variants of hydroxyl-terminated PDMS in the form of 20 mm x 10 mm x 1.5 mm blocks to measure swelling in the presence of pure solvents as well as binary and ternary mixtures. Of most relevance are the data for pure n-hexane, n-heptane and cyclohexane solvents where swelling ratios in the region of 4 were noted (i.e. ~300 % expansion). Geens *et al.* [11] also showed significant swelling with a range of solvents where prior to testing the selective top layer from three hydrophilic polymer membranes was removed using liquid nitrogen. In contrast, Piccinini *et al.* [12] describe an alternative, and relatively complex, technique where a quartz spring microbalance was used to simultaneously measure solubility, diffusion coefficient and swelling for a solvent/polymer combination of acetonitrile/polyetherurethane.

The current authors have taken an approach to determinations of swelling that does not require the weighing of a sample. A commercially available inductive probe was used to directly measure the lateral swelling of PDMS layers on composite membranes both with and without an imposed pressure.

EXPERIMENTAL

Membrane and Solvents

All swelling experiments used samples of a flat sheet polyacrylonitrile (PAN)/PDMS composite membrane supplied by GKSS Forschungszentrum (see Figure 1). The PAN substrate had a quoted thickness of 40 μm , although SEM micrographs suggested a manufacturing tolerance of up to $\pm 10\%$. Membranes with a nominal PDMS layer thickness of 10 μm were available to the authors. The hydrophobic PDMS, which achieves the separation in SRNF, was radiation crosslinked during manufacture and a typical sample exhibited a thickness tolerance of $\pm 0.5 \mu\text{m}$ as determined by SEM. The radiation crosslinking precluded the use of a conventional gravimetric method for swelling determination as a block of PDMS treated in such a way would not exhibit the same degree of crosslinking as a thin PDMS layer from a composite membrane.

The solvents shown in Table 1 were used in the swelling experiments. These are representative of the alkane, aromatic and alcohol solvents that some of the authors have previously investigated in SRNF experiments [13-15] and span a range of polarity, and thus potential swelling capability, as evidenced by the quoted solubility parameter (δ). In many cases a solvent was used in its pure state, however, for a smaller number of experiments appropriately proportioned mixtures of alcohol with either xylene or heptane were generated. All solvents had initial purities in excess of 99% and were obtained from Sigma-Aldrich, Fisher Scientific or Shell Global Solutions.

Apparatus and Procedure

Membrane swelling was determined using the apparatus shown schematically in Figures 2(a) and 2(b). Referring to Figure 2(a), in an experiment with no applied pressure, a 2 cm x 2 cm square of PAN or composite membrane was placed in a short, flat-bottomed, round dish. A 10 mm diameter spacer was placed on top of this sample to prevent direct, and potentially sensor damaging, contact between the measurement probe and the subsequently introduced solvent. The extent of swelling was determined using a freshly calibrated Mahr P2004 M inductive probe connected to a Millitron S1840 electronic column gauge; this arrangement essentially comprises a sensitive dial comparator and is more normally used by metrologists to determine the eccentricity of rotating components. The probe was rigidly mounted in a standard 820N, screw adjustable, comparator stand that was also able to accommodate the flat-bottomed dish. The probe/gauge combination had a manufacturer quoted resolution of 0.1 μm , a displacement range of 4 mm and required a force of 1 N to induce a detectable linear movement of the measurement tip. Whilst the probe

could be considered to impose a small pressure on a sample this was taken to be negligible for the current purpose.

Referring to Figure 2(b), using a modified apparatus comprising of an additional support frame and a cantilever bar that pivoted about a bearing mount in one end, it was possible to impose a pressure upon a test sample. The cantilever bar was arranged to rest horizontally between the inductive probe and the spacer. By adjusting the distance between the sample and pivot, and/or adding weight to the free end of the cantilever bar, it was possible to vary the applied pressure and values up to 20 bar were investigated.

