

1 Towards azeotropic MeOH-MTBE separation using pervaporation chitosan-based 2 deep eutectic solvent membranes

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28

29 **Abstract**

30 Deep eutectic solvents (DESs) are a new class of solvents that can offset some of the
31 major drawbacks of common solvents and ionic liquids. When dealing with the
32 preparation of dense membranes, the use of DESs is still challenging due to their low
33 compatibility with the polymer phase. In this research, a novel L-proline:sulfolane (molar
34 ratio 1:2) DES was synthesized and used for the preparation of more sustainable bio-
35 based membranes using chitosan (CS) as a polymer phase. The compatibility among
36 both phases (polymer and DESs) and their ability to form homogenous membranes was
37 preliminary studied. In this regard, scanning electron and confocal microscopies were
38 used to completely map the structure of the resulting membranes evidencing a complete
39 homogenous structure. The membranes were also characterized in terms of contact
40 angle (CA), Fourier transformed infrared spectroscopy (FTIR), mechanical resistance and
41 swelling degree (uptake). Preliminary pervaporation tests for the separation of a methanol
42 (MeOH)- methyl *tert*-butyl ether (MTBE) azeotropic mixture were, thus, performed. In this
43 regard, the addition of DESs provided an enhanced separation efficiency in comparison
44 to pristine CS membranes. Thanks to the morphology and properties exhibited, the newly
45 developed membranes can be considered as excellent bio-based candidates to be
46 explored in other gas selective and solvent oriented membrane operations.

47

48 **Keywords:** Deep eutectic solvents; membrane preparation; chitosan; methanol/MTBE;
49 pervaporation.

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52 **1. Introduction**

53 According to the “*Twelve Principles of Green Chemistry*” established by Anastas and
54 Warner [1], there is a big need of implementing green materials and processes in the
55 manufacturing of new products. Therefore, the research community is continuously
56 exploring the potentialities of new feedstocks to follow such principles aiming at the
57 preservation of the environment [2]. Today, deep eutectic solvents (DESs), which are a
58 new class of solvents, have been categorized as “green alternatives” to conventional
59 solvents for various applications, including metal plating and coatings [3], sustainable
60 media in organic reactions [4], extraction and separation of biologically active compounds
61 from natural sources [5], CO₂ capture [6], desulfurization [7], as stationary phases for
62 chromatography [8], enzymatic biodiesel production [9], chemical and biocatalysis [10],
63 to mention just a few. DESs overcome most of the major drawbacks of common solvents
64 and ionic liquids, together with several advantages, such as low toxicity, low cost, easy
65 handling, biodegradability, biocompatibility and reusability [11]. Typically, DESs are
66 synthesized by combining hydrogen bond acceptor (HBA), like quaternary ammonium
67 salt, with hydrogen bond donor (HBD) compounds [3].

68 When dealing with membrane preparation, DESs have been primarily proposed and used
69 as additives in the manufacture of DES-liquid supported membranes [12,13], with the aim
70 of enhancing the separation properties of polymeric membranes. The superior



71 performance exhibited by DESs based membranes are generally attributed to a facilitated
72 molecule transport and adsorption through the functional groups of DESs [14–16]. DESs
73 have been also explored as pore forming agents in the fabrication of asymmetric
74 membranes via phase-inversion method [17].

75 To the best of our knowledge, there are no studies employing DESs in the preparation of
76 non-porous (well-known as dense) membranes. This is because, fundamentally, the
77 compatibility of DESs and polymer phases, for their complete merging, is still a challenge.
78 Therefore, in this work, we describe the successful incorporation of a specific DES (L-
79 proline:sulfolane) into chitosan (CS) membranes surmounting one of the most common
80 constraints related to the proper dispersion of the DES into the polymer matrix.

81 In order to achieve this goal, a hydrophilic and water-soluble DES, such as L-
82 proline:sulfolane (molar ratio 1:2), was firstly synthesized. Afterward, its ability to form
83 dense homogenous membranes was evaluated using CS as a continuous polymer phase.
84 The cross-linking effect on membrane properties and performance was also evaluated
85 using glutaraldehyde (GA). To evaluate their miscibility, the complete blending of both
86 phases (DES and polymer) was studied by mapping the complete membrane structure.
87 For this purpose, scanning electron microscopy (SEM) and scanning confocal electron
88 microscopy (SCEM), were employed. Secondly, the generated membranes were also
89 characterized in terms of contact angle (CA), Fourier transformed infrared spectroscopy
90 (FTIR), mechanical test and swelling degree (uptake). Preliminary pervaporation tests
91 towards the methanol (MeOH)- methyl *tert*-butyl ether (MTBE) separation have been
92 performed in order to prove the applicability of the new synthesised membranes.

