Organic Solvent Nanofiltration of Binary Vegetable Oil/Terpene Mixtures:

Experiments and Modelling

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Abstract

Bio-derived solvents such as *p*-cymene, d-limonene and α -pinene represent feasible alternatives to *n*-hexane for the extraction of vegetable oils. However, the large-scale utilization of these solvents is still limited mainly owing to their high boiling points and latent heats of vaporization. In this work, the performance of composite polydimethylsiloxane/polyacrylonitrile (PDMS/PAN) organic solvent nanofiltration membranes in the recovery of these solvents from their binary mixtures with canola oil is investigated. The sorption isotherms of the mixtures were first studied using free-standing PDMS films and the multicomponent Flory-Huggins model used to determine the resulting interaction parameters. The partial solvent uptake decreased with increasing oil concentration in the mixture. On the other hand, the partial oil uptake in the solvent mixture was higher than that of the pure oil which was attributed to the swelling effects induced by solvents. The effects of feed concentration (10-30 wt. % oil), feed temperature (25-40 °C), transmembrane pressure (5-30 bar), and cross-flow velocity (18-52 cm s⁻¹) on the membrane performance were then studied in a cross-flow membrane setup. Maxwell-Stefan formulations were combined with the ternary Flory-Huggins solubility model to successfully describe these flux data.

Keywords: cymene; limonene; pinene; solvent resistant nanofiltration; Maxwell-Stefan.

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1. Introduction

Vegetable oil extraction and purification is an important industry, with an average annual production of more than 380 million metric tonnes [1]. In the primary stages, the crude oil is extracted from oilseeds by means of an organic solvent; typically n-hexane. N-hexane has been used for many years due to its high solubility for oil, availability and low price. Importantly, its low boiling point (69 °C) and heat of vaporisation (30 KJ mol⁻¹) make the recovery by conventional evaporation feasible[2]. However, n-hexane has recently been classified as a CMR (carcinogenic, mutagenic and reprotoxic) solvent and may be banned for industrial use in the future[3–5]. Moreover, the high volatility and low flash point of n-hexane increase the risk of fire and explosion[6]. Therefore, finding environmentally friendly alternative solvents has become imperative.

Bio-derived solvents, particularly terpenes represent promising substitutes for n-hexane [7]. These solvents are extracted from sustainable agricultural materials and have been proved to be safer to humans and the environment [8]. These solvents are used widely in perfumes, pharmaceuticals and in the food industry as flavouring agents [9–11]. Several studies have reported the utilization of terpenes for the extraction of vegetable oil and microalgae lipids[12–18]. These studies concluded that terpenes can replace n-hexane as extractive solvents due to their affinity for oil and lipids constituents. However, their high boiling points and heats of vaporization restrict their utilization at an industrial scale [19]. Furthermore, exposure to high temperatures during the recovery of these solvents using conventional evaporation results in the thermal decomposition of heat sensitive components such as natural antioxidants and the formation of harmful peroxides and unsaturated aldehydes [19,20]. Therefore, finding an alternative solvent recovery process with minimal energy consumption has become inevitable.

Membrane separation technologies are increasingly used for aqueous separations in the food industry. This success has triggered interest in such membrane technology for organic solutions, an

approach known as solvent resistant nanofiltration (SRNF), or organic solvent nanofiltration (OSN). SRNF represents a feasible alternative for energy-intensive conventional separation processes such as distillation, evaporation and liquid-liquid extraction. SRNF has advantages over these conventional processes of low energy consumption, mild operating temperatures, ease of installation and operation and low operating cost[21]. It is also considered as an environmentally friendly technology that minimizes harmful emissions as well as carbon dioxide to the atmosphere [1,22,23]. In the vegetable oil industry, SRNF has the potential to replace different stages of crude oil processing such as solvent recovery, degumming, de-acidification, deodorization and decolourisation[22].

The utilisation of membrane technology in the recovery of solvents from vegetable oil mixtures has been reported in some studies [20,24–31]. Kuk et al. [32] investigated the recovery of ethanol from ethanol-cotton oil mixtures using a commercial reverse osmosis membrane. Tres et al.[33] used a polymeric ultrafiltration membrane for the separation of refined soybean-hexane mixtures and observed a permeate flux up to $65 \text{ kg m}^{-2} \text{ hr}^{-1}$ and oil rejections up to 30 %. In another study, Tres et al. [34] observed higher rejections and fluxes for soybean oil/n-butane mixtures relative to oil/n-hexane mixtures using ceramic membranes (MWCO 5 and 10 kDa), Raman et al.[35] investigated the separation of 20 wt. % soybean oil in hexane using a polymeric nanofiltration membrane in a multistage process which resulted in a net oil recovery of 99 %. In our own prior work, we investigated the permeation of pure terpenes through a polydimethylsiloxane (PDMS) membrane and observed a non-linear increase in permeate flux that was readily explained using the solution-diffusion model. However, this work considered the permeation of terpenes alone and not oil/solvent mixtures[36].

