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ORGANIC SOLVENT NANOFILTRATION TECHNOLOGY IN FUEL PROCESSING

E.S. Tarleton[1] (e.s.tarleton@lboro.ac.uk, www.stevetarleton.com) and J.P. Robinson[2]
[1]*Department of Chemical Engineering, Loughborough University, Loughborough, LE11 3TU, UK.*
[2]*now at School of Chemical and Environmental Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*

Traditionally, membrane nanofiltration has been largely confined to aqueous applications such as the treatment of drinking water and the removal of contaminants from effluent streams. In recent years a new generation of polymeric membrane materials has been developed which can process organic streams, in particular those similar in nature to common gasoline and diesel fuels.

By utilising a system of representative model compounds, this study explores the effectiveness of organic solvent nanofiltration (OSN) for fuel treatment, and highlights the prevalent permeation and separation mechanisms when poly(dimethylsiloxane) (PDMS) membranes are used to process non-polar and polar feed streams (including the alcohols found in biofuels). It is shown that membrane performance, e.g. solvent flux and solute rejection, is governed by both molecular size and polarity. Potential methods to tailor a membrane material to a specific application via crosslinking are also discussed.

INTRODUCTION

Nanofiltration (NF) is a process largely associated with the separation of nanometre size and/or charged species from aqueous systems, with examples ranging from the removal of pesticides from effluent water to the concentration of fruit juices. The suitability of ceramic membrane materials to perform separations in organic media has been studied by a number of workers, with titania, silica and zirconia identified as promising materials[1,2]. However, the large surface areas which can be required with ceramic nanofiltration membranes (of the order of several hundreds of square metres in some industrial applications) have lead many researchers to look towards polymeric NF membranes. Apart from the relative ease with which polymeric membranes with large surface areas can be manufactured, advantages include the ability to be produce very thin films (thereby reducing the resistance to mass transfer), and the wide range of chemical groups that can be substituted onto the surface of the polymer to alter its separation characteristics.

In recent years a number of polymeric membrane materials have been developed which can withstand the more aggressive environments associated with organic solvents such as toluene, dichloromethane (DCM) and tetrahydrofuran (THF), and this study focuses on the use of such membranes for applications related to the processing of liquid hydrocarbon fuels. Potential benefits include the removal of polycyclic aromatic hydrocarbons (PAHs), high molecular weight and gum forming species, organometallic and sulphur bearing compounds that impact upon the performance and emissions characteristics.

Basic Principles

A membrane selectively permeates one substance over another, for instance, based on its size or charge. There are two principal operating regimes which are commonly used, namely deadend filtration and crossflow filtration as depicted in Figure 1.

In deadend filtration the entire process stream is permeated through the membrane, the technique does not directly apply any shear at the membrane surface. As such, any solid or retained solute molecules accumulate at the membrane surface to form a resistant layer (e.g. cake, gel) which hinders permeability, the process being known as fouling. Crossflow filtration on the other hand passes the feed across the surface of the membrane whilst under pressure. The pressure acts to permeate the solvent through the membrane, whilst the crossflow hinders the formation of a fouling layer. Performance is dependent on the hydrodynamic regime induced by the design of the membrane housing module. For continuous applications or solvent-solute mixtures crossflow filtration systems are almost always employed.

As can be seen from Figure 1 there are two products when crossflow filtration is employed; that which passes through the membrane (permeate) and the fraction retained (retentate). The process can be operated on a continuous ‘once through’ basis, or the retentate can be recirculated back to the feed tank as a batch operation. An important parameter in crossflow filtration is the ‘stage cut’ or ‘recovery’, which describes the fraction of the feed that permeates the membrane, and is typically controlled by adjusting the operating pressure and feed flow rate. The separation potential of the membrane is quantified using the ratio of the solute concentration in the permeate (C_{iP}) and feed (C_{iF}), and is usually expressed as the rejection, R, rather than a transmission or penetration:

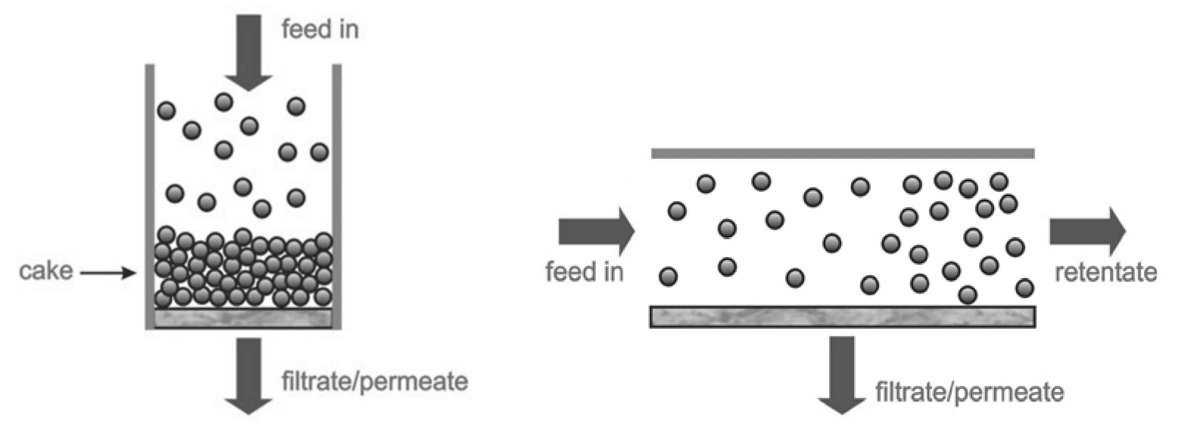

Figure 1: Schematic representations of deadend (*left*) and crossflow filtration (*right*) techniques.

$$R = 1 - \frac{C_{iP}}{C_{iF}} \quad (1)$$

Polymeric membrane materials themselves can be classified as either porous or dense. Porous membranes have a well-defined pore structure or distribution of pore sizes within the material, which promote separation primarily based on the size of the permeating species or charge relative to the membrane surface. Dense membranes have no manufactured pores, instead the selectivity is governed by differential rates of sorption into the membrane material and permeation through it, with solvent/polymer phase equilibria being an important parameter. Porous membranes are generally used for solid/liquid or solid/gas separations, whereas dense membranes are used for molecular level separations such as the removal of dissolved salts and solutes from liquids, vapour permeation and gas separation. The nature of the membrane material partially dictates the fundamental transport mechanisms, of which hydraulic or diffusive transport may be prevalent. Transport through porous materials is governed by a hydraulic mechanism consistent with the Hagen-Poisuelle equation:

$$J = \left(\frac{\varepsilon r^2}{8x\tau}\right)\left(\frac{\Delta P}{\mu}\right) \quad (2)$$

where the component flux, J, is a function of membrane properties such as porosity (ε), pore radius (r), thickness (x) and tortuosity (τ) and system parameters such as differential pressure (ΔP) and fluid viscosity (μ).