93



94 **2. Methodologies**

95 *2.1. Reactants and materials*

96 L-proline (purity ≥ 98 %, Sigma Aldrich), sulfolane (purity ≥ 99 %, Alfa Aesar), phosphoric
97 acid (purity ≥ 85 %, POCH S.A.) and GA (grade II, 25 wt%) were acquired and used
98 without further purification. CS (medium molecular weight) was acquired from Sigma
99 Aldrich. MeOH (99.8%) and MTBE (99.7%) were also purchased from Sigma-Aldrich (St.
100 Louis, USA) and used without further purification.

101

102 *2.2. DES synthesis*

103 *L-proline:sulfolane*, at a molar ratio (1:2), was synthesized. Basically, 32.4 g of L-proline
104 (0.282 mol), 67.6 g of sulfolane (0.564mol) and 705 mL of phosphoric acid 1M (0.705
105 mol) were mixed at 1000 rpm (70°C) until obtaining a transparent solution. Lately, the
106 excess of water was removed out by means of a rotary vacuum evaporator (Rotavapor
107 R-300 with a V-300 vacuum pump, BUCHI).

108

109 *2.3. Membrane preparation*

110 CS-DES membranes were prepared via dense-film casting method and solvent
111 evaporation. The CS dope solutions (1.5 wt.%) in acidic water solutions were prepared.
112 Herein, an acetic acid solution (2wt.% in distilled water) was preliminarily prepared. The
113 polymer dope solutions were stirred over 24 h (at room temperature). Later, 5 wt.% of
114 DES (L-proline:sulfolane), with respect to CS concentration, was separately added in the
115 respective dope solutions. The resulting mixture was stirred for 4 h before applying the
116 *in-situ* cross-linking procedure. The latter procedure was utilized to ensure the entrapment



117 of the DES into the polymer phase, in which chemical cross-linking with GA was used
118 [18]. Here, *in situ* cross-linking procedure was carried out by adding 100 μL of GA and
119 100 μL of HCl (to speed up the reaction) to every dope. This was stirred for 15 min, cast
120 on clean Petri dishes and then dried at room temperature for 2 days. The final appearance
121 of membranes was of a homogeneous and transparent film with approximately 25 μm of
122 thickness. To sum up, the prepared membranes were labelled as follows: pristine CS,
123 cross-linked CS (xCS), chitosan:L-proline:sulfolane (CS:PRO:SUF) and cross-linked
124 chitosan: L-proline:sulfolane (xCS:PRO:SUF).

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126 2.4. Membrane characterization

127 2.4.1. *Scanning electron microscopy (SEM)*. The morphological structure of the
128 membrane surface and cross-section was preliminarily analysed using a SEM instrument
129 (Hitachi S-3400N, Japan), operating with a tungsten electron source. The secondary
130 electron detector was used for the analysis, and micrographs were made under 5 kV
131 accelerating voltage. Before the microanalysis, a 10 nm layer of metallic gold was
132 sputtered at each sample surface to compensate the low surface conductivity. The
133 corresponding images were acquired at suitable magnification. In the case of cross-
134 section analysis, all samples were prepared by cryogenic fracture after immersion in liquid
135 N_2 .

136 2.4.2. *Scanning confocal electron microscopy (SCEM)*. In order to assess the
137 homogeneity and dense structure of the resulting membranes, a complete scanning of
138 the structure was performed using a LSM 800 T-PMT confocal microscope (Carl Zeiss
139 AG, Oberkochen, Germany) with a CCD camera [19]. Images were acquired and



140 processed with ZEN Blue software.

141 2.4.3. *Fourier transformed infrared spectroscopy (FTIR)*. FTIR was performed on all
142 membrane formulations described previously using a Nicolet iS10 FTIR (Thermo Fisher
143 Scientific) spectrometer equipped with a DTGS detector and a Golden Gate diamond ATR
144 accessory. The spectra were recorded in the 4000–400 cm^{-1} wave number range at a
145 resolution of 16 cm^{-1} .

146 2.4.4. *Water contact angle (CA)*. The water contact angle measurements were performed
147 using ultrapure water by the method of the sessile drop using a goniometer OCA15 (Data
148 Physics). The average and standard deviation values were determined for three
149 measurements.