While the solution-diffusion model is effective for single component systems, it ignores coupling effects between penetrants that occur in binary mixtures[37]. For this reason, it fails to predict the negative solute rejection which is observed in some studies[38,39]. The Maxwell-Stefan (M-S) approach overcomes these limitations[40]. These equations were originally developed to describe multicomponent diffusion through low-density gases but have since been extended successfully to

dense gases, liquids and polymers[40,41]. The approach has been widely used for describing transport in reverse osmosis, pervaporation, gas permeation and organic solvent nanofiltration systems[42–46]. The M-S equations originate from applying an inter-species force balance and can be written as follows[47].

$$\frac{x_i}{RT} \nabla_{T,P} \mu_i = - \sum_{\substack{j=1 \\ j \neq i}}^m \frac{x_i x_j (u_i - u_j)}{\mathcal{D}_{ij}} \quad (1)$$

where x_i , μ_i and u_i are the mole fraction, chemical potential (J mol^{-1}) and velocity (m s^{-1}) of component i , respectively. $\mathcal{D}_{ij}$ ($\text{m}^2 \text{s}^{-1}$) are the M-S diffusivities which represent the inverse of the drag coefficient between species i and j . In dealing with a system where a polymer is one component, it is more convenient to express the M-S equations in terms of volume fractions to be consistent with the thermodynamic models that describe species interactions with polymers[48]. Heintz and co-workers [49] adapted the M-S equations to be in terms of species volume fraction (ϕ_i) as follows:

$$\frac{\phi_i}{RT} \nabla_{T,P} \mu_i = - \sum_{\substack{j=1 \\ j \neq i}}^m \frac{\phi_i \phi_j (u_i - u_j)}{\mathcal{D}_{ij}} \quad (2)$$

The formula developed by Heintz has been widely used in modelling multicomponent transport in pervaporation[50–53]. However, the formula does not satisfy the Gibbs-Duhem relationship as pointed out by Fornasiero et al.[54]. To overcome the drawback of **Eq. 2**, Fornasiero et al.[54] reformulated the original M-S equation (**Eq. 1**) in terms of the molar segment concentration. With the assumption of no volume change of the multicomponent system upon mixing, Fornasiero obtained the following expression:

$$\frac{C_i}{RT} \nabla_{T,P} \mu_i = - \sum_{\substack{j=1 \\ j \neq i}}^m \frac{\phi_i \phi_j (u_i - u_j)}{v D_{ij}^\circ} \quad (3)$$

where C_i is the molar concentration of the segment i (mol cm^{-3}), v is the segment molar volume ($\text{cm}^3 \text{mol}^{-1}$) and D_{ij}° is the MS diffusivity of the segments comprising species i and j . Several studies have reported the application of **Eq. 3** to modelling the transport of water through polymeric materials [55–57], diffusion of asphaltene[58–60], and the formation of polymeric nanoparticles[61]. The only limitation of **Eq. 3** is that a reference molar volume consistent with the thermodynamic model must be chosen. Ribeiro et al. [42] adapted the original M-S equations in terms of volume fraction to overcome the limitations of Heintz[49] and Fornasiero [54] and the following relation is obtained:

$$\frac{\phi_i}{\bar{V}_i RT} \nabla_{T,P} \mu_i = - \sum_{\substack{j=1 \\ j \neq i}}^m \left(\frac{N_i \phi_j}{D_{ij}} - \frac{N_j \phi_i \bar{V}_j}{D_{ij} \bar{V}_i} \right) \quad (4)$$

where $\bar{V}_i$ and N_i are the partial molar volume ($\text{cm}^3 \text{mol}^{-1}$) and the molar flux ($\text{mol cm}^{-2} \text{s}^{-1}$) of component i , respectively. D_{ij} is the modified M-S diffusivity, $\text{cm}^2 \text{s}^{-1}$. This formulation assumes that the friction factor between species are not symmetric (i.e. $D_{ij} \neq D_{ji}$)[42]. While this is generally not an issue for steady-state transport through a membrane ($N_m=0$), it would make difficult a treatment of transient phenomena with $N_m \neq 0$. Ribeiro et al.[42] used **Eq. 4** combined with the Flory-Huggins model to develop a set of ordinary differential equations to describe the steady-state transport of $\text{CO}_2/\text{C}_2\text{H}_6$ mixtures in a cross-linked poly(ethylene oxide) membrane. These differential equations were solved by numerical methods. In an attempt to avoid the complexity associated with solving such differential equations, Krishna [44] used a linearized M-S formulation for the transmembrane fluxes. This expression combines the original M-S equations and the Flory-Huggins model and it provides comparable accuracy.

