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Poly[1-(trimethylsilyl)-1-propyne] as a solvent resistance nanofiltration membrane material

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Abstract

In this work, poly[1-(trimethylsily])-1-propyne] (PTMSP) has been considered as a new membrane material for non-aqueous nanofiltration applications in ethanol media (SRNF), and compared with other silicone-based commercially available membranes (MPF-50 and Membrane D). Noticeable membrane swelling in ethanol media ($66 \pm 4\%$) provides rather high ethanol permeation and the ethanol permeability normalized by the dry membrane thickness ($P \cdot d_{dry}$, kg m/(m² h × 10⁵ Pa) (kg m/(m² h bar))) exceeds those of the two commercially silicone-based membranes. Based on WAXS analysis, it seems that the swollen PTMSP membranes in ethanol still possess some nanoscale order and probably ethanol exists in PTMSP as clusters or even as a liquid phase. It was found that the retention of negatively charged Remazol Brilliant Blue R is higher than 90% (94.2% at 30 × 10⁵ Pa (30 bar)). Furthermore, the negative retention of the neutral dye Solvent Blue 35 (MW 350.4; -4.6%) shows that membrane–solute interaction is important and simple sieve mechanism cannot always explain the retention behavior for non-aqueous systems. It was found that higher dye–membrane interaction (distribution coefficient *K*) leads to lower retention of dyes with low molecular weight (around 350 Da).

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1. Introduction

The society is facing an acute problem of technogenic pollutions due to the use of hazardous organic solvents, such as toluene, hexane, chloroform etc., in chemical and food industries. From environmental point of view, a new way of solving this problem would be their replacement with environmental more friendly media (water, alcohols, ionic liquids, supercritical carbon dioxide, etc.). For example, the extraction efficiency of ethanol is twice as much of n-hexane in an accelerated solvent extraction of wheat germ oil [1]; over 92% of the corn oil can be extracted by ethanol at a temperature of 65 °C [2]. In organic synthesis, Suzuki aryl–aryl coupling reaction can also proceed in ethanol [3]. Moreover, fermentation derived alcohols (e.g. bioethanol and biobutanol) are more preferable for food industry because of the absence of traces of harmful organic

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chemicals, which are usually present in solvents produced from petroleum.

The effective recovery and re-use of chemicals (solvents and catalysts) in industrial processes can achieve reduction of air and other pollutions, of the required amount of chemicals, of industrial costs and, hence, of product's prime cost. In comparison to conventional separation technologies (e.g. distillation), the solvent resistance nanofiltration (SRNF) is more promising separation method due to absence of phase separation and energy saving. An excellent example of the industrial application perspectiveness of SRNF is the solvent recovery in dewaxing process [4]. In this case, the integration of SRNF modules based on asymmetric polyimide membranes achieves increased oil production by over 25% and reduction of energy consumption up to 20% per volume unit of product.

Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) is a hydrophobic glassy polymer ($T_g > 300$ °C) with an extremely high freevolume fraction (up to 25%), and exhibits intrinsic nanoporosity [5]. The nanoporosity of PTMSP is formed during polymer solution casting and no subsequent treatment is required. This is an

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advantage in comparison to other membrane formation methods (immersion precipitation, cross-linking, stretching, tracketching, etc. [6]). Besides, PTMSP has obvious advantages over commercially available hydrophobic solvent resistant membranes (e.g. MPF-50 (Koch), Membrane D (Osmonics)): the latter always contain residual solvents (e.g. water, ethanol, glycerol, etc.) acting as a pore preserving solution. Prior to the permeation experiments through these membranes, the porepreserving solvent should be removed. PTMSP has already been studied in liquid separation process, namely, reverse osmosis of ethanol from aqueous solutions [7,8] and pervaporation separation [5] of organics (e.g. alcohols and acetone) from water. In this work, PTMSP-material is evaluated for nanofiltration applications in ethanol media, and compared with silicone-based commercially available SRNF membranes (MPF-50, MPF-60 and Membrane D), in terms of membrane conditioning, solvent flux and solute retention.