150 2.4.5. *Mechanical test*. Mechanical properties of pristine CS and xCS:PRO:SUF
151 membranes were measured using a Zwick/Roell Z2.5 test unit (BTC-FR2.5TN-D09,
152 Germany). Measurements were performed at room temperature (25 °C) using a
153 membrane sample of 1 × 5 cm. The samples were extended at the constant elongation
154 rate of 5 mm min^{-1} until their break. Elongation at break, Young's modulus and tensile
155 strength were, then, determined. Each sample was analyzed at least four times, the
156 results were expressed as the average and standard deviation. Mechanical tests were
157 carried out on all the investigated membranes before and after use in PV tests (14.3 wt%
158 MeOH; 85.7 wt% MTBE).

159 2.4.6. *Uptake*. The degree of swelling (uptake) of the membranes was determined for pure
160 feed components (MeOH, MTBE), various MeOH-MTBE mixtures (5, 10 25, 50, wt.%
161 MeOH) as well as azeotropic mixture (14.3% MeOH and 85.7% MTBE). Three small
162 pieces of membranes (1 × 5 cm) were weighed and immersed in the solvent mixtures at



163 30 °C for 48 h. The wet membrane samples were quickly wiped with tissue paper to
164 remove the excess free liquid on their surface and immediately weighed with a digital
165 balance (Gibertini, Crystal 500, Italy, Crystal 500, Gibertini Elettronica srl, Milan, Italy)
166 with an accuracy of 0.001 g. In general, the uptake was calculated as follows:

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$$168 \quad \text{Uptake (\%)} = \frac{W_w - W_d}{W_d} \cdot 100 \quad \text{Eq. (1)}$$

169 where W_w and W_d correspond to the weight of the wet and dry membranes, respectively.

170

171 2.5. Pervaporation tests

172 The PV experiments were performed in a laboratory-scale setup, whose graphical
173 drawing and details can be found elsewhere [20]. Basically, a mixture (250 mL) of an
174 azeotropic MeOH-MTBE (14.3–85.7 wt.%, respectively) solution was poured in the
175 pervaporation cell. The feed operating temperature was varied (at 25, 35, 45 °C) and
176 controlled with an accuracy of 0.01 °C using a thermo digital circulating bath (Neslab RTE-
177 201, USA). The vacuum on the permeate side (at 0.05 mbar) was maintained by using a
178 RV5 two-stage vacuum pump (Edwards, UK).

179 The membrane, having an active area of 9.6 cm², was placed on a porous support within
180 the membrane cell. The permeated vapour was condensed and collected in a glass trap
181 placed in a liquid nitrogen condenser. Once reached the steady-state, the permeates
182 were collected for 5 h of experiment and immediately weighted to determine the total
183 permeate flux. The permeate flux (J) was determined as follows:

$$184 \quad J = \frac{Q}{A \cdot t} \quad \text{Eq. (2)}$$

185 where Q corresponds to the weight of the permeate (expressed in kg), A corresponds to
186 the membrane area (m^2) and t is the operating time (h). The partial flux (J_i) for each
187 component i was calculated by multiplying its weight fraction (y_i) in the collected permeate
188 sample by the total permeate flux (J), as follows:

$$189 \quad J = Y_i \cdot J \quad \text{Eq. (3)}$$

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191 The separation factor (α) was calculated according to the following equation:

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$$193 \quad \alpha = \frac{y_{MeOH}/y_{MTBE}}{x_{MeOH}/x_{MTBE}} \quad \text{Eq. (4)}$$

194 where y and x correspond to the weight fractions of the components in the permeate and
195 feed, respectively. The permeate composition was determined by an Abbe 60 type direct
196 reading refractometer (Bellingham + Stanley Ltd., UK) at 25 °C. The J and α values were
197 expressed as the average of more than two runs to ensure the accuracy of the outcomes.

198

199 **3. Results and discussion**

200 **3.1. Scanning electron microscopy (SEM).**

201 In general, all resulting membranes showed a smooth and uniform surface pattern without
202 signs of plastic deformation, being common for dense polymeric membranes [21].
203 Particular attention has been devoted to the cross-section analyses of the membranes,
204 as shown in **Figure 1**. For instance, the pristine CS membrane (Figure 1a) displayed a
205 crater-like pattern, which is commonly generated during deformation caused by the
206 freeze-fracture of polymer membranes. Such a pattern has been well documented in



207 pristine [22] and cross-linked CS membranes [18]. Regarding the CS blend with
208 PRO:SUF (Figure 1c), the membrane exhibited a more homogeneous dense pattern
209 structure with non-visible pores. Similarly, cross-linked CS-DESs membranes (Figure 1d)
210 confirmed a dense structure with non-visible defects among the phases and additives
211 (like DES agent). Particularly, such characteristics can be used as an evidence of the
212 good miscibility of the hydrophilic PRO:SUF DES in CS, as demonstrated in other
213 polymer/polyethylene glycol blends [23,24].