In this work, we aim to investigate the feasibility of SRNF for the recovery of terpenes from their binary mixture with canola (rapeseed) oil under different experimental conditions. Free-standing PDMS films are prepared and used to determine the sorption isotherm of terpenes and their binary mixtures. The performance of PDMS/PAN composite membranes for the recovery of terpenes from canola oil

solutions is then investigated. The linearized Maxwell-Stefan formulation combined with the Flory-Huggins model is used to model these results.

2. Model development

According to the Flory-Huggins model for a ternary system (polymer (m), solvent (s) and oil(o)), the activity of the solvent (a_s) and the oil (a_o) are related to volume fractions assuming concentration independent interaction parameters as follows[48,62]:

$$\ln a_s = \ln \phi_s + (1 - \phi_s) - \frac{\phi_o \bar{V}_s}{\bar{V}_o} - \frac{\phi_m \bar{V}_s}{\bar{V}_m} + (\chi_{os} \phi_o + \chi_{sm} \phi_m)(\phi_o + \phi_m) - \chi_{om} \frac{\bar{V}_s}{\bar{V}_o} \phi_o \phi_m \quad (5)$$

$$\ln a_o = \ln \phi_o + (1 - \phi_o) - \frac{\phi_s \bar{V}_o}{\bar{V}_s} - \frac{\phi_m \bar{V}_o}{\bar{V}_m} + (\chi_{os} \frac{\phi_s \bar{V}_o}{\bar{V}_s} + \chi_{om} \phi_m)(\phi_s + \phi_m) - \chi_{sm} \frac{\bar{V}_o}{\bar{V}_s} \phi_s \phi_m \quad (6)$$

and

$$\phi_o + \phi_s + \phi_m = 1 \quad (7)$$

where χ_{os} is the mutual interaction parameter between the oil and the solvent.

For unidimensional binary mixture permeation across a polymeric membrane given that the membrane is a stationary phase ($N_m^V = 0$), **Eq. 4** can be rewritten as follows:

$$-\frac{\phi_s}{RT} \frac{d\mu_s}{dz} = \frac{N_s^V \phi_o - N_o^V \phi_s}{D_{so}} + \frac{N_s^V \phi_m}{D_{sm}} \quad (8)$$

$$-\frac{\phi_o}{RT} \frac{d\mu_o}{dz} = \frac{N_o^V \phi_s - N_s^V \phi_o}{D_{os}} + \frac{N_o^V \phi_m}{D_{om}} \quad (9)$$

where N_s^V and N_o^V are the volumetric flux of the solvent and the oil ($L m^{-2} hr^{-1}$), respectively.

Starting with **Eqs. 8 and 9** Krishna [44] developed a linearized solution for the volumetric fluxes of a binary mixture which can be adapted for the solvent and oil fluxes as follows:

$$N_s^V = \frac{1}{A L} [B_1(\Gamma_{11}\Delta\phi_s + \Gamma_{12}\Delta\phi_o) + B_2(\Gamma_{21}\Delta\phi_s + \Gamma_{22}\Delta\phi_o)] \quad (10)$$

$$N_o^V = \frac{1}{A \phi_m L} [B_3(\Gamma_{11}\Delta\phi_s + \Gamma_{12}\Delta\phi_o) + B_4(\Gamma_{21}\Delta\phi_s + \Gamma_{22}\Delta\phi_o)] \quad (11)$$

where $B_1 = \frac{\phi_s}{D_{os}} + \frac{\phi_m}{D_{om}}$, $B_2 = \frac{\phi_s}{D_{so}}$, $B_3 = \frac{\phi_o}{D_{os}}$, $B_4 = \frac{\phi_o}{D_{so}} + \frac{\phi_m}{D_{sm}}$, $\Gamma_{11} = \phi_s \frac{\partial \ln a_s}{\partial \phi_s}$, $\Gamma_{12} = \phi_s \frac{\partial \ln a_s}{\partial \phi_o}$, $\Gamma_{21} = \phi_o \frac{\partial \ln a_o}{\partial \phi_s}$, $\Gamma_{22} = \phi_o \frac{\partial \ln a_o}{\partial \phi_o}$, $A = \phi_m \left(\frac{\phi_s}{D_{os}D_{sm}} + \frac{\phi_o}{D_{so}D_{om}} + \frac{\phi_m}{D_{sm}D_{om}} \right)$, $\frac{D_{so}}{V_o} = \frac{D_{os}}{V_s}$, L is the membrane thickness, $\Delta\phi_s$ and $\Delta\phi_o$ are the volume fraction difference across the membrane for the solvent and the oil, respectively.