2. Experimental part

2.1. Chemicals

The following chemicals were used as received: ethanol (100%; Acros Organics), chloroform (>99%; Merck), Solvent Blue 35 (dye content 98%; Aldrich), Safranin O (high purity biological stain, 95%; Acros Organics) and Remazol Brilliant Blue R (Acros Organics).

2.2. Membranes

The PTMSP polymer ($M_w = 190,000, M_n = 125,000;$ $[\eta] = 0.45 \text{ dl/g}$; cis/trans ratio: 63/37) was synthesized using NbCl₅, as a catalyst, and toluene as a solvent [9]. It has been chosen due to its good stability in time [10–12] and stable performance in pervaporation separation of ethanol [13]. The dense PTMSP-membranes were cast from 2 wt.% chloroform solution onto a commercial cellophane film. This allowed preparing membranes with dry thickness of 24-30 µm. The membranes were soaked in ethanol overnight at room temperature and atmospheric pressure and the cellophane support was removed before the NF experiment. Then, the PTMSP membrane films were cut and placed into the permeation cells in swollen state. The thickness of swollen membranes was used to calculate the permeability of ethanol through membranes; the thickness of dry membranes was used to compare with the other commercial available SRNF membranes. Prior to filtration studies with pure ethanol and ethanol-dye solutions, all membranes were conditioned with pure ethanol at 30×10^5 Pa (30 bar) until the alcohol flux was constant within deviation of 5%.

2.3. Permeation study

The experimental set-up is described in detail elsewhere [14]. The permeate collector was arranged in such a way to minimize the evaporation of ethanol during experiments. The effective surface area of each cell was 1.45×10^{-3} m². The liquid in the cells was stirred at 628.3188×10^{-1} rad/s (600 rpm). The total

flux, $J [kg/(m^2 h)]$ was measured as a function of pressure (up to of 30×10^5 Pa (30 bar)) at room temperature (24 ± 2 °C). The results, reported here, are the average values for two membrane cells with error no more than 5%. The measurements at each pressure were repeated to obtain fluxes with deviation up to 5%. Helium has been chosen to pressurize the liquid above the membrane due to insignificant difference in solubility of the gas in ethanol at different pressures. When nitrogen was applied, noticeable amount of gas bubbles were observed in the permeate (ethanol) due to difference in nitrogen solubility in ethanol [15].

2.4. Retention study

Experimental evaluation of MWCO of PTMSP in ethanol was performed using three dyes with different molecular weight and charge: Solvent Blue 35 (MW 350.4; neutral), Safranin O (MW 350.8; positively charged) and Remazol Brilliant Blue R (MW 624.5; negatively charged). Some characteristics of these dyes are listed in Table 1. For the retention studies, the concentration of each dye was 86 mM due to low solubility of some of them in ethanol. An ultrasonic water bath was used, for 15 min, for complete dissolving of the dyes, especially the charged ones, in ethanol. The analysis of the dye concentration was performed using UV-vis spectrophotometer Cary 300 Scan. Table 1 shows the wavelength used (λ_{max}) and the linearity of the calibration lines for each dye solution. For the UV-vis calibration lines, six solutions of different concentrations in the range of 0-86 mM were prepared from mother solution (86 mM) using the dilution method. Additional solution with concentration of 100 mM was prepared for Solvent Blue 35 dye. The dye retention values were calculated using Eq. (1):

$$R(\%) = \left(1 - \frac{C_{\rm p}}{C_{\rm f}}\right) \times 100\% \tag{1}$$

where C_p and C_f are the dye concentration (g/g) in the permeate and the feed, respectively. The dense PTMSP-membranes were pre-conditioned in pure ethanol at 30×10^5 Pa (30 bar) and then were used in the retention investigation. Tests for each dye were performed at pressures of 18×10^5 and 30×10^5 Pa (18 and 30 bar) at 24 ± 2 °C; for Solvent Blue 35 tests were done only at a pressure of 30×10^5 Pa (30 bar). The measurements were repeated to obtain the total flux and dye retention values with maximum deviation of 5%.