In a typical swelling experiment the pure PAN or composite membrane sample was mounted dry in the flat-bottomed dish, the requisite spacer was positioned and, if necessary, a pressure was imposed by adding weight to the cantilever bar*. The measurement probe was then lowered to contact either the top of the spacer or the cantilever bar. With the probe reset to zero, 5-10 ml of solvent was quickly added to the dish to completely immerse the sample whence swelling started immediately. Sixty seconds was typically allowed for a sample to reach an equilibrium thickness in the solvent(s) before the final displacement measurement was taken; preliminary experiments showed that a time of 5-10 s was required in the absence of any imposed pressure. When mixtures of solvents were investigated it was necessary to shroud the measurement area in order to minimise changes in composition by component evaporation. As only a limited supply of membrane was available to the authors it was necessary to re-use some of the tested samples that had not been previously exposed to an applied pressure. Following an experiment, such membranes were vacuum dried for 30 minutes to remove any residual solvent and then left overnight to re-acclimatise to atmospheric conditions. In this way membranes were restored to their original state, as evidenced by repeat swelling experiments under otherwise identical conditions.

RESULTS AND DISCUSSION

Experiments were performed to assess the capability and limitations of the new apparatus by determining the swelling of PAN and the PAN/PDMS composite membrane in both pure solvents and mixtures of solvents. In all cases repeat measurements were required to give a level of data consistency. For the PAN substrate alone, at least 4 repeats were performed whereas with the PAN/PDMS composite this was raised to at least 9 repeats for all the data reported in Figures 3-7. When evaluating swelling of the PDMS layer in a composite membrane it was assumed that dimension changes in the PAN layer were the same as determined in a corresponding experiment with the PAN alone. The test samples, as assessed by visual inspection at the end of an experiment, were completely wetted.

Pure Solvents

Table 1 presents typical results of experiments with no applied pressure using the apparatus shown schematically in Figure 2(a). The data demonstrate the ability of the apparatus to quantify swelling and comprise average values for sample expansion/shrinkage and respective standard deviations for the displacement measurements; the latter are also representative of the ranges obtained in all experiments.

When the PAN backing alone was tested, with low polarity solvents such as n-heptane and xylene there was no change in lateral dimension. However, with higher polarity (alcohol) solvents some shrinkage was observed, the extent of which was seemingly dictated by the solubility parameter (δ)

* When an additional pressure was applied via the cantilever bar/weight system a typical sample would compress in the absence of solvent. In an experiment this compression was allowed to continue to equilibrium before solvent was introduced; the duration could be up to 10 minutes.

of the solvent once a threshold value of δ had been exceeded. Experiments using the PAN/PDMS composite showed appreciable swelling with all tested solvents. For low polarity solvents the extent of swelling was exclusively dictated by expansion of the PDMS layer, whereas with the highest polarity solvents shrinkage of the PAN layer became progressively more comparable to expansion of the PDMS layer.

It is worth noting that measurements with the PAN/PDMS composite membrane were generally more difficult to perform consistently, and potentially influenced by two factors. Firstly, for a given experiment sequence, e.g. with one pure solvent, ten distinct membrane samples were typically chosen at random in order to facilitate repeat measurements. Secondly, a limitation of the new technique is that only displacement from a starting point (i.e. the non-swollen state) can be measured rather than absolute sample thickness during swelling. Bearing in mind the variability in PAN thickness and the PDMS thickness imparted to a membrane during manufacture, these two factors combine to introduce scatter to a measured value. In some cases the standard deviation in measurements was significant compared to the average value, and for methanol in particular sufficiently large to render the absolute result unreliable at this stage of apparatus development.

Although the results presented in Table 1 and Figures 3-7 should be viewed within the context of overall accuracy, the standard deviations of measurements appear to be comparable to those reported by Stafie *et al.* [8] using the Ho and Sirkar method [7] and demonstrate the potential of the new technique for membrane characterisation. Moreover, the new method offers several advantages including the ability to test membranes in their manufactured state, in a variety of physical arrangements (e.g. clamped, with/without imposed pressure) and the potential to determine transient measurements of swelling (e.g. as solvent progressively wets a membrane or as solvent composition is altered).

The relationship between δ and swelling of the PDMS membrane layer is plotted in Figure 3. For solvents with δ values in the range 14.3-15.3 MPa^{0.5}, the average expansion of the PDMS layer increased from 148% to 169% where the latter represents the peak value. Over the region $\delta = 15.3-23.6$ MPa^{0.5} the solvent polarity increases to induce progressively less swelling in the PDMS layer and for i-propanol the average expansion was limited to 14%. At values of δ greater than 23.6 MPa^{0.5} the membrane swelling was reduced still further, although reliable absolute values were difficult to determine. The peak in membrane swelling that occurred in the region $\delta \approx 15.3$ MPa^{0.5} corresponds favourably with the literature reported value of solubility parameter for PDMS at $\delta = 15.5$ MPa^{0.5}. In some of the authors previous works with low polarity systems, maximum solvent fluxes and minimum solute rejections were reported for the GKSS membrane when δ_{solvent} was similar to δ_{PDMS} and their data suggest that the relationship of these two parameters closely follows swelling propensity over the region $\delta = 14.3-18.2$ MPa^{0.5} [13-15].