The thermodynamic factor Γ can be evaluated by the differentiation of the Flory-Huggins model (**Eqs. 5 -7**). Mulder et al.[62] provided explicit expressions for the derivatives $\partial \ln a_i / \partial \phi_j$. The arithmetic mean of the volume fractions of the penetrant inside the membrane at the feed and permeate interface $\frac{\phi_i^F + \phi_i^P}{2}$ is used to calculate (B) and (Γ) values as proposed by Krishna[44].

D_{so} and D_{os} represent mutual solvent-oil interactions and are termed exchange coefficients[63,64]. All numerical simulations were conducted using MATLAB® R2014b.

3. Materials and methods

3.1. Materials

Polyacrylonitrile (PAN) membranes (MWCO=20 kDa) were purchased from AMI, USA. A PDMS kit consisting of a pre-polymer (KE106) and a crosslinker (CAT-RG) was supplied by Shin-Etsu Chemicals (Japan). Food grade p -cymene, d -limonene and α -pinene were obtained from Sigma-Aldrich. A refined canola oil (Pure Vita - Australia) was used for the preparation of solvent-oil mixtures. The oil consists

of a mixture of triglycerides (6 wt. % unsaturated C₁₆ and C₁₈, 67 wt. % monounsaturated C₁₈ and 26 wt. % polyunsaturated C₁₈) with an average molecular weight of 877 g mol⁻¹. N-hexane and n-heptane were purchased from ChemSupply. All chemicals were used as received without further purification.

3.2. Preparation and characterisation of PDMS/PAN membranes

Composite PDMS/PAN membranes were prepared by the solution casting method and described in detail in our earlier work [36]. A 500-μm polymer film of a pre-crosslinked 7 % PDMS solution was cast on a wet PAN ultrafiltration support. The polymer solution was prepared in n-heptane with a polymer to crosslinker ratio of 2:1 (w/w). The membrane was thermally cured at 70 °C for 2 hrs, then at 120 °C for another 2 hrs. The final thickness of the PDMS layer was 23 ± 3 μm[36]. For the sorption study, free-standing PDMS films (average dry thickness 1.97 ± 0.04 mm) were prepared from 50 wt. % polymer solution in n-hexane with the same polymer to crosslinker mass ratio. The films were thermally cured at the same conditions used for the preparation of the composite membranes. The average density of PDMS films at 25 °C was estimated from mass measurements in air and distilled water as 1.022 ± 0.005 g cm⁻³.

3.3. Sorption and swelling study

The sorption isotherm was studied by the gravimetric method at atmospheric pressure at 25 °C and 40 °C. Pre-weighed PDMS films were soaked in oil-solvent mixtures of concentrations ranging from 0 to 100 wt. % oil and kept in an oven at the specified temperature. After a specified interval of time (24 hrs), the films were taken out, wiped gently with a tissue paper and reweighed. Each measurement was conducted within 30 seconds at most to minimize the experimental error resulting from solvent losses. The process was continued until a constant weight of the films was observed. The total degree of swelling (% SD) was calculated from the equilibrium masses as follows:

$$\%SD = \frac{m_a - m_b}{m_b} \times 100 \quad (12)$$

166 where m_a and m_b are the equilibrium and initial masses (g) of the PDMS film, respectively.