2.5. Sorption and swelling experiments

Dense PTMSP membrane samples with diameter of 63.2 mmand thickness of 500 μ m were used for the sorption and swelling

Table	1				
Some	characteristics	of dyes	and their	ethanol	solutions

Dye	Charge	MW	λ _{max} (EtOH) (nm)	Concentration (mM); <i>R</i> ²
Solvent Blue 35	Neutral	350.4	644	0-100; 0.9998
Safranin 0	Positive	350.8	533	0-51; 0.9994
Remazol Brilliant Blue R	Negative	624.5	582	0–86; 0.9994

tests in ethanol. Soaking in ethanol was carried out for 2 days to reach equilibrium. After removal of the excess of ethanol from the surface, the membrane sizes and weight were measured.

Dense PTMSP-membranes with thickness of about 500 μ m were also placed into 86 mM ethanol–dye solutions. Total sorption value was estimated from the difference in weight between the swollen and dry sample. The concentration of dye into the membrane was determined from the difference in solution concentration before and after sorption. The distribution coefficient of the dye between solution (C_S) and membrane (C_M) was expressed as:

$$K = \frac{C_{\rm M}}{C_{\rm S}} \tag{2}$$

$$C_{\rm M} = \frac{m_{\rm dye}}{m_{\rm ethanol} + m_{\rm dye} + m_{\rm PTMSP}} \tag{3}$$

$$C_{\rm S} = \frac{m_{\rm dye}}{m_{\rm ethanol} + m_{\rm dye}} \tag{4}$$

where m_{ethanol} , m_{dye} , m_{PTMSP} are the weight of ethanol, dye and PTMSP, respectively (g), C_{M} the equilibrium dye concentration in the membrane (g/g) and C_{S} is the equilibrium dye concentration in the solution in contact with membrane (g/g).

2.6. WAXS-analysis

PTMSP membranes with thickness of 500 μ m were used for wide-angle X-ray diffraction analysis. PTMSP-samples were immersed in ethanol or n-octanol overnight and then placed in plastic bag (transparent for X-rays) for analysis to avoid alcohol evaporation. The WAXS analysis was carried out in transmission mode using Rigaku diffractometer "RU-200 Rotaflex", 40 kV, 140 mA with radiation Cu K α , λ = 0.154 nm.

3. Results and discussions

In this part, PTMSP-membranes will be evaluated as a new material for non-aqueous nanofiltration applications in ethanol media, and will be compared with other commercially available solvent resistant nanofiltration membranes (MPF-50, MPF-60 and Membrane D).

3.1. Pure ethanol nanofiltration

In this study, all dense PTMSP membranes were soaked in ethanol overnight, and installed into the cell in swollen state. The swelling degree of PTMSP in ethanol is $66 \pm 4\%$, and the ethanol sorption is 0.89 ± 0.02 g/g. To compare the membrane performances for samples with different thickness, the ethanol flux has been normalized by the thickness of swollen PTMSP-membranes, measured directly after soaking in ethanol and before installation into the cells. All PTMSP-samples in the range of thickness of 24–30 µm (dry thickness) have ethanol permeability normalized by swollen membrane thickness $P \cdot d_{sw}$ with deviation up to 5%.

Fig. 1 shows that the typical PTMSP membranes have constant ethanol permeability ($P \cdot d_{sw}$) even after 3 days of experi-



Fig. 1. Pure ethanol permeability through swollen PTMSP-membranes at pressure of 10×10^5 Pa (10 bar).

ment at transmembrane pressure of 10×10^5 Pa (10 bar). Fig. 2 presents the normalized ethanol flux through swollen membranes in time at various pressures. As shown, a steady state ethanol flux is obtained after 1–2 h of filtration.