Whilst a direct comparison of the authors results with those in the open literature is difficult due to limited availability and knowing the extent of crosslinking in a particular PDMS sample, when data for n-heptane, cyclohexane and n-hexane are compared with independent measurements then a potentially interesting observation can be made. For the three solvents, Yoo *et al.* [10] report PDMS swellings in the region of 260-310% which are significantly greater than the corresponding values shown in Table 1 (158-169%). Stafie *et al.* report PDMS swelling in pure hexane of ~205%, again well above the 164% recorded by the authors. Whilst these workers crosslinked their block PDMS samples thermally, and thus the degree of crosslinking is likely to differ from that exhibited by the GKSS membrane, the possibility that swelling is hindered by the presence of a backing cannot be excluded. It was not feasible to test the PDMS from the GKSS membrane in isolation for the reasons already described, however, if the backing does impair swelling, which the authors results suggest, then the Ho and Sirkar method [7] for swelling determination may not give representative values for a membrane comprising two or more different polymers.

Figure 4 shows swelling data for pure xylene and n-heptane solvents obtained over the pressure range 0-20 bar with the apparatus shown in Figure 2(b). As could be expected from Figure 3, n-

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heptane swelled the PDMS layer to a greater extent than xylene and the differences in expansion were more evident at low pressures, say 0-2 bar. At pressures higher than 5 bar such differences were less pronounced. Although average values for n-heptane were always above those for xylene, the measurement standard deviations were sufficiently large to view the results with caution. For example, at 15 bar the average expansion and standard deviation for n-heptane were 4.7 μm and 0.9 μm respectively whereas with xylene the corresponding values were 3.8 μm and 0.6 μm . It is clear, however, that swelling propensity with both solvents followed a similar form as pressure was increased. The degree of swelling was apparently affected from the onset with pressure and there was greater effect on swelling from (say) 0-10 bar than over the range 10-20 bar. This result is perhaps to be expected as polymer chains in the PDMS come ever closer together, however, the change in swelling with pressure is interesting in the wider context.

Several researchers have reported increasing solute rejection at raised pressures [3,4,8,16], and some have taken this to be indicative of a solution-diffusion transport mechanism [17]. Other workers have reported non-linear solvent flux/pressure relationships that deviate from Darcy's Law [18-20] and some have attributed deviations to membrane compaction [18]. In crossflow nanofiltration experiments with the GKSS membrane, the authors also showed improved rejection with pressure for a number of solvent/solute systems, however this was not accompanied by a declining flux and the solvent-flux relationships remained linear up to the maximum tested 20 bar. It is interesting that simultaneous with an increasing pressure, membrane compaction and increasing rejection a linear flux-pressure relationship in accordance with Darcy's Law can exist. The authors have suggested that the polymer chains move further apart during swelling to allow a greater free volume in the membrane structure thereby promoting higher convective flows and lower rejections [13-15]; evidence for the rearrangement of PDMS membrane structure has been previously reported by van der Bruggen [21]. When the pressure is raised the subsequent reduction in free volume, which can also be interpreted as a tightening of a non-regular pore structure, naturally brings polymer chains closer together again to enhance rejection by a size exclusion mechanism. For this to happen simultaneously with a linear flux-pressure relationship, the free volume/flow paths in the PDMS would have to remain sufficiently large so as not to adversely affect flow. Whilst such a scenario, and any other, is conjecture with the current level of knowledge the situation is undoubtedly complex and the link between inherent membrane properties, swelling, flux and rejection will tax researchers for some time to come.