The permeation mechanism through dense membranes is somewhat different. In the majority of cases the permeating species are considered to dissolve in the membrane material and diffuse through it via a solution-diffusion mechanism, with the separation potential being governed by differences in solubility and diffusivity. A common representation of the Solution-Diffusion model is shown in equation (3), which is in essence a combination of solvent/polymer phase equilibria with Fick's Law of diffusion.

$$J_i = \frac{D_i K_i}{x}\left[C_{iF} - C_{iP}\exp\left(\frac{-u_i \Delta P}{R_G T}\right)\right] \quad (3)$$

where R_G is the universal gas constant, T is temperature and u is molar volume. The partition coefficient, K_i, is derived from phase equilibria and D_i is the diffusion coefficient of the penetrating species in the swollen polymer.

The two models differ in the way the pressure gradient across the membrane is expressed. A hydraulic mechanism assumes a pressure drop across the thickness of the membrane material, which acts as the driving force for permeation. With the solution-diffusion model the pressure is constant throughout the selective layer, with the driving force for transport arising from an activity gradient induced by the differential pressure. A thorough discussion of the application and validity of both approaches has been conducted by several membrane researchers, e.g.[3-5], so will not be covered here.

Existing Processes and Recent Research

A new generation of polymeric membrane materials has substantially widened the potential applications of membrane separation technology to industries which utilise non-aqueous liquids. For example, in pharmaceutical applications Scarpello *et al.*[6] studied the separation performance of a range of catalysts from organic solvents such as DCM, THF and acetone. The membrane based recovery of solvents after extraction processes is desirable as a non-thermal method, and this has been investigated by Stafie *et al.*[7] in the extraction of vegetable oils with hexane. The potential for using membrane technology in the petrochemical industry is being realised, with Gould *et al.*[8] reporting a process for the dewaxing of lubricating oil and White *et al.*[9] for the removal of sulphur from naphtha. The application to fuels is realised by, for instance, Bitter *et al.*[10], who demonstrated that the concentration of metallic compounds in kerosene and gas-oil can be reduced using membranes and Tarleton *et al.*[11] who reported the use of membranes to remove heavier components from gasoline based fuels. Although specific details of applications can be difficult to identify, in recent years several companies including Koch (SelRO membranes), W.R. Grace (Starmem), SolSep, Evonik (Duramem and Puramem), PoroGen and AMS Technologies have all commercialised membrane products suited to OSN. The interested reader is referred to the extensive review of Marchetti *et al.*[12] for more details of previous works and applications.

Studies to date serve to highlight progress; however, many of the reports are exclusive to a particular feed stream and yield little technical information which could be used to gauge wider implications of the technology. The current study aims to address the imbalance by presenting nanofiltration results for a range of organic liquids and solute molecules which are representative of fuel components, and to highlight the prevalent transport and separation mechanisms. An understanding of the fundamental principles will potentially allow the technology to be realised more widely than at present.

MATERIALS

The membranes used in the current study were composite materials with a dense poly(dimethylsiloxane) (PDMS) selective layer and a porous poly(acrylonitrile) (PAN) substrate layer. The membranes were supplied by GKSS Forschungszentrum (Geesthacht, Germany), and manufactured according to[13]. A micrograph of a cross-section of the material is shown in Figure 2, in this case showing a 10 µm PDMS layer on top of a 40 µm porous substrate. Beneath the substrate is a cellulose fibre support layer which provides additional mechanical strength; however, the resistance to mass transfer in this region is negligible compared with the selective PDMS layer.

Most of the membranes were manufactured with a PDMS layer of 2 µm thickness, although some with a PDMS thickness of 1 µm, 1.5 µm or 10 µm were also available. A range of alkane, aromatic and oxygenated solvents were studied. Solute compounds (used only with non-polar solvents) were chosen to be representative of those commonly associated with fuels processing applications, and are shown in Table 1, along with their respective molecular weight and molecular sizes calculated from bond lengths and covalent radii. The molecular size when dissolved in the solvents is likely to be similar given that the majority of the solvents are non-polar in nature.

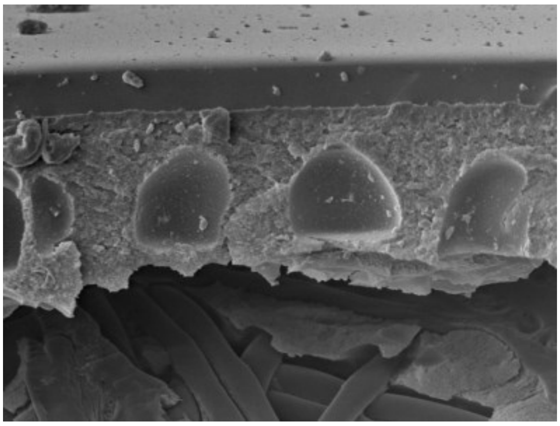

Figure 2: SEM image of PDMS composite membrane, with 10 µm PDMS layer and 40 µm PAN substrate clearly visible. Picture width corresponds to *ca.* 100 µm.

EXPERIMENTAL

The separation characteristics of the solvent/solute systems were studied in the crossflow membrane filtration apparatus shown schematically in Figure 3.