167 At the end of the sorption study, the partial uptake of both the oil and the solvent was obtained by a
 168 complete evaporation of the solvent sorbed by the films. This was accomplished by placing the films
 169 under vacuum at 50 °C for a sufficient time (4 days) until a stable mass of the films was observed. The
 170 difference between the mass after drying (m_{ad}) and the initial mass of the film (m_b) gives the partial
 171 oil uptake (m_o) as follows:

$$m_o = m_{ad} - m_b \quad (13)$$

172 Accordingly, the partial solvent uptake (m_s) is calculated as follows:

$$m_s = m_a - m_{ad} \quad (14)$$

173 3.4. Nanofiltration experiments

174 Nanofiltration of solvent/oil mixtures was conducted in a cross-flow cell (Sterlitech-CF042) as
 175 described in our earlier work [36]. The feed mixture was circulated by a high-pressure diaphragm
 176 pump (Hydra cell P200). A needle valve was mounted on the retentate line and used to control the
 177 pressure acting on the membrane which was measured by a pressure gauge (Floyd). To maintain a
 178 constant feed temperature, the feed line was immersed in a temperature-controlled water bath. A
 179 PTFE high foulant (65 mils, Sterlitech) feed side spacer was placed on the membrane feed side to
 180 minimise the concentration polarisation effects. A fresh membrane was used for each of the solvent-
 181 oil mixtures. Prior to the experiment, this membrane was conditioned by permeating n-hexane at 30
 182 bar for 3 hours followed by the pure terpene solvent for 3 hrs. The binary oil/solvent mixture was then
 183 filtered for another 3 hrs at the same pressure. The retentate was circulated back to the feed tank.

184 The permeate was collected and weighed on a digital balance (Ohaus) connected to a PC to record the
 185 mass measurements at intervals of 5 mins using the TWedge data acquisition software. In order to
 186 maintain consistent feed concentration, the permeate collected was returned back to the feed tank
 187 after collecting 100 ml.

188 The membrane performance was evaluated in terms of the permeate flux and the oil rejection. The
 189 permeate volumetric flux (N_p^V) was calculated as follows,

$$N_p^V = \frac{\Delta m_p}{\rho_p \Delta t A} \quad (\text{L m}^{-2} \text{ hr}^{-1}) \quad (15)$$

190 where Δm_p is the mass (kg) of the permeate collected at time Δt (hr), A is the membrane active area
 191 ($42 \times 10^{-4} \text{ m}^2$) and ρ_p (kg L^{-1}) is the permeate density. The oil retention in the permeate solution was
 192 determined by the solvent evaporation method [26,27,34,65]. A 3-ml sample was weighed and placed
 193 in a vacuum oven at 120 °C for 4 hours to remove the residual solvent. Afterwards, the sample was
 194 left to cool down at ambient conditions in a desiccator, then reweighed. The apparent oil rejection
 195 ($\% R_a$) was calculated from Eq. 16a, while the true rejection ($\% R_t$) was calculated from Eq. 16b:

$$\% R_a = \frac{c_B - c_P}{c_B} \times 100 \quad (16a)$$

$$\% R_t = \frac{c_F - c_P}{c_F} \times 100 \quad (16b)$$

196 where c_B , c_F and c_P are the oil concentrations (w/w) in the bulk feed, at the feed side of the membrane
 197 interface and in the permeate respectively.

4. Results and discussion

4.1. Sorption and swelling

The average uptakes of pure pinene, limonene, cymene and canola oil in PDMS films at both 25 °C and 40 °C were determined in our previous paper as 3.13, 2.77, 2.58 g/g dry membrane [36]. In the present case, we determined that the uptake of pure canola oil was three orders of magnitude lower at 3.90×10^{-3} g/g dry membrane. Stafie et al.[31] reported similar behaviour and attributed this to the large molecular size of the oil compared with the solvent. The partial uptakes of the solvents/canola oil from their binary mixtures in PDMS films are depicted in **Fig.1**.

Figure 1. Partial uptakes of A) pinene/ canola oil, B) limonene/canola oil and C) cymene/canola oil from their binary mixtures in PDMS films. Symbols represent experimental data while lines are the predictions from the Flory-Huggins model.

In the entire range of concentrations, the oil sorption levels were significantly lower than those of the solvents (note the different y-axis scales in **Fig. 1**). However, the partial oil uptake in oil/solvent mixtures was higher than that of the pure oil, reaching a maximum at 70 wt. % solvent. With the addition of solvent to the oil the degree of polymer swelling increases which in turn enhances the

sorption levels of oil. Similar behaviour has been observed during the sorption of ethanol/water and propanol/water mixtures in PDMS[66–68].

The ternary Flory-Huggins model was used to predict these sorption isotherms (**Fig. 1**). The binary Flory-Huggins interaction parameters for the pure solvents, as determined from our prior work were used directly, and the solvent/oil interaction parameters then determined by minimising the error between predicted and experimental data (**Table 1**) [48,66,69]. All interaction parameters used here were assumed concentration independent. The liquid phase oil/solvent solutions are assumed to behave ideally[31][70] so that the activity coefficient for the liquid mixture was assumed unity.