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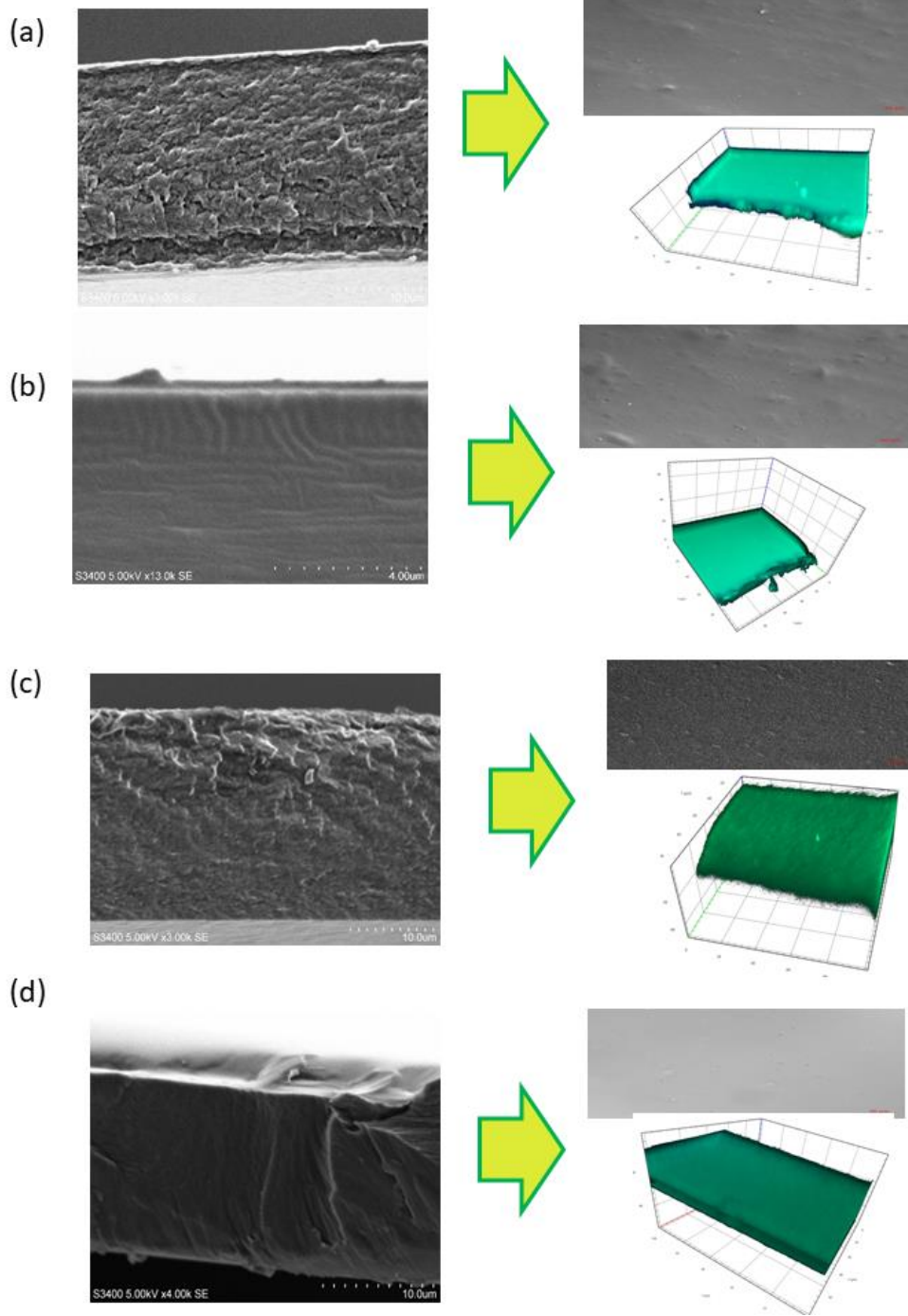


Figure 1. SEM cross-section, surface view and 3D view images of the prepared membranes based on CS and DES. (a) pristine CS (CS), (b) cross-linked chitosan (xCS) (c) chitosan:L-proline:sulfolane (CS:PRO:SUF), (d) cross-linked chitosan:L-proline:sulfolane (xCS:PRO:SUF).