The solvent/solute mixture was added to the 2.5 litre capacity reservoir (A) from which an air driven pump (B) delivered the fluid to the membrane module (C) via a variable area flow meter (F), a flow control valve (V6) and a 15 µm rated prefilter (D). The permeate could either be circulated back to the reservoir or collected separately for subsequent sample analysis. The retentate stream returned to the reservoir through a cooler (E) which employed the exhaust air stream from the pump to maintain the temperature of the circulating fluid. Trans-membrane pressure and crossflow rate were controlled primarily by the back pressure regulator (V7) and the air regulator to the pump (V2). The circular, flat sheet membrane was mounted in an Osmonics DESAL membrane cell to give a wetted surface area of 75 cm^2.

The membranes were mounted dry, with 100 ml of the process fluid being used to flush away any residual solvent from the manufacturing process. When the desired process conditions were set, the permeate was returned to the reservoir to allow a steady state to be achieved. The permeate was then diverted to a separate collecting vessel for a set time, which allowed flux measurements to be obtained. Samples of permeate were subsequently used to determine the concentration of the desired solute. The amount of permeate collected was such that recovery was in the order of

		Solute dimensions	
Solute	Molecular weight (g/mol)	Min size (nm)	Max size (nm)
Thiophene	84	0.30	0.52
1-butanethiol	90	0.33	0.83
Acenaphthene	154	0.67	0.73
Phenanthrene	178	0.77	0.85
Anthracene	178	0.56	0.97
Ferrocene	186	0.52	0.54
Pyrene	202	0.77	0.85
Coronene	300	0.97	0.98
9,10-diphenylanthracene	330	0.97	1.27
Tetraphenylethylene	332	0.71	1.00
Iron (III) acetyl acetonate	353	1.29	1.29
Iron (III) naphthenate	373	1.82	1.82
Rubrene	532	1.21	1.27
Copper (II) naphthenate	611	0.92	3.52

Table 1: Organic solute compounds, including molecular weight and calculated dimensions.

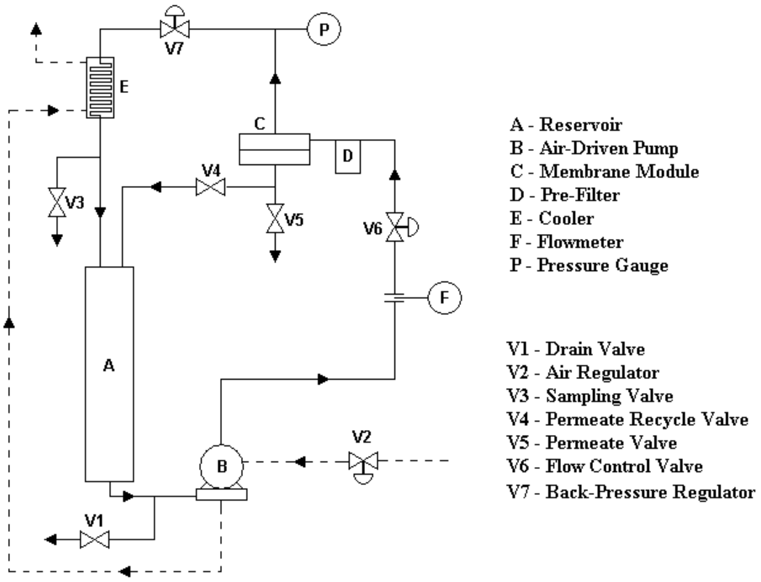

Figure 3: Schematic of the crossflow nanofiltration apparatus.

10%. In all cases, a solute mass balance was obtained to within 1% based on concentrations and mass of feed, permeate and retentate.

RESULTS AND DISCUSSION

Membrane Stability

A primary concern with polymeric membranes is their stability in organic solvents, an issue which is compounded by the fact that polymeric NF membranes are usually composite materials. Variations in the rate of swelling in the selective and substrate layers can result in differing levels of volumetric expansion which may cause the selective layer to detach from its substrate. Elaborate conditioning procedures have been reported by a number of workers[6,14] where the membrane is sequentially contacted with different solvents in order to enhance its stability. In the current work, for the membrane with a 2 μm PDMS thickness no conditioning was necessary.

A single sample of membrane was used intermittently for several months, during which time the permeating solvent was changed on several occasions. The solvent permeability was monitored throughout and the results for xylene and n-heptane are shown in Figure 4. The data clearly show that the integrity of the membrane material remains intact. Had the permeability progressively increased with time, or shown an upward step change, this would have indicated a defect in the selective layer. The essentially constant permeability of the two solvents indicates that no deterioration of the PDMS layer has taken place over a range of operating conditions. Also of note from Figure 4 is that there are no effects of hysteresis when switching between different solvents, the region between 750 and 1000 L/m^2 shows that the same permeability is maintained when tests on the previous solvent are resumed. Given that the data shown in Figure 4 were obtained over a period of seven months, it is clear that membranes of this type are a good candidate for larger scale industrial applications.

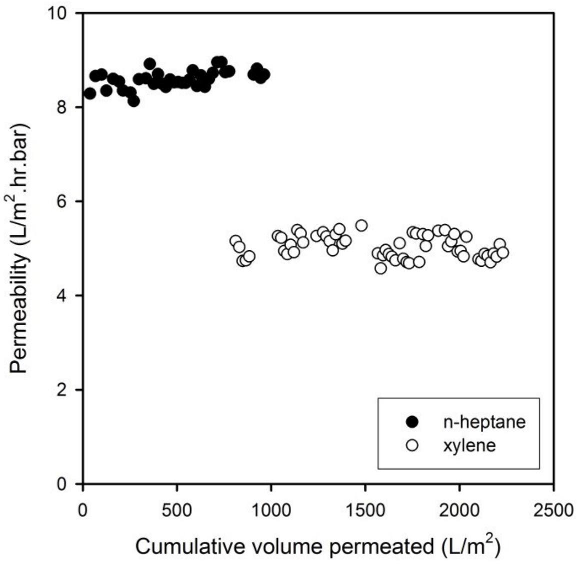

Figure 4: Solvent permeability plotted against volume of solvent permeated; results were obtained over seven months.