Mixtures of Solvents

The influence of solvent mixtures on the swelling of the PDMS membrane layer with no applied pressure is presented in Figures 5 and 6. Figure 5 shows the effect of varying the amount of ethanol in either a xylene/ethanol or n-heptane/ethanol mixture. It is apparent that the mixture containing n-heptane swelled PDMS to the greatest extent throughout the entire range of mixture composition, which reflects the findings presented in Figure 4 (i.e. n-heptane has a δ value closer to PDMS than xylene). The data indicate that swelling decreased as the amount of ethanol in the mixture was increased which is to be expected given that $\delta_{\text{ethanol}} > (\delta_{\text{xylene}} \text{ and } \delta_{\text{n-heptane}})$ and the swelling propensity of PDMS is relatively low in pure ethanol (see also Figure 3). The data also possibly suggest that a threshold amount of ethanol may be required to significantly alter swelling of the PDMS layer. Although caution should be exercised, up to 20 %w/w ethanol may be required to bring about a more rapid change with xylene whilst the threshold for n-heptane appears to be lower and in the region of 10% w/w. The data in Figure 5 are broadly in-line with those of Yoo *et al.* [10] for a n-hexane/ethanol/PDMS system, as are those in Figure 6.

Figure 6 presents swelling results for xylene mixtures with the homologous series of methanol, ethanol or n-propanol solvents. Each combination of xylene/alcohol follows a similar form and it is tempting to show a single correlation for all the data. On the basis of solubility parameter alone, $\delta_{\text{methanol}} > \delta_{\text{ethanol}} > \delta_{\text{n-propanol}}$ and greater swelling of the PDMS would be expected with n-propanol. Although some scatter is present, the swelling values measured for n-propanol are generally above those for methanol across much of the spectrum of concentration and ethanol falls somewhere

between these two. With n-propanol, there is also more evidence to suggest that a threshold level of alcohol may be required to influence PDMS swelling (c.f. Figure 5). The inference from the overall dataset is that the type of alcohol has a relatively minor effect on the swelling of PDMS when a good swelling solvent such as xylene is present, however, it cannot be excluded that even small differences in swelling could significantly effect transport of alcohol during nanofiltration. It is noted that the differences between alcohol types were more emphasised when the values of PDMS expansion from Figure 6 were plotted against solubility parameter calculated by $\delta_{mixture} = \sum V_i \delta_i$ where V_i and δ_i are the component volume fraction and solubility parameter respectively. For a given value of $\delta_{mixture}$, and particularly at alcohol concentrations >50% w/w, methanol showed the greatest swelling followed in sequence by ethanol and n-propanol; limited tests with i-propanol showed even further reduced swelling for a given $\delta_{mixture}$.

For completeness, Figure 7 shows swelling data for two xylene/ethanol mixtures over the pressure range 0-20 bar. Similar to Figure 4, the swelling propensity of the PDMS was affected immediately that pressure was applied and the change progressively lessened at higher pressures. The greatest swelling occurred with pure xylene over the entire range of tested pressures and reduced as the amount of ethanol in the mixture increased as a consequence of the raised mixture polarity.

CONCLUSIONS

A new apparatus for characterising nanofiltration membranes has been described and data representative of its capability have been shown. Although the approach is still being developed, particularly for determinations with thinner membranes, the initial results are sufficiently encouraging to warrant further investigations. There will always be inherent difficulties in taking reliable swelling measurements for the small dimensions characteristic of SRNF membranes. However, in the authors opinion, the new method offers several potential advantages over the more conventional approach. These include the ability to make transient measurements of swelling and the possibility of relating swelling propensity to filtration performance over a more significant and wider range of conditions.

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TABLES AND FIGURES

Solvent	Hildebrand solubility parameter (δ , MPa ^{0.5})	Expansion PAN alone (μm) [*]	Expansion of 10 μm PDMS + PAN (μm) ^{**}
i-octane	14.3	0	14.8 (0.82)
i-hexane	14.7	0	16.0 (1.59)
n-hexane	14.9	0	16.4 (1.59)
n-heptane	15.3	0	16.9 (1.80)
cyclohexane	16.8	0	15.8 (0.95)
xylene	18.2	0	11.9 (0.94)
i-propanol	23.6	-0.1	1.40 (0.30)
n-propanol	24.9	-0.2 (0)	1.24 (0.34)
ethanol	26.5	-0.24 (0.09)	0.75 (0.26)
methanol	29.2	-0.64 (0.09)	0.07 (0.30)

At least: * 4 measurements; ** 9 measurements

Table 1: Lateral expansion (swelling) of PAN and PDMS/PAN composite membranes in pure solvents with zero applied pressure; standard deviation of measurements are shown in brackets.