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221 In this work, the addition of the DES has evidenced to provide a tighter and smoother
222 structure in CS membranes. However, in literature it has been reported that DESs are
223 employed in the fabrication of porous membranes by acting as pore forming agents
224 [17,25]. In general, the use of pore formers is aimed, in phase-inversion techniques, to
225 generate large pores and voids in the membrane matrix [26]. The pore formers (such as
226 polyethylene glycol and polyvinyl pyrrolidone) are generally removed by the membranes
227 after its formation by washing them with water.

228 In our case, the approach was oriented to physically entrap the selected DES into the
229 membrane thus exploiting the benefits that it may offer once preserved in the membrane
230 structure. DESs have been successfully applied for the extraction, separation and
231 purification of biomolecules due to their ability to form hydrogen bonds via dipole-dipole
232 and other specific solute-solvent interactions [27,28].

233 The resulting CS-based membranes visually exhibited a dense structure. However, there
234 is still a possibility that the used DESs can also be supported (or encapsulated) within the
235 polymeric structure. Therefore, further analysis of the overall membrane structure were
236 performed. In this case, SCEM was used for mapping the structures of the membranes,
237 as detailed in **Figure 1** (right side). It is known that polymer blending with other phases
238 strongly depends on its available chemical functionalities. If functional groups are not
239 present between phases, a poor interaction and hence low miscibility will be obtained
240 [29]. This is also fundamental for blending polymers with inorganic phases (e.g.,
241 nanoparticles), in which the nano-sized materials tend to be chemically functionalized to
242 reach a good compatibility and contact between polymer and filler interfaces [30].

243 In particular, CS owns a plenty of amino and hydroxyl groups, making it an excellent



244 candidate for polymer blending [31]. Also, in the case of DESs, they may also offer a
245 series of functional groups which can interact with CS giving to the final membrane
246 specific properties. At this point, it is likely that this new DES employed (PRO:SUF),
247 bearing different functional groups (such as amino, hydroxyl, and carbonyl), can interact
248 with CS. For instance, **Figure 1** shows the surface view of the synthesized membranes
249 confirming their smooth and homogenous surfaces with absence of pinholes and defects.
250 Regarding the 3D view, the images were created by stacking together 210 fluorescence
251 intensity scans of each membrane. Every single scan is a picture representation of a 0.25
252 μm cross-section of each membrane, each scan is created by merging green and blue
253 from two fluorescence channels (DAPI and AF488, excitation: 353 and 493 nm, emission
254 465 and 517 nm, detection 400-580 nm). By scanning the membrane structure, the
255 complete blending between CS and DES was confirmed, evidencing a dense-like
256 morphology. Also, there was no evidence of DES phase separation or encapsulation in
257 the polymer matrix.