Solvent Permeability

The flux of a range of organic solvents was measured at pressures ranging from 1-10 bar. In all cases the flux/pressure relationship was found to be linear, allowing data to be expressed as a permeability (see Table 2). Permeabilities ranged from 4 to 10 L/m^2.hr.bar, and are dependent on a number of factors and physical properties. This range is generally high for nanofiltration membranes which typically[6] exhibit permeabilities in the order of 0.05-1.0 L/m^2.hr.bar. A primary factor governing solvent permeability is the degree of swelling imparted by the solvent. Solvents such as n-alkanes swell the PDMS membrane to as much as 270% of the original volume, whereas alcohols and water impart very little swelling.

The degree of swelling is governed theoretically by the thermodynamic activity within the PDMS matrix; however, an estimate can be gained from inspection of the solubility parameter (δ) of the solvent relative to that of the membrane[15]. Generally, solvents whose solubility parameter is closer to that of the PDMS membrane (15.5 MPa$^{0.5}$) will induce the most swelling. In the current work the degree of swelling was measured using a technique described in[16,17], and is expressed as a ratio of the volume of the swollen PDMS relative to the dry polymer. It can be clearly seen that those solvents which swell the membrane to a large degree exhibit high permeabilities relative to those which do not swell the membrane. Also included in Table 2 are parameters from both hydraulic and Solution-Diffusion models. The swelling data allow the true thickness of the selective layer to be calculated (as it is different for each solvent), and also allows the partition coefficient, K_i, to

	Physical properties	Experimental data		Model parameters	
Solvent (i)	δ_i - δ_{PDMS} (MPa$^{0.5}$)	Permeability (l/m^2.hr.bar)	Swelling ratio (-)	D_i (x10^{-9} m^2/s)	$\varepsilon r^2/8\tau$ (x10^{-20} m^2)
n-hexane	-0.6	9.97	1.64	4.25	4.62
n-heptane	-0.2	8.30	1.69	3.04	4.90
i-hexane	-0.8	9.25	1.60	3.72	3.56
i-octane	-1.2	5.53	1.48	1.75	3.46
cyclohexane	1.3	4.34	1.58	2.32	5.83
xylene	2.7	5.61	1.19	2.38	4.38
C_1-C_3 alcohols	8.1-13.7	<0.1	0.05-0.2	-	-
water	32.0	0	0	-	-

Table 2: Permeability for a range of solvents with PDMS membranes of 2 μm selective layer thickness. Measured swelling properties and model parameters are also shown.

be estimated.

Diffusion coefficients were calculated by fitting equation (3) to the experimental permeability data, and it can be seen that they are in the order of 10^{-9} m^2/s, i.e. of the same order as diffusion in liquids rather than in a dense polymeric membrane. The hydraulic coefficients were calculated using equation (2), along with the bulk solvent viscosity and swollen thickness of the selective layer, and are generally quite low. The permeabilities appear to lie at the upper end of what might be considered as diffusion and the lower end of what can be said to be hydraulic.

The high permeability of PDMS can, to some extent, be understood by considering the degree of swelling of the membrane. PDMS swells to a greater extent than most other commercially available polymer membranes, and by swelling the polymer chains move further apart to promote volumetric expansion. In doing so, the regions in between the polymer chains are expanded, allowing for improved passage of the permeating species. Hence, those substances which do not swell the membrane to a great extent (e.g. alcohols) have a very low, or zero permeability. In the case of the PDMS membrane being investigated, the degree of swelling is sufficiently large that the transport regions induce a flow which is difficult to accurately characterise as being truly hydraulic or diffusive in nature, and has reignited a previous debate as to the validity of the solution-diffusion approach[18]. Irrespective of the permeation mechanism, the degree of swelling is an important factor which governs solvent transport in this, and other solvent resistant membranes.

The separation of solute molecules from organic solvents is dependent on a range of parameters. Of note is that the mechanism does not appear to be one of adsorption, even though the previous section discusses swelling of the membrane material. Any sorption in this case is dynamic, and is followed by permeation and subsequent desorption into the permeate stream. No evidence of permanent adsorption was observed with the PDMS membranes over many years of operation using a range of different solvents and solutes.

As one would expect of a mass transfer process, the hydrodynamic conditions at the surface of the membrane play an important role in defining the boundary layer resistances and pressure drops, and hence impact upon the sorption and overall solute retention. The operating pressure also affects the solute rejection, with higher operating pressures generally being beneficial in terms of solute removal. Whilst of interest to the membrane scientist such parameters are of limited concern to this discussion, which will instead focus on the size and polarity of the molecules present. A thorough discussion of the effects of various operating parameters on the filtration performance of solvent resistant membranes and associated mechanisms can be found in, for instance[6,18,19].

Rejection Based on Size

In order to differentiate between separations based on size and polarity it was necessary to use a range of low polarity solutes (non-OH containing) such as PAHs and organometallic components as detailed in Table 1. Traditionally, the molecular weight of a solute is used to characterise the separation capabilities of a particular membrane, however, the validity of this approach diminishes when the solutes are small so the solute size is considered as an alternative. Figure 5 demonstrates the separation performance of the PDMS membrane by plotting fractional rejection against solute size for two different solvents, measured at equivalent operating conditions.

There is a distinct region between 1-1.5 nm, below which there is no separation and above which the separation is close to 100%. Such a relationship is indicative of a sieving mechanism, albeit at a molecular level. Substances below 1 nm include the smaller PAHs, sulphur bearing compounds and the majority of the solvents themselves, whereas above 1.5 nm are the copper and iron naphthenic acid derivatives. The 1-1.5 nm region contains the larger PAHs and organometallic compounds, and it is these compounds which can be used to characterise the separation potential of different solvents or different membrane materials.