Fig. 3 shows the ethanol flux normalized by the swollen membrane thickness versus the applied transmembrane pressure in the range of $0-30 \times 10^5$ Pa (0-30 bar). The relation is linear and reproducible when the applied pressure is increased stepwise from 0 to 30×10^5 Pa (0 to 30 bar) or decreased from 0 to 30×10^5 Pa (0 to 30 bar). From the slope of graph (Fig. 3), the pure ethanol permeability for swollen PTMSP-membrane $P \cdot d_{sw}$ is $8.3 \times 10^{-6} \text{ kg m/(m^2 h \times 10^5 \text{ Pa})}$ $(8.3 \times 10^{-6} \text{ kg m/(m^2 h bar)})$. In contrast to published data for MPF-50 [16] (dry thickness of top layer is 100 nm range [17]), the PTMSP dense membranes do not exhibit membrane compaction up to pressure of 30×10^5 Pa (30 bar) in ethanol. The ethanol flux through the commercially available silicone-based Membrane D (Osmonics; dry thickness of top layer is 600 nm range [18]) increases linearly with pressure up to 54×10^5 Pa (54 bar) [19].



Fig. 2. Normalized ethanol flux through dense PTMSP membranes in time at various pressure.



Fig. 3. Effect of pressure on pure ethanol flux normalized by thickness of swollen PTMSP-membranes (filled symbols: pressure increases stepwise, open symbols: pressure decreases stepwise).

Table 2 presents a comparison of the ethanol permeation through our membranes and various commercial membranes. To recalculate the permeability $(kg/(m^2 h \times 10^5 Pa) (kg/(m^2 h bar)))$ from the literature data, ethanol density of 0.789 g/cm³ was used. For the composite membranes, the ethanol flux is basically determined by the transport through the top-selective layer; the resistance in the support layers should be negligible [20]. To directly compare the performance of PTMSP to the other membranes, one has to normalize the permeability P by the top-layer thickness. For the commercial membranes, only the thickness of dry top-layer could be obtained based on SEM analysis: MPF-50–100 nm [17] and Membrane D—about 600 nm [18]. It is known that the drying required to take SEM pictures can lead to irreversible changing in membrane structure, but nevertheless the SEM analysis gives us a sufficiently accurate estimation of the membrane thickness for the comparison. The variations of ethanol permeability reported for the MPF-50 and MPF-60 membranes may be explained by the difference in pretreated history and experimental conditions. Furthermore, the operated

pressure may also play significant role due to possible membrane compaction [16] at high pressure.

The normalized ethanol permeability measured in this work $(P \cdot d_{dry} = 495.7 \text{ kg m/(m^2 h \times 10^5 Pa)} (495.7 \text{ kg m/(m^2 h bar)}))$ is comparable with that for n-hexyldimethylsilylated PTMSP (498.8 kg m/(m^2 h \times 10^5 Pa) (498.8 kg m/(m^2 h bar)) [8]) and somewhat higher that the one for dense PTMSP-membranes (431.7 kg m/(m^2 h \times 10^5 Pa) (431.7 kg m/(m^2 h bar)) [7]), used in reverse osmosis. Unfortunately, the authors of ref. [7] did not give further details for the PTMSP samples in order to explain the difference.

For the PTMSP membranes, the ethanol permeability normalized by the dry membrane thickness $P \cdot d_{dry}$ exceeds those of MPF-50 and Membrane D membranes. Unfortunately, no published data concerning the top-layer thickness for MPF-60 or SolSep-030505 could be found in order to make the comparison.