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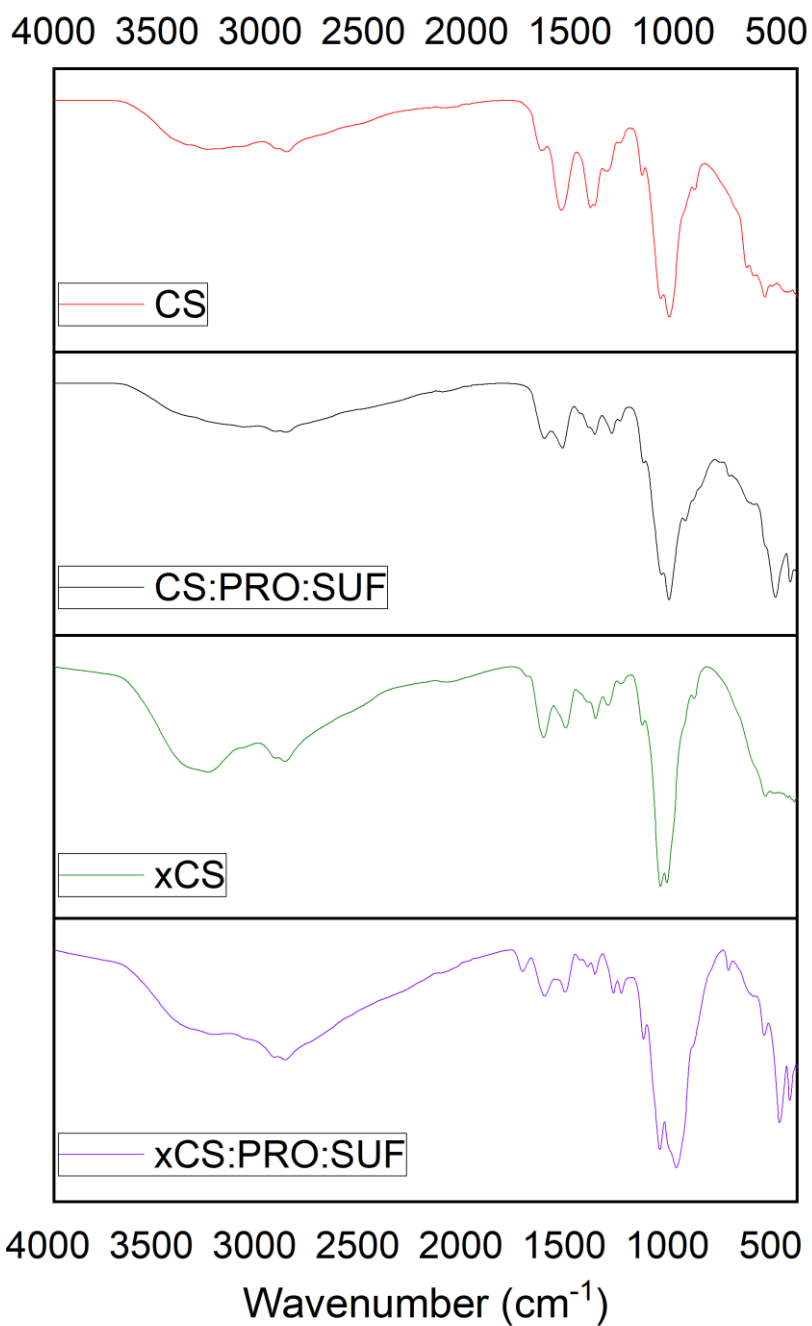
260 3.2. *Water contact angle (CA) and Fourier transformed infrared spectroscopy* 261 *(FTIR)*

262 The FTIR results (shown in Figure 2) can be the evidence of the affective blending of the
263 DES into the CS polymer membrane matrix. All spectra exhibit a strong and broad non-
264 symmetric band at about 3400 cm^{-1} that results from overlapping of the O-H and N-H
265 stretching vibrations of functional groups engaged in hydrogen bonds. The spectrum of
266 CS shows typical absorption bands at 1600 cm^{-1} (for C=O stretching in amide group),



267 1550 cm^{-1} (for N-H bending in no acetylated 2-aminoglucose) and 1560 cm^{-1} (for N-H
268 bending in amide group), as reported in literature [32]. Absorption bands at 1100 cm^{-1} ,
269 corresponding to an antisymmetric stretching of the C-O-C bridge, 1050 cm^{-1} and 1000
270 cm^{-1} , related to skeletal vibrations implying the C-O stretching, are typical for CS.
271 Interestingly, the blending of CS with DES provoked a slight shift on such characteristic
272 polymer bands, giving a proof of the good interaction among the phases and thus
273 compatibility. For the cross-linked CS-DES membranes with GA, they exhibit an increase
274 in the absorption between 1600-1650 cm^{-1} which can be attributed to imine bonds N=C
275 [33,34]. The stretching at 1540 cm^{-1} , 1710 cm^{-1} and 2900 cm^{-1} corresponds to free-
276 aldehydic bonds and increased C-H stretch, respectively. Also, the presence of aliphatic
277 amino groups diminishes as much as the peak 1100 cm^{-1} does. These shifts may be the
278 reason of the more hydrophobic nature of the membranes compared to the pristine and
279 CS-DES blends (non-cross linked) [18], which is in agreement with the CA data.

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Figure 2. FTIR spectra for pristine and cross-linked CS membranes and their blends with DESs.

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An important aspect to address during the incorporation of DESs in membranes deals with the possible effect on the membrane hydrophilicity/hydrophobicity. The pristine CS membrane showed a CA value of 90° , in line with the data reported in literature which place the CA of CS polymer between $84-88^\circ$ [32,35]. The variability in the hydrophilic/hydrophobic nature of CS strongly depends on the deacetylation degree of the polymer; for instance, a high degree of deacetylation provides highly hydrophilic CS membranes [36], meaning more amine groups available on the CS molecule which can promote the water transport through the membrane matrix [37]. In principle, the hydrophilicity of CS belongs to its hydrophilic groups, such as -OH and -NH₂; however, such hydrophilicity decreases when cross-linking is applied. For this reason, the CA value reached up to 95° when CS was cross-linked.