To assess the sub 1 nm region in more detail, a gasoline fuel was permeated through the membrane and the composition determined by GC analysis both before and after permeation. Inspection of Table 3 shows that there may be some loss of the lighter components after permeation as evidenced by the compositions of C_3-C_5. This is most likely a consequence of the experimental setup rather than a direct effect of the filtration process as some loss to evaporation was inevitable. Overall, however, it appears that the base composition of the feed fuel and that permeated through the membrane is the same, with no selectivity toward paraffinic, olefinic or aromatic constituents in the case of the particular PDMS membrane material.

The experimental evidence presented in Figure 5 and Table 3 suggests that the mechanism of separation of non-polar (i.e. those without OH containing groups) solutes is governed by size exclusion. However, this presents something of a paradox given the membrane is a dense material, with no manufactured pore structure. Once again the key to the separation capability of the PDMS membrane is the degree of swelling that the solvent imparts. When the membrane swells to a greater extent so the size of the transport regions within the material increases; whilst no defined pore structure exists, the term ‘transport regions’ is introduced to refer to the areas between the polymer chains through which a species is able to permeate, and does not in

C number	Feed (% v/v)	Permeate (% v/v)		Hydrocarbon type	Feed (% v/v)	Permeate (% v/v)
C_3	0.18	0.15		n-paraffin	10.08	9.11
C_4	7.36	6.2		i-paraffin	26.95	27.10
C_5	9.12	8.9		n-olefin	3.13	3.04
C_6	10.09	10.16		i-olefin	4.20	4.21
C_7	22.82	23.29		aromatic	50.49	51.48
C_8	28.97	29.56				
C_9	14.32	14.61				
C_{10}	5.44	5.55				
C_{11}	1.16	1.18				

Table 3: Selected GC analysis of feed and permeate for membrane filtered gasoline fuel.

itself imply any particular flow mechanism. Referring to Figure 5, the greater swelling solvent of the two shown is n-heptane (see Table 2), hence larger transport regions exist which allow for greater permeation of the solute molecules and therefore a lower rejection. The smaller transport regions occurring with xylene result in lower solute permeation and hence a higher rejection.

The overall degree of swelling effectively determines the structure of the membrane material, and impacts on the passage or retention of larger molecules. This is an important finding given that the manufacture of nano-structured porous materials for such separations is likely to be extremely difficult – in this case one only needs to form a crosslinked polymer which will swell to the desired degree in the presence of a solvent. Indeed, the polymers could be said to exhibit an intrinsic microporosity. The extent to which a membrane swells is dependent not only on the process solvent but also on the degree of crosslinking of the polymer, which are bonds that join adjacent polymer chains. With no crosslinking the PDMS chains will effectively dissolve in the solvent, so the polymer chains need to be held together by use of a crosslinking agent, similar to a conventional thermosetting or curing process. The addition of crosslinking bonds limits the expansion of the polymer chains upon swelling, with more crosslinking resulting in a more rigid structure. As well as the process solvent, the degree of crosslinking of the polymeric material will also impact upon the size of the transport regions within the membrane, and will hence affect the filtration performance.

A range of PDMS membranes with different degrees of crosslinking were studied. The degree of crosslinking arose from the type of manufacturing process and the manner in which the crosslinking was imparted. Quantification of crosslinking is usually expressed in terms of the average molecular weight between crosslinking bonds; however, the very thin films of PDMS used in the current membranes prevented an accurate measurement. As an alternative results for the range of membranes are shown in Figure 6 where the solvent permeance (permeability rationalised by the thickness of the PDMS layer) is presented along with the corresponding solute rejection for each particular membrane.

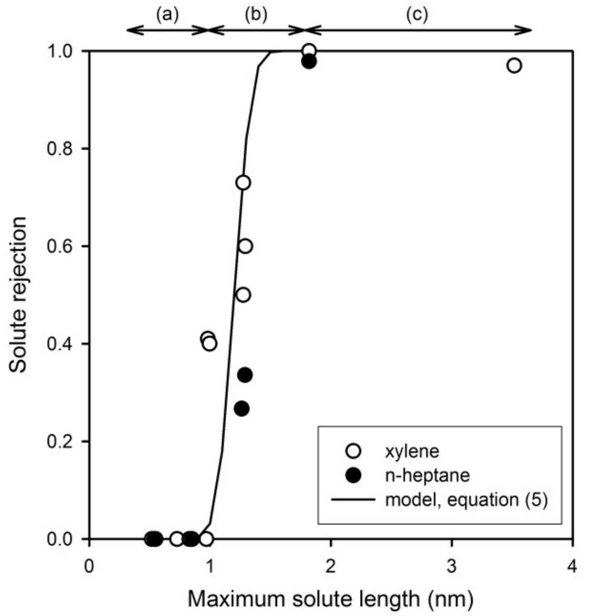

Figure 5: Rejection of organic solute compounds in xylene and n-heptane as a function of maximum solute size. The solid line represents model predictions using equation (5). (a) = small PAH's, sulphur containing; (b) = larger PAH's; (c) = naphthenates.

Generally, membranes whose selective PDMS layer is subjected to the highest degree of crosslinking yield a high solute rejection but a relatively low permeance. In this case the degree of swelling is low, so the size of the transport regions within the membrane is the smallest. The result is that solute rejection is high (due to

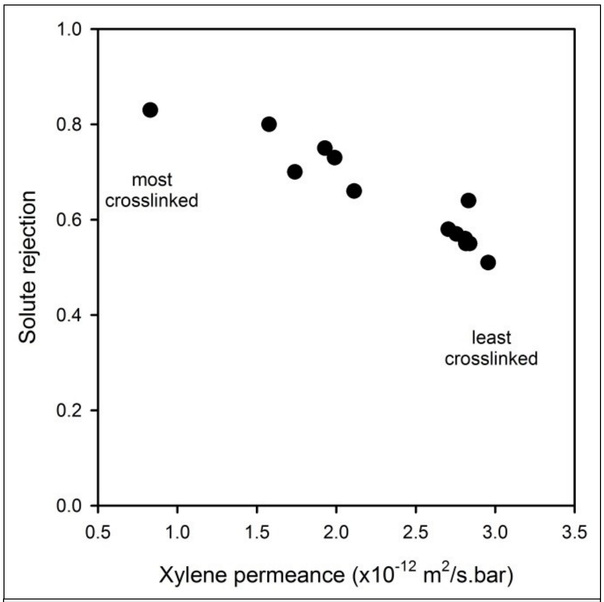

Figure 6: A typical profile of solvent permeance vs. solute rejection (9,10-diphenylanthracene) for PDMS membranes with different degrees of crosslinking. For the data shown, the membrane crosslinking was achieved via exposure to radiation and/or thermal techniques with individual PDMS thickness in the range 1 to 10 μm.

the restricted size of the membrane transport network), whereas the solvent permeance is low for the very same reason. Likewise, the least crosslinked membrane swells the most which results in a more open network structure with larger gaps between the polymer chains. In this case the solute retention is the lowest and the solvent permeance highest.