Table 1. Molar volumes and Flory Huggins interaction parameters for the solvents and the canola oil

	Molar volume, $\bar{V}_i$ (cm ³ mol ⁻¹)	Interaction parameter, χ_{im}	Interaction parameter, χ_{so}
α -pinene	161	0.58 ± 0.01 [36]	0.46 ± 0.02
d-limonene	163	0.59 ± 0.01 [36]	0.38 ± 0.02
p-cymene	158	0.60 ± 0.01 [36]	0.32 ± 0.01
Canola oil	960	4.51 ± 0.03	-----

4.2. Nanofiltration experiments

4.2.1. Concentration polarisation

Concentration polarisation results from the build-up of solute molecules in the boundary layer at the membrane interface[71]. This layer of solute introduces an additional mass transfer resistance which in turn reduce the permeate flux along the operation. Moreover, it contributes into the deterioration

of the membrane selectivity due to the increased solute concentration at the membrane surface, thus increasing the solute concentration driving force across the membrane. The effects of concentration polarisation can be minimised by operating at high cross-flow velocities and utilisation of a feed spacer [71]. Although several studies have reported the existence of concentration polarisation effects in organic solvent nanofiltration[27,65,72–74], only the work done by Peeva et al. reported a detailed investigation of concentration polarisation effects [75].

The effect of feed cross-flow velocities on the permeate flux was studied in the range of 18-52 cm s⁻¹ using hexane as the solvent. An increase in the permeate flux, particularly at higher pressures and feed concentration was observed with increasing the cross-flow velocity of the feed solution (**Supplementary Information, Fig. S1**). The mass transfer coefficients of the oil within the mass transfer boundary layer were determined using the approach developed by Sutzkover et al.[76].

$$k = \frac{N_p^V}{\ln \left\{ \frac{\Delta P}{\pi_F - \pi_P} \times \left[1 - \frac{N_p^V}{N_s^V} \right] \right\}} \times \frac{1}{36000} \quad (17)$$

where k is the oil mass transfer coefficient (cm s⁻¹), N_p^V and N_s^V are the permeate and the pure solvent fluxes (L m⁻² hr⁻¹), respectively, and π_F and π_P are the osmotic pressures of the feed and permeate solutions, respectively. The osmotic pressures were calculated using the Van't Hoff equation as follows:

$$\pi = RTC \quad (18)$$

where R is the universal gas constant, T is the absolute temperature and C is the molar concentration of the oil.

Using **Eq. 17**, the mass transfer coefficients of the oil at various experimental conditions were estimated graphically from the straight-line fit of N_p^V versus the $\ln \left\{ \frac{\Delta P}{\pi_F - \pi_P} \times \left[1 - \frac{N_p^V}{N_s^V} \right] \right\}$ as shown in **Fig. S2 (Supplementary information)**.

The mass transfer coefficients were then used to develop the mass transfer correlation of the system as (**see Supplementary Information**):

$$Sh = 0.569 Re^{0.56} Sc^{0.30} \left(\frac{d_h}{L} \right)^{0.5} \quad (19)$$

where Sh is the Sherwood number $\left(\frac{k d_h}{D_o} \right)$, Re is the Reynolds number $\left(\frac{\rho v d_h}{\mu} \right)$, Sc is the Schmidt number $\left(\frac{\mu}{\rho D_o} \right)$, d_h is the hydraulic diameter (cm) of the flow channel, L is the length of the flow channel (cm), ρ is the feed solution density ($g\ cm^{-3}$), μ is the dynamic viscosity of the feed solution (cP), v is the crossflow velocity of the feed solution ($cm\ s^{-1}$) and D_o is the diffusivity of the oil in the solution ($cm^2\ s^{-1}$).

4.2.2. Binary mixture filtration

The permeate flux of 10 wt. % and 30 wt. % oil solutions in the different solvents as a function of the net driving force (transmembrane pressure minus the osmotic pressure difference $\Delta P - (\pi_F - \pi_P)$) are provided in **Fig. 2 and 3**. As with our earlier work, the flux change with pressure is clearly non-linear reflecting the change in solvent concentration within the membrane as pressure increases.

Consistent with our prior work, oil/limonene solutions showed the highest permeate flux followed by oil/cymene, then oil/pinene. Increasing the oil content in the feed solution resulted in a significant decline in the permeate flux reflecting the greater viscosity of the solution and the lower degree of swelling (**Supplementary Information, Table S3**). The nonlinear flux-pressure behaviour observed in our previous work is also less evident with increasing oil content in the feed solution, reflecting reduced swelling in these systems. Increasing the temperature resulted in increased flux due to the

266 lower viscosity. These results are consistent with other workers[19,27,31,35] who have used similar
 267 silicone based polymers.