The incorporation of the PRO:SUF DES in the CS membrane led to a drastic decrease of the contact angle value (34°). This may suggest that the polar groups provided by the DES (such as amino and carboxyl) have a big impact in enhancing the hydrophilicity of the overall membrane.

308 **Table 1.** CA values and mechanical properties of the pure CS membranes and its
 309 blends with DES.

Membrane	CA (°)	Image:	Before PV			After PV		
			Young's modulus (N/mm ²)	Tensile strength (N/mm ²)	Elongation at break (%)	Young's Modulus (N/mm ²)	Tensile strength (N/mm ²)	Elongation at break (%)
CS	90±0.5		415 ± 32	61 ± 9	11 ± 7	632 ± 3	65 ± 11	12 ± 4
xCS	95±0.5		1467 ± 41	40 ± 11	6 ± 2	853 ± 206	45 ± 12	9 ± 2
CS:PRO:SUF	34±2		163 ± 10	38 ± 10	16 ± 4	164 ± 19	41 ± 2	12 ± 1
xCS:PRO:SUF	89±7		226 ± 47	50 ± 13	11 ± 2	205 ± 66	35 ± 13	8 ± 1

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 311 Surprisingly, the cross-linking of the CS membrane containing DES (xCS:PRO:SUF
 312 membrane) led to an increase of the CA value (89°) close to the pristine CS membrane.
 313 It is worth mentioning that, after a cross-linking protocol, the reaction of GA with primary
 314 amino groups results in the formation of two Schiff bases involving both aldehyde groups
 315 of the GA molecule [32,38]. Herein, the decrease of the number of the -NH₂ groups could
 316 be the responsible of the contact angle increase in the xCS:PRO:SUF membrane.
 317 As can be seen in **Table 1**, the blending of the DES with CS decreased specific
 318 mechanical properties, such as Young's modulus and tensile strength (with a decrease

319 of about 61 and 38%, respectively). However, the impact of DES addition on membrane
320 mechanical properties was observed to be reduced when the cross-linking was adopted.
321 In this case, the reduction of Young's modulus and tensile strength, in comparison to the
322 pristine CS membrane, was much reduced (45 and 18%, respectively). DESs can act as
323 plasticizers into a CS polymer matrix causing a decrease in the intermolecular
324 interactions. The addition of plasticizers in CS, in fact, conducts to a transition from a
325 rigid to a softer material with elastic properties [39]. In particular, the loss of tensile
326 strength is associated to the breakup of the film network provoked by the incorporation of
327 the additive into the polymer. Similar results have been documented in literature in CS
328 films when mixed with different additives [40] and natural chlorine chloride/ malonic acid
329 eutectic mixtures [41]. It has been, in fact, documented that the increase in DES
330 concentration is responsible of the decrease of Young's modulus and tensile strength in
331 CS [41]. On the contrary, elongation at break was surprisingly preserved by the DES
332 addition, which has been associated with the increase in the free volume in the polymer
333 matrix. According to Jakubowska et al. [41], a possible expansion of a free volume fosters
334 polymeric chain translation, being worthy in the stabilization of films in the elastic flow
335 regime. In this case, the cross-linking could have re-established the original free volume
336 of CS films after DES blending since the elongation at break was comparable to the initial
337 value of the CS membrane.

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339 3.3. *Pervaporation performance*

340 3.3.1. *Effect of operating temperature on permeation and separation factor.*