It appears from Figure 6 that altering the degree of membrane crosslinking has a greater effect on solvent transport than solute transport. For example, between the two extremes the solute rejection varies by less than 0.4 whereas the permeance varies by a factor of about 3. When considered along with the overall size exclusion curve in Figure 5, it is apparent that large changes in solvent permeability may be obtained with relatively little change in the overall separation characteristics of the membrane. This may be particularly important in an industrial process, where large gains in permeability may be obtained without excessive detriment to the overall product quality, thus reducing the capital cost (membrane area required) and/or operating costs (pressure).

If a sieving mechanism is assumed to be the exclusive factor governing solute retention, then the effective size of the transport regions within the membrane can be estimated. A number of models based on porous membranes are available. For example, the Ferry[20] model and Steric-Hindrance Pore (SHP) model[21] have been used to characterise similar membranes, however, they generally assume a uniform pore structure which is difficult to infer with the swollen polymer membranes used in this study. If it is assumed that the swollen PDMS network is a mesh, through which solvent and solute transport can occur, then the mesh can be characterised in terms of an average mesh size and a standard deviation.

Assuming that a solute molecule is retained only if its size is greater than the mesh, and passes freely when smaller than the mesh then a sharp cut-off will be obtained with infinite gradient, i.e. the cut-off will occur exactly at the solute size. If a standard deviation (S_p) is introduced, a small standard deviation of mesh size will result in a sharp cut-off over a small size range, whereas a larger value will yield a smaller gradient, with the cut-off spanning a greater range of solute sizes. This can be developed mathematically by considering the distribution of mesh sizes to be normally distributed, in which case the frequency (y) of transport regions above a certain effective radius, r_p, can be described by:

$$y = \frac{1}{S_p\sqrt{2\pi}}\exp\left(-\frac{\left[r_p - r_{p,av}\right]^2}{2S_p^2}\right) \qquad (4)$$

The rejection for any given size of solute can be obtained by integration since this corresponds to the position of that solute on the size exclusion curve:

$$R(r_S) = \int_0^{r_S} \frac{1}{S_p\sqrt{2\pi}}\exp\left(-\frac{\left[r_S - r_{p,av}\right]^2}{2S_p^2}\right)dr \qquad (5)$$

If equation (5) is integrated numerically, with $r_{p,av}$ equal to 0.6 nm and S_p 0.05 nm, then good agreement is obtained between the model and the experimental data for xylene solvent as shown in Figure 5. The standard deviation is small in order to reflect the sharp cut-off in rejection; however, this is also what would be expected on a physical basis. Crosslinking is achieved, primarily, by the addition of a chemical crosslinking agent with energy then being supplied by various means. It is reasonable to assume that the chemical crosslinking agent disperses evenly throughout the PDMS, in which case the mesh that is created upon crosslinking is likely to be regular, with a small standard deviation.

Using the approach described for the membranes of various crosslinking and PDMS thickness (Figure 6), and assuming the standard deviation remains the same in each case, then the membranes can be characterised in terms of their equivalent mesh diameter as shown in Figure 7. The estimation from equation (5) suggests the equivalent mesh diameter is around 1.2

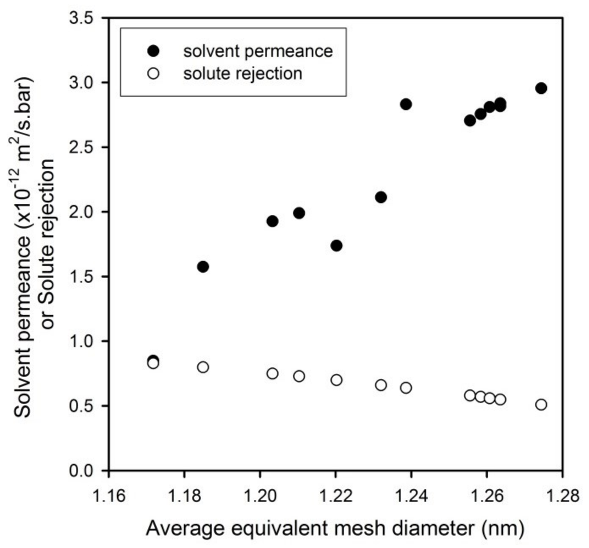

Figure 7: Solvent permeance and solute rejection obtained with PDMS membranes characterised in terms of average equivalent mesh diameter.

nm, and this varies by just over 0.1 nm across the range of membranes studied. Although an estimate, the data help to further illustrate the importance of swelling in these membrane/solvent systems. It is conceivable that the permeance could be further improved with progressively less crosslinking. However, there exists a minimum degree of crosslinking, below which the PDMS material will just dissolve in the solvent. For applications such as in kerosene or diesel the degree of swelling is likely to be reasonably low and in these cases it may be possible to use lightly crosslinked membranes which would otherwise be unstable in greater swelling solvents.