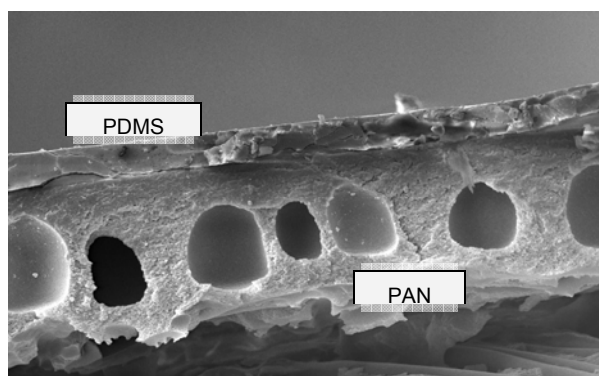


Figure 1: SEM micrograph of a composite PAN/PDMS membrane.

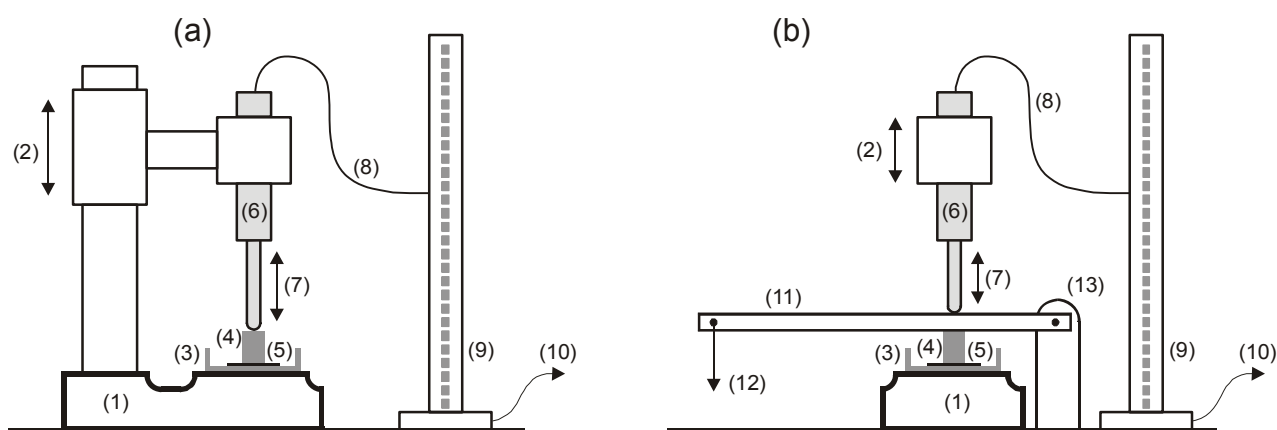


Figure 2: Schematics of apparatus for measurements of membrane swelling (a) no applied pressure (b) with applied pressure. *Legend:* (1) comparator stand; (2) overall height adjustment via screw adjustment; (3) flat-bottomed round dish; (4) spacer; (5) membrane or substrate sample to be tested; (6) inductive probe; (7) measurement tip (linear movement); (8) connecting cable; (9) electronic gauge column; (10) optional interface to PC; (11) cantilever bar; (12) weight; (13) support frame and bearing mount for cantilever bar.