268 **Figure 2.** Permeate flux and true oil rejection ($\% R_t$) of 10 wt. % oil solutions as a function the pressure driving force at A) 25
 269 °C and B) 40 °C. The apparent oil rejection (based on the bulk oil concentrations) is provided in Fig. S5.

271 **Figure 3.** Permeate flux and true oil rejection ($\% R_t$) of 30 wt. % oil solutions as a function the pressure driving force at A) 25
 272 °C and B) 40 °C. The apparent oil rejection (based on the bulk oil concentrations) is provided in Fig. S6.

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The apparent oil rejection (Eq. 16a) is provided in **Fig. S5 and S6** in the **Supplementary Information** as a function of the driving force for the different oil-solvent solutions. The true oil rejection (Eq. 16b) is presented in **Fig. 2 and 3**. This rejection is calculated based on the oil concentration at the feed side of the membrane interface (c_F), that is, after taking account of concentration polarisation. This oil concentration was calculated from Eq. 20 using **the oil** mass transfer coefficients determined using **Eq. 19** and presented in **Table. S4** in the **Supplementary Information**.

$$\frac{c_F - c_P}{c_B - c_P} = \exp\left(\frac{N_P^V}{k}\right) \quad (20)$$

An increase in the oil rejection (%) was observed with increasing pressure, reflecting the increase in the solvent flux through the membrane with increasing pressure, while the oil flux remains relatively unchanged. Importantly, the rejection exceeds 80 % for pressures beyond 20 Bar which indicates that SRNF is a viable approach for solvent removal up to 30 wt. % oil. No significant difference in oil rejection between the different oil-solvent mixtures can be observed. Increasing the feed temperature resulted in a slight deterioration in the membrane selectivity. This may result from the lower viscosity of the oil at these temperatures, or the greater free volume inside the membrane. A decrease in oil rejection was also observed with increasing feed oil concentration.

4.2.3. Maxwell-Stefan Model simulations

The linearized M-S formulations developed by Krishna were then used to simulate the steady-state mass transfer of the oil/solvent binary mixture across the PDMS/PAN membrane at the different experimental conditions. The volume fractions of the oil and solvent at the upstream and downstream faces were obtained by solving the ternary Flory-Huggins model (**Eqs. 5-7**) using the interaction parameters χ_{sm} , χ_{om} , and χ_{so} presented in **Table 1** and after accounting for concentration polarisation on the upstream side.

In initial simulations, the solvent diffusivity in the membrane (D_{sm}) was taken as an adjustable parameter and allowed to vary at each pressure condition. The exchange coefficients D_{om} and D_{os} did

not vary with pressure, but were allowed to change with temperature and feed oil concentration. This approach gave an excellent fit to all data sets as shown in **Fig 4**.

Figure 4. Flux of pinene and oil obtained from the initial set of simulations where the diffusion coefficient was allowed to vary with pressure A) 10 wt. % oil with $D_{om} = 1.4 \pm 0.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{os} = 3.5 \pm 0.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and B) 30 wt. % oil with $D_{om} = 0.94 \pm 0.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{os} = 2.2 \pm 0.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Symbols represent experimental data where lines represent simulation results.

These preliminary simulations revealed a clear dependency of the solvent diffusivity (D_{sm}) and the average volume fraction of solvent in the membrane (**Fig. 5**). Such concentration-dependent diffusion coefficients are commonly observed in the literature and relate to the degree of membrane swelling. They are often described by an exponential relationship as follows [42,77–81]:

$$D_{sm} = D_{sm}^0 \exp(\beta_s \phi_s) \quad (21)$$

where D_{sm}^0 is the penetrant diffusivity in the limit $\phi_s \rightarrow 0$, β_s is an empirical constant reflecting the effect of penetrant concentration on the membrane swelling. As shown in **Fig. 5**, such a relationship would appear valid here across all oil concentrations (0, 10 and 30 wt. %), although there is clearly some variability related to experimental error.

Figure 5. Pinene diffusivity (D_{sm}) for 0, 10 and 30 wt. % oil solutions at 25 °C through PDMS/PAN composite membrane as a function of solvent volume fraction in the membrane, determined from the initial set of simulations.