Rejection Based on Polarity

The previous discussion has focussed on non-polar or low polarity solvents and solutes which were chosen specifically to illustrate the effects of molecular size in OSN. Likewise, to best study the influence of polarity, substances must be used which are below 1 nm in size (i.e. well below the membrane cut-off due to size exclusion). The organic solvents used in this study will not promote dissociation into ions, hence polarity must be assessed through a selective study of OH containing compounds which are miscible with the non-polar solvents. In this instance alcohols have been chosen, partly due to their importance in biofuels. Results for MTBE (methyl tert-butyl ether) are also discussed in an attempt to understand the wider filtration behaviour of oxygenated compounds.

A similar range of experiments were performed for the xylene/oxygenate mixtures as for the solvent/solute mixtures discussed previously. In this case, however, concentrations were studied up to 75% oxygenate instead of within the ppm range used for the non-polar solutes. Again, operating parameters such as pressure and crossflow rate affected the permeability and separation performance of the membrane, although these data are not included here (see[22]). The PDMS membrane was found to favour the permeation of the less-polar substance, in this case xylene, n-heptane and cyclohexane solvents rather than the alcohols. The choice of non-polar solvent with which the alcohols were mixed also affected the separation performance, however, for simplicity the remainder of the discussion will focus on the behaviour of oxygenate/ xylene mixtures which is representative.

Alcohol rejection was found to be dependent on both the type of alcohol and its concentration; the experimental findings are summarised in Figure 8. Of note is that in all cases the rejections are relatively low when compared with those obtained for larger solute molecules, with a maximum rejection of 0.28 being observed for methanol. The most striking observation is that the rejection of alcohol follows the sequence of the homologous series, i.e. methanol > ethanol > propanol. This can be explained by considering the oxygenate polarity. For example, methanol is the most polar and exhibits the highest rejection whilst MTBE is the least polar and does not separate from the xylene co-solvent. As the PDMS membrane is inherently hydrophobic it is likely to reject the more polar species, and similarly a hydrophilic membrane would be expected to behave conversely.

Polarity is a convenient parameter in this discussion because the xylene solvent and PDMS membrane are inherently non-polar. However, to progress the depth of the discussion terms like polarity, charge, hydrophobicity and hydrophilicity are potentially misleading. Instead, the phase equilibria between the liquid and swollen polymer must be considered (hydrophobicity and hydrophilicity represent a simplified consideration of phase equilibria). Whilst one may intuitively comprehend the rejection of a polar species by a non-polar membrane, the process can be quantified using the principles of phase equilibria, in this case the Flory-Huggins theory which relates the activity (*a*) of a substance within the swollen polymer to its activity in the feed liquid[23]. The expression for a three component system (solvent 1, solvent 2, polymer) is necessarily complex as shown by the Flory-Huggins ternary equations (6-8), and cannot be solved analytically.

$$\begin{aligned}\ln a_1 = {} & \ln\varphi_1 + (1-\varphi_1) - \left(\frac{\upsilon_1}{\upsilon_2}\right)\varphi_2 - \left(\frac{\upsilon_1}{\upsilon_P}\right)\varphi_P \\ & + (\chi_{12}\varphi_2 + \chi_{1P}\varphi_P)(\varphi_2 + \varphi_P) - \chi_{2P}\left(\frac{\upsilon_1}{\upsilon_2}\right)\varphi_2\varphi_P \end{aligned} \qquad (6)$$

$$\ln a_2 = \ln\varphi_2 + (1-\varphi_2) - \left(\frac{\upsilon_2}{\upsilon_1}\right)\varphi_1 - \left(\frac{\upsilon_2}{\upsilon_P}\right)\varphi_P + (\chi_{12}\varphi_1 + \chi_{2P}\varphi_P)(\varphi_1 + \varphi_P) - \chi_{1P}\left(\frac{\upsilon_2}{\upsilon_1}\right)\varphi_1\varphi_P \quad (7)$$

$$\varphi_1 + \varphi_2 + \varphi_P = 1 \quad (8)$$

The right hand side of equation (6) equates to the natural logarithm of the activity of solvent 1 in the polymer, and likewise equation (7) shows the expression for solvent 2. Briefly, φ is the volume fraction of each species in the swollen polymer, υ the molar volume and χ is an interaction parameter. Experimental data are required at the boundary conditions with pure solvents to establish χ_{1P} and χ_{2P} values, and χ_{12} is estimated using vapour-liquid equilibrium data. a_1 and a_2 are equated to the activity of each component in the liquid phase, which leaves three equations with three unknowns φ_1, φ_2 and φ_P. Using the ternary equations, the fractionation or partitioning which occurs upon swelling can be estimated by comparing the ratio of components 1 and 2 in the liquid phase with that in the swollen polymer phase. Table 4 gives an example of the predictions obtained for mixtures of 75% xylene and 25% co-solvent.

It appears that there is a good correlation (in terms of trend) between the rejection that occurs at equilibrium swelling and that determined experimentally. In the case of the alcohols the rejection determined from phase equilibria is much higher than those measured in filtration experiments, which may be due to a further separation/selectivity upon permeation and desorption which will be influenced by the viscosity or diffusion coefficient of each species. Interestingly, when considering MTBE and n-heptane in phase equilibria calculations the predicted rejections are very low, and mirror the experimental case where mixtures containing these solvents did not separate.

Considering also the case of the gasoline fuel in Table 3, the chemical nature of the individual alkane and aromatic fuel components is such that very little fractionation occurs due to phase equilibria, and hence the composition of the fuel remains unchanged after permeation. In the case of PDMS the correlation can also be obtained with solubility parameter data, where the greater the difference between the δ values of the membrane and co-solvent so the greater is the rejection. When the value of δ_I - δ_{PDMS} is low this suggests that little separation will occur.

The bell-shaped curves in Figure 8 for methanol and ethanol rejection are particularly interesting, and perhaps difficult to rationalise conceptually using the physical properties of the solvent mixture. Insufficient data exist to calculate the phase equilibria across the range of alcohol concentrations, however, a study by Favre *et al.*[24] showed experimentally determined equilibria for a PDMS-ethanol-toluene system, which is conceivably similar to the PDMS-ethanol-xylene system used in the current study. Their data have been used as a basis for calculating the rejection due to swelling equilibria, R_0, and is shown in Figure 9. The separation of ethanol from toluene upon swelling shows a very similar trend to the experimentally determined alcohol rejections in Figure 8, where a clear bell-shaped trend is evident. This provides further evidence of the importance of phase equilibria when the separation is governed by polarity rather than size, and again it is of note that the rejection from phase equilibria alone is much higher than those observed experimentally.