Wijmans and Baker in their review [26] refer to PTMSP as an extremely high free volume polymer (up to 25%) and suggest that the transport mechanism is in transition range between the pore-flow and the solution-diffusion models. It should be emphasized that PTMSP cannot be clearly characterized in terms of porosity. Diffusion coefficient of ethanol D_i for swollen PTMSPmembrane estimated from the slope of linear dependence of normalized flux on pressure (Fig. 3) using an approximation of the solution-diffusion model for pure solvent [26]:

$$J_{\rm i} = \frac{D_{\rm i} K_{\rm i} \Delta p}{d_{\rm sw} R_{\rm g} T} \tag{5}$$

The diffusion coefficient calculated is 1.27×10^{-8} m²/s and higher by an order of magnitude than the value of ethanol selfdiffusion (1.1×10^{-9} m²/s), which was estimated for a temperature of 25 °C [27]. This marked difference can be explained that assumption of the model, polymer is dense non-porous membrane, is not obviously applicable for PTMSP.

The solvent transport depends on the polymer structure and the polymer–solvent interaction. The structure of PTMSP

Table 2

Comparison of pure ethanol permeabilit	y through various	hydrophobic n	anofiltration membranes
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Membrane	Manufacturer	d _{dry} selective layer	<i>T</i> (°C)	p (×10 ⁵ Pa (bar))	$P (kg/(m^2 h \times 10^5 Pa) (kg/(m^2 h bar)))$	$\begin{aligned} & P \cdot d_{\rm dry} \times 10^8 \\ & (\text{kg m}/(\text{m}^2 \text{ h} \times 10^5 \text{ Pa}) \\ & (\text{kg m}/(\text{m}^2 \text{ h} \text{ bar}))) \end{aligned}$	Ref.
MPF-50	Koch	100 nm	25	20	5.17	51.7	[21]
			25	7	4.10	41.0	[22]
			RT	10	3.31	33.1	[23]
			RT	30	3.13	31.3	[16]
MPF-60	Koch	NK ^a	21	27.6	1.43	_	[24]
			RT	30	0.79	-	[16]
SolSep-030505	SolSep BV	NK	RT	10	0.94	_	[23]
Membrane D	Osmonics	600 nm	23	0–54	0.02	1.4	[19,25]
PTMSP	_	40 µm	30	77	0.21	431.7	[7]
Co-polymer PTMSPb	_	20 µm	25	38.5	0.25	495.7	[8]
PTMSP	-	20 µm	24 ± 2	0-30	0.25	498.8	This work

^a NK, not known.

^b n-Hexyldimethylsilylated PTMSP.



Fig. 4. WAXS-spectroscopy: (1) dry PTMSP-membrane, (2) PTMSP swollen in ethanol and (3) ethanol.

was studied with wide-angle X-ray scattering (WAXS). X-ray diffraction patterns for dry PTMSP show a major maximum at d = 9.0 Å (2Θ is 9.8°) and additional maxima at about d = 3.2, 4.5 Å (2Θ is 19.5° and 27°, respectively) (Fig. 4). This can be explained by the appearance of supramolecular ordering in PTMSP, which differs from the common short-range order of amorphous polymer. Despite the relatively high swelling degree in ethanol media ($66 \pm 4\%$), the swollen PTMSP still possesses some nanoscale order (8.2 Å; $2\Theta = 10.6^{\circ}$), which corresponds to the one for glassy PTMSP in the dry state. Furthermore, the WAXS analysis might suggest that the ethanol molecules form clusters in PTMSP or even exist as a liquid phase (see peak corresponding to ethanol in the liquid state at $2\Theta = 21.2^{\circ}$, 4.2 Å). However, definite conclusions about clustering can only be drawn after further investigation (e.g. IR-spectroscopy, DSC).

This investigation, however, is beyond the scope of the present study.