A second set of simulations was thus carried out where (D_{sm}) was determined from **Eq.21**. It would have been preferable to determine the D_{om} exchange coefficient from filtration experiments using pure oil. However, the flux of oil in such experiments was below the level of detection, as the oil solubility in the absence of solvents is extremely low (**Table 1**). As a result, D_{om} was set as a fitted parameter. It is worthwhile noting that if the ‘friction’ between oil and solvents was ignored (i.e.) $D_{so} \gg D_{sm}$, $D_{os} \gg D_{om}$), negative fluxes were obtained, highlighting the importance of ‘friction’ on the oil transport. A choice of $\frac{D_{om}}{D_{os}} = 10$ for all experimental conditions provided robust simulation results and it further reduced the number of fitted parameters. The resulting model parameters are given in **Table 4** while typical results showing the fit to the experimental data are presented in **Figs. 6-8**. As it can be seen, both experimental and predicted flux data show a similar trend with deviations due to experimental error. The trend of constant oil flux with pressure occurs because this flux relates mostly to the concentration gradient across the membrane, which does not vary with pressure. On the other hand, the solvent fluxes show a non-linear increase with increasing pressure driving force which can be explained by the membrane swelling as reported by others[36,82].

Table 4. Fitting parameters of Eqs. 15 and 16 for permeation of oil/solvent binary mixtures through PDMS/PAN membrane.

The simulations were conducted for 0, 10 and 30 wt. % oil. $D_{os} = D_{om}/10$.

	T (°C)	$D_{sm}^0(\text{cm}^2 \text{s}^{-1}) \times 10^6$	β_s	Wt. % oil	$D_{om}(\text{cm}^2 \text{s}^{-1}) \times 10^6$
Pinene	25	0.9 ± 0.3	3.1 ± 0.6	10	3.1 ± 0.5
				30	1.2 ± 0.7
	40	1.7 ± 0.7	2.5 ± 0.6	10	4.0 ± 1.0
				30	2.3 ± 1.4
Cymene	25	0.8 ± 0.5	4.0 ± 1.0	10	3.8 ± 1.8
				30	2.5 ± 0.4
	40	2.1 ± 0.4	2.6 ± 0.3	10	6.0 ± 3.0
				30	3.6 ± 1.3
Limonene	25	1.5 ± 0.6	3.2 ± 0.6	10	6.0 ± 2.0
				30	2.6 ± 0.8
	40	3.2 ± 0.6	2.3 ± 0.3	10	7.6 ± 4.7
				30	5.7 ± 1.7

As shown in **Table 4**, the pre-exponential term for the solvent/membrane (D_{sm}^0) is highest for limonene, consistent with the higher flux observed with this solvent. The oil membrane exchange coefficients are also highest for limonene, indicative of greater solvent concentrations when this solvent was used. The oil diffusivity (D_{om}) and the pre-exponential term in **Eq. 21** (D_{sm}^0) increased with increasing the temperature as expected. The oil diffusivity (D_{om}) also decreased as the solvent concentration fell (i.e. the oil concentration increased) as expected from swelling effects.

Figure 6. Flux of pinene and oil through the PDMS/PAN membrane from A) 10 wt. % oil and B) 30 wt. % oil mixtures. Symbols represent experimental data and lines are the simulation results.

Figure 7. Flux of cymene and oil through the PDMS/PAN membrane from A) 10 wt. % oil and B) 30 wt. % oil mixtures. Symbols represent experimental data and lines are the simulation results.

Figure 8. Flux of limonene and oil through the PDMS/PAN membrane from A) 10 wt. % oil and B) 30 wt. % oil mixtures. Symbols represent experimental data and lines are the simulation results.

5. Conclusions

In this work composite PDMS/PAN membranes were prepared and used for the recovering of pinene, limonene and cymene from their binary mixtures with canola oil as a solute. The highest solvent fluxes were observed with oil/limonene mixtures whereas the oil rejections were comparable in the different oil/solvent mixtures and up to 90 % was achieved. The concentration polarisation effects on the system were studied and the mass transfer correlation of the system was developed. The sorption levels of the oil and the solvents were studied and were successfully predicted by the ternary Flory-Huggins model with concentration independent interaction parameters. Using linearized MS formulations, the oil and solvent fluxes across the membrane were calculated and were in a good agreement with the experimental observations. The results of this study indicate that SRNF has potential as an alternative to evaporation for the recovery of terpenes from vegetable oil mixtures. Future research will focus on improving the membrane selectivity to meet the industry requirement of more than 95 % oil rejection. This can be achieved by varying the cross-linking density and/or the membrane hydrophobicity by using functionalised PDMS.

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