In summary, although the mechanisms of this type of separation are still to be understood, it is shown that multicomponent solvents/polymer phase equilibria

Co-solvent (*i*)	δ_i - δ_{PDMS}	R_0	R_{obs}
methanol	13.7	0.947	0.25
ethanol	11.0	0.747	0.14
n-propanol	9.4	0.567	0.11
i-propanol	8.1	0.559	0.08
MTBE	2.9	0.029	0
n-heptane	-0.2	-0.034	0

Table 4: Comparison of experimental rejection data (R_{obs}) with phase equilibria (R_0) and solubility parameter data for xylene/co-solvent mixtures.

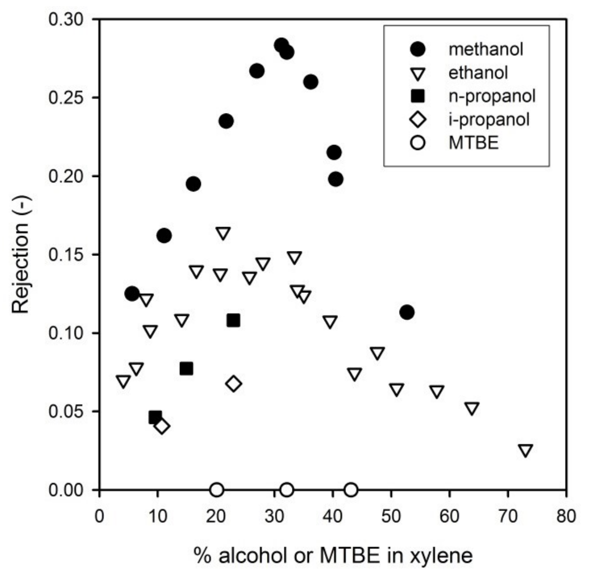

Figure 8: Rejection of alcohols and MTBE at 5 bar from solutions with xylene.

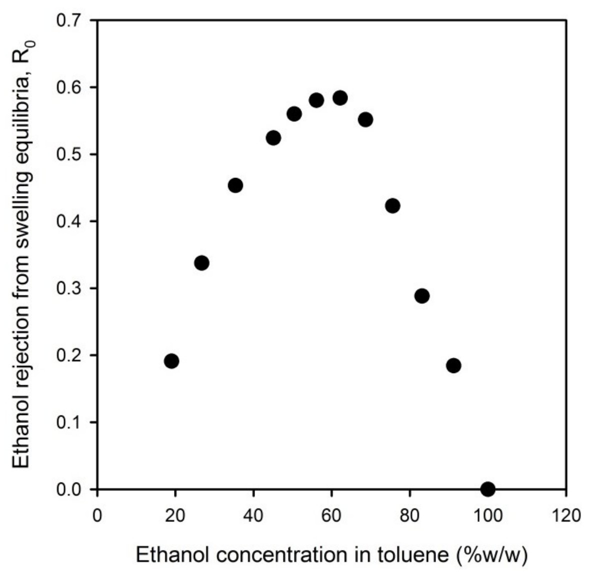

Figure 9: Experimentally determined rejection of ethanol from toluene using multicomponent phase equilibria. Data derived from Favre *et al.*[24].

appears to be the main driving force behind the separation potential of PDMS membranes when polar solvents are used. When non-polar or low polarity solvents are used the degree of fractionation from phase equilibria is very small, to the extent that the separation of a multicomponent mixture such as a gasoline fuel will be negligible. When a mixture of polar and non-polar solvents is used, a separation will occur based on the phase equilibria.

CONCLUSIONS

The potential of PDMS as a membrane material for organic separations has been demonstrated, and the importance of swelling, size exclusion and phase equilibria have been discussed in some detail. It is shown how a dense membrane can exhibit many of the characteristics of a porous membrane and perform separations based on molecular size, whilst at the same time being able to separate a mixture of polar/non-polar components based on multicomponent solvent/polymer phase equilibria. Altering the degree of crosslinking may allow compounds of a specific size to be targeted or an improvement in permeability, in both cases by altering the mesh size of the swollen polymer network.

PDMS is a good candidate in OSN but it is by no means the only polymeric membrane material which could be used, other examples include polyimide and polyether ether ketone (PEEK). The representative model compounds used as part of this study were chosen to simulate a gasoline fuel. It has been shown that a gasoline fuel can be permeated through the membrane with little separation of the base hydrocarbon mixture, and that the membrane can potentially remove all impurities above 1.5 nm in size such as large PAHs, polymerised species and organometallic components.

NOMENCLATURE

a	activity
C	concentration
D	diffusion coefficient (m^2/s)
J	flux (m^3/m^2.s)
K	partition coefficient
P	pressure (Pa)
r	pore radius (m)
r_p	effective mesh radius (m)
R	rejection
R_0	rejection due to phase equilibria
R_G	universal gas constant (m^3.bar/mol.K)
R_{obs}	experimentally observed rejection
S_p	standard deviation (m)
T	temperature (K)
x	thickness (m)
y	frequency

Greek letters

ε	porosity
δ	solubility parameter (MPa$^{0.5}$)
μ	viscosity (Pa s)
τ	tortuosity
υ	molar volume (m^3/mol)
φ	volume fraction in swollen polymer
χ	Flory-Huggins interaction parameter

Subscripts

i	component i
F	feed
P	permeate

Acronyms

DCM	dichloromethane
GC	gas chromatograhy
MTBE	methyl tert-butyl ether
NF	nanofiltration
OSN	organic solvent nanofiltration
PAH	polycyclic aromatic hydrocarbon
PAN	poly(acrylonitrile)
PDMS	poly(dimethylsiloxane)
SHP	steric-hindrance pore
THF	tetrahydrofuran

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