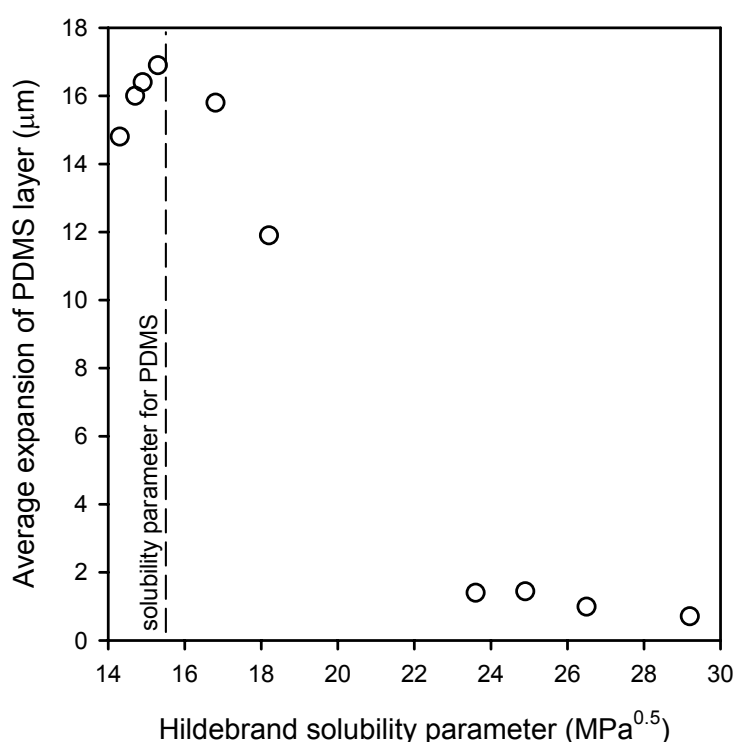


Figure 3: Swelling of the PDMS layer in a PAN/PDMS composite membrane as induced by pure solvents.

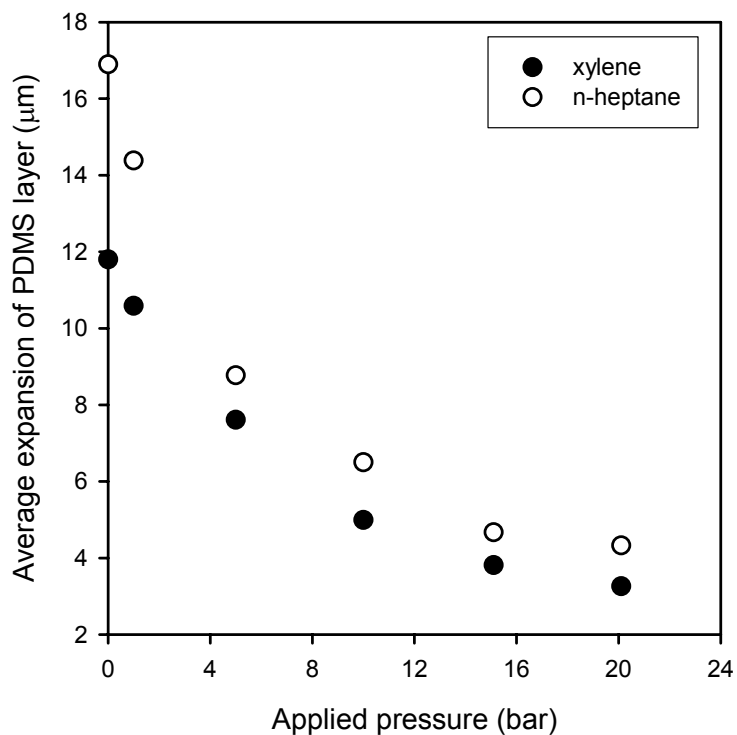


Figure 4: Swelling of the PDMS layer in a composite PDMS/PAN membrane for two pure solvents over a range of applied pressures.

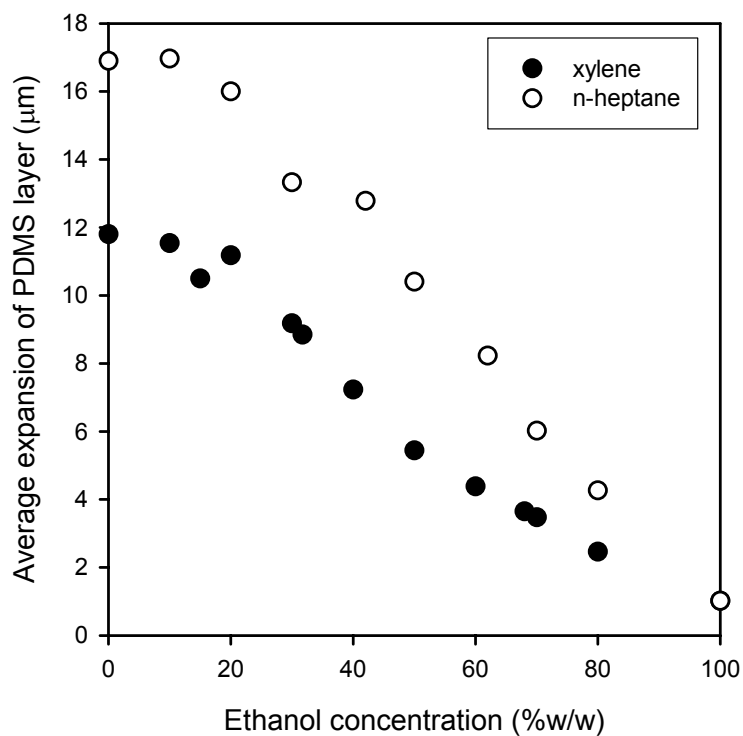


Figure 5: Swelling of the PDMS layer in a composite PDMS/PAN membrane for two alkyl solvent/ethanol mixtures.