3.2. Retention studies

Solvent Blue 35 and Safranin O with almost the same molecular weight (MW 350) but different charge have been chosen to evaluate the solutes interaction with the PTMSP. The negatively charged Remazol Brilliant Blue R (MW 624.5) was also used as a model solute to study the effect of solute molecular weight. The concentration of each individual dye in ethanol was low (86 mM) to avoid osmotic, polarization and fouling effects. The experiments for each dye solution were performed for several hours at each pressure. No change in permeability or rejection was observed during these tests (error less than 5%). Table 3 presents the total flux of ethanol–dye solutions through the PTMSP membranes normalized by the swollen thickness and the dye retention by PTMSP at pressures of 18×10^5 and 30×10^5 Pa (18 and 30 bar), at 24 ± 2 °C.

Table 3 shows that the total flux is comparable with that of pure ethanol through the PTMSP membranes. The retention of the neutral Solvent Blue 35 is negative at a pressure of 30×10^5 Pa (30 bar), while the positively charged Safranin O with same molecular weight is partially retained (71.3%) by the PTMSP membranes. The retention of the negatively charged dye Brilliant Blue R (MW 624.5) is 94.2% at 30×10^5 Pa (30 bar). The negative retention of Solvent Blue 35 shows that a simple sieving mechanism is not enough to explain the retention behavior for PTMSP performance. Based on the above, one can anticipate that the MWCO is in the range of 600 Da. However, solute transport in organic nanofiltration may significantly depend on solute nature, solute dissociation, transmembrane pressure, type of solvent and therefore the exact value for the

Table 3

Nanofiltration of Solvent Blue 35, Safranin O and Brilliant Blue R; total flux normalized by swollen membrane thickness and retention characteristics of PTMSP in ethanol media at a temperature of 24 ± 2 °C

	MW (dye charge)	PTMSP-sample (after sorption)	Total sorption (g/g)	K ^a	$J \cdot d_{\rm sw} \times 10^{-4}$ kg m/(m ² h)		Retention (%)	
					$18 \times 10^5 \text{ Pa}$ (18 bar)	$30 \times 10^5 \text{ Pa}$ (30 bar)	$18 \times 10^5 \mathrm{Pa}$ (18 bar)	$30 \times 10^5 \text{ Pa}$ (30 bar)
Ethanol	46.1	Colorless transparent	0.89	_	1.53	2.43	_	_
Solvent Blue 35	350.4 (neutral)	Blue transparent	0.82	11.4	-	2.48	-	-4.6
Safranin 0	350.8 (positive)	Red transparent	0.82	4.5	1.54	2.46	74.0	71.3
Brilliant Blue R	624.5 (negative)	Colorless transparent	0.80	0 ^b	1.64	2.46	94.3	94.2

^a K is the distribution coefficient of the dye between solution and polymer.

^b No dye presence in PTMSP is observed with regard to experimental error.

Table 4

Retention properties of commercially available membranes MPF-50 and Membrane D in ethanol media (literature data)

Membrane	Solute	MW (charge)	$p (\times 10^5 \text{ Pa (bar)})$	<i>T</i> (°C)	Retention (%)	Ref
MPF-50	2,2'-Methylenebis-(6-tert-butyl-4-methyl phenol)	340 (neutral)	20	25	2.7	[21]
	DL-Alpha-tocopherol hydrogen succinate	531 (neutral)	20	25	1.4	[21]
	Raffinose	504 (neutral)	15	30	41	[23]
	Raffinose	504 (neutral)	7–45	25	30	[22]
Membrane D	Sudan IV Fast Green FCF	384 (neutral) 808 (negative)	15 20	$\begin{array}{c} 25\pm2\\ 25\pm2 \end{array}$	-5 98	[25] [25]

MWCO can not be really given. Fractional retention curves data for neutral molecules are needed to determine the MWCO of these PTMSP-membranes.

Table 4 shows literature data for silicone-based membranes MPF-50 and Membrane D in ethanol. Negative retention of the neutral dye Sudan IV (MW 384) in polar solvents, such as methanol (-10%) and ethanol (-5%) at 20×10^5 Pa (20 bar) has been also reported for hydrophobic Membrane D, while a positive retention of the same dye has been reported for the non-polar solvent n-hexane (25% at 15×10^5 Pa (15 bar)) [25]. Using the surface force-pore flow model, it was shown that lower retention in alcohol media is a result of higher attractive force between Sudan IV and the membrane in alcohol compare with hexane.