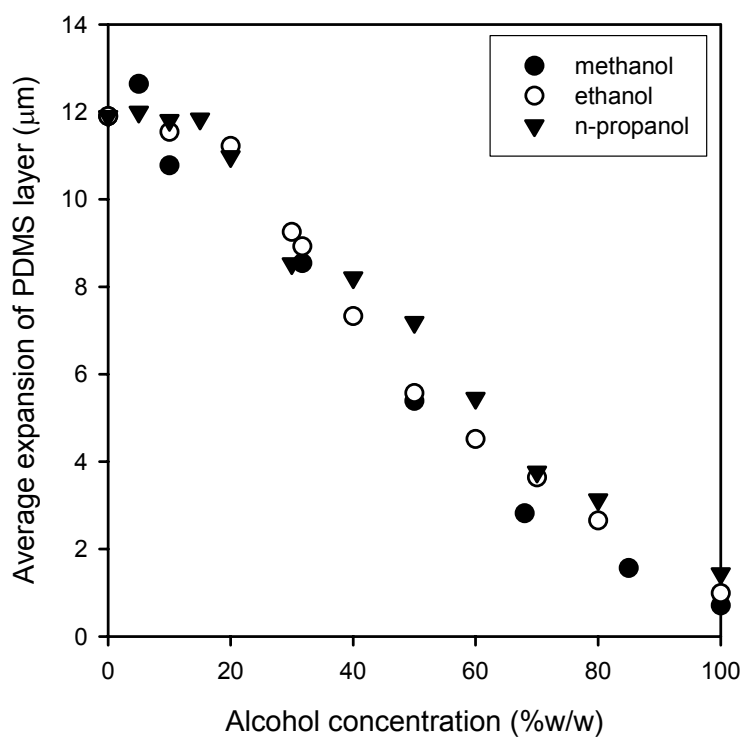


Figure 6: Swelling of the PDMS layer in a composite PDMS/PAN membrane with xylene/alcohol mixtures.

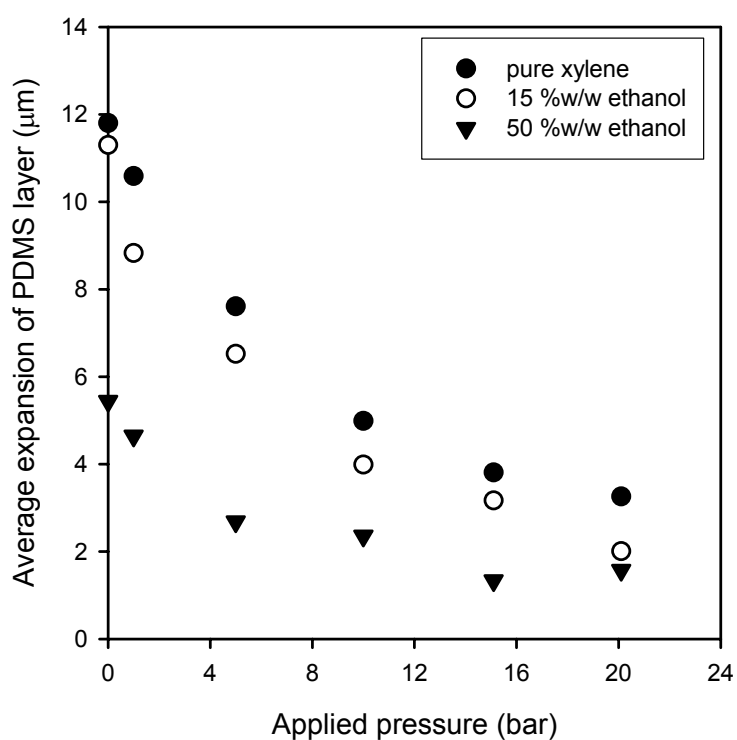


Figure 7: Swelling of the PDMS layer in a composite PDMS/PAN membrane for xylene/ethanol mixtures over a range of applied pressures.