Preferable sorption of one component over the others often determines the overall selectivity in nanofiltration with dense separation layers. For example, it was reported that sorption of high concentration solution of carboxylic acids can significantly decrease the hexane transport through asymmetric cellulose acetate membranes in reverse osmosis process [28]. It should be mentioned that the PTMSP samples after sorption experiment with Solvent Blue 35 or Safranin O were colored. However, the membrane was still colorless after immersion in Remazol Brilliant Blue R solution, and this indicates an absence of sorption of the dye into PTMSP. The equilibrium distribution coefficient K of individual dye between ethanol solution (86 mM) and PTMSP are presented in Table 3. The explanation of absence of Remazol Brilliant Blue R sorption in membrane and, therefore, high retention of that by PTMSP (>90%) might be a sieving effect next to exclusion based on less favorable interaction. In the case of the other two dyes, higher dye-membrane interaction for Solvent Blue 35 (K = 11.4) compare with Safranin O (K = 4.5) leads to lower retention by PTMSP, -4.6 and 71.3%, respectively. In other words, retention of the dyes with low molecular weight is determined by sorption selectivity.

4. Conclusions

In this work, poly[1-(trimethylsilyl)-1-propyne] (PTMSP) has been considered as a new membrane material for nonaqueous nanofiltration applications in ethanol media, and compared with other silicone-based commercially available membranes (MPF-50 and Membrane D). Noticeable membrane swelling in ethanol media ($66 \pm 4\%$) provides rather high ethanol permeation and the ethanol permeability normalized by the dry membrane thickness ($P \cdot d_{dry}$, kg m/(m² h × 10⁵ Pa) (kg m/(m² h bar))) exceeds those of the two commercially silicone-based membranes. Based on WAXS analysis, it seems that the swollen PTMSP membranes in ethanol still possess some nanoscale order and probably ethanol exists in PTMSP as clusters or even as a liquid phase. It was found that the retention of negatively charged Remazol Brilliant Blue R is higher than 90% (94.2% at 30×10^5 Pa (30 bar)). Furthermore, the negative retention of the neutral dye Solvent Blue 35 (MW 350.4; -4.6%) shows that membrane-solute interaction is important and simple sieve mechanism cannot always explain the retention behavior for non-aqueous systems. It was found that higher dye-membrane interaction (distribution coefficient K) leads to lower retention of dyes with low molecular weight (around 350 Da).

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Nomenclature

$C_{\rm S}$	equilibrium dye concentration in the solution with
	contact with membrane (g/g)
C_{f}	dye concentration in the feed (g/g)
$C_{\rm p}$	dye concentration in the permeate (g/g)
$\dot{C_{M}}$	equilibrium solute concentration in the membrane
	(g/g)
$d_{\rm dry}$	dry membrane thickness (m)
$d_{\rm sw}$	swollen membrane thickness (m)
$D_{\rm i}$	diffusion coefficient of ethanol (m ² /s)
J	flux through membrane $(kg/m^2 h)$
Κ	distribution coefficient of solute
Ki	distribution coefficient of ethanol
methanol	ethanol weight (g)
m _{dye}	dye weight (g)
<i>m</i> _{PTMSP}	PTMSP weight (g)
MW	molecular weight of the solute
MWCO	molecular weight cut-off (g/mol)
p	pressure ($\times 10^5$ Pa (bar))
Р	permeability $(kg/m^2 h \times 10^5 Pa (kg/(m^2 h bar)))$
R	membrane retention (%)
Rg	gas constant (J/(mol K))
Т	temperature (K)
Greek le	tters
[<i>n</i>]	intrinsic viscosity (dl/g)

λ_{max} wavelength with maximum absorbance (nm)

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