341 The PV separation data for all tested membranes is reported in **Table 2**.

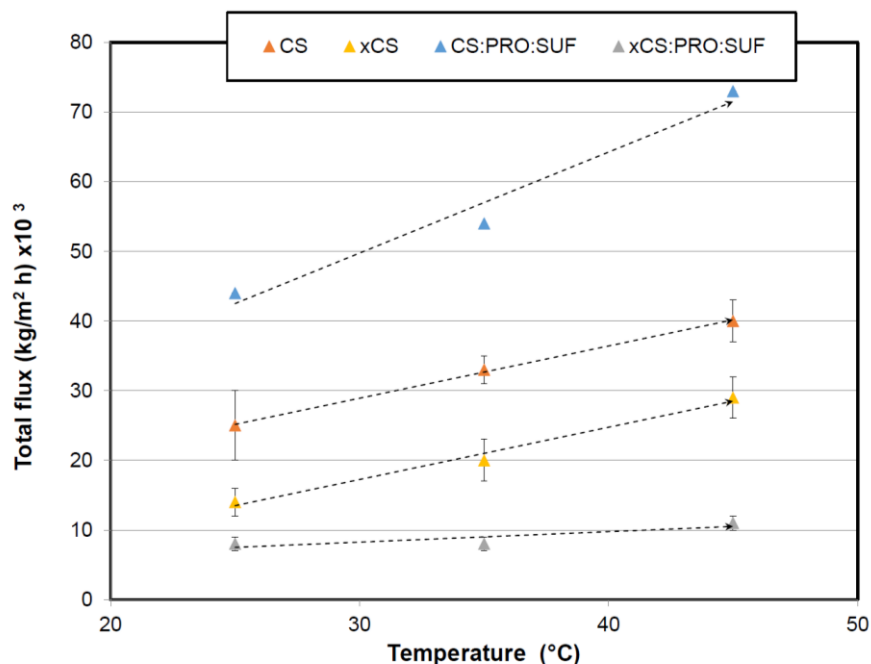


342 **Table 2.** Performance of CS-DES membranes as a function of temperature (feed
 343 composition: 14.3 wt.% MeOH; 85.7 wt.% MTBE).

Temperature	CS			
	Total flux (kg m ⁻² h ⁻¹) × 10 ³	Separation factor (α)	MeOH partial flux (kg m ⁻² h ⁻¹) × 10 ³	MTBE partial flux (kg m ⁻² h ⁻¹) × 10 ³
25°C	25±5	12.2± 0.11	16.9±3	8.2±2
35°C	33±2	5.6± 0.10	16.4±3	17±3
45°C	40±3	2.7± 0.09	17.4±2	27±4
xCS				
25°C	14±2	28.8± 0.10	11±2	2±0.2
35°C	20±3	27.6± 0.10	16±3	3±0.3
45°C	29±3	24.9± 0.11	24±2	5±0.5
CS:PRO:SUF				
25°C	44±1.5	1.3±0.21	7±0.1	33±1.7
35°C	54±0.0	1.1±0.06	8±5.7	45±0.4
45°C	73±3	1.0±0.029	11±0.8	62±2.8
xCS:PRO:SUF				
25°C	8±2	35.4±0.15	6.8±2	1±1
35°C	8±1	31.5±0.25	7±2	1.4±1
45°C	11±3	28.5±0.22	9.2±1	2.1±1

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 345 **Figure 3** graphically illustrates the effect of the feed temperature on the total permeate
 346 flux, where a permeation increase, as a function of temperature, was observed in pristine

347 CS membrane and its blend with DES. Such a behaviour is a typical trend in polymeric
 348 membranes since polymer chains are more flexible at higher temperatures fostering the
 349 sorption ability of the solvent molecules, conducting to an increase in permeation of
 350 compounds across the intermolecular distances of the polymeric membrane [42].
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 353 **Figure 3.** Effect of feed temperature on total flux (feed composition: 14.3 wt.% MeOH;
 354 85.7 wt.% MTBE, pressure: 0.05 mbar). The curves are only guides to the eye.

355
 356 The temperature dependence on permeate flux was determined by means of the
 357 Arrhenius model, as expressed in Equation 5.

$$J = J_0 \cdot \exp\left(-\frac{E_A}{R \cdot T}\right) \quad \text{Eq. (5)}$$

358
 359 where J_0 corresponds to the pre-exponential factor, E_a refers to the apparent

361 activation energy for permeation (for the mixture and each compounds)
362 and $R \cdot T$ corresponds to the common energy term. Using the logarithms for Eq. 5.
363 E_A can be calculated in a linear function, which confirms that an Arrhenius relationship
364 occurs between total fluxes and operating temperature; in other words, an increase in
365 total permeation takes places by increasing temperature. From **Table 3**, it can be seen
366 that crosslinked CS membrane display lower E_a values for methanol (ca. 13.34 kJ/mol)
367 than MTBE (ca. 15.66 kJ/mol), which gives an input of methanol selectivity of CS.
368 Interestingly, the incorporation of the hydrophilic DES lowered the E_a value for
369 methanol up to 0.49 kJ/mol in xCS:PRO:SUF membrane, while the E_a value for MTBE
370 was less affected. At this point, the E_a decreased substantially towards MeOH
371 compared with MTBE in the range of 25-45 °C. It is worth mentioning that the PV
372 process in the operating temperature affects primarily the permeation rate of MeOH,
373 and does influence minimally the MTBE transport. It is clear that the presence of DES
374 lowers the energy needed for the molecules to permeate across the membranes and
375 this is particularly evident for MeOH molecules. This also can be supported by the
376 hydrophilic nature of the DES, which definitely may display a preference for polar
377 compounds (like MeOH) [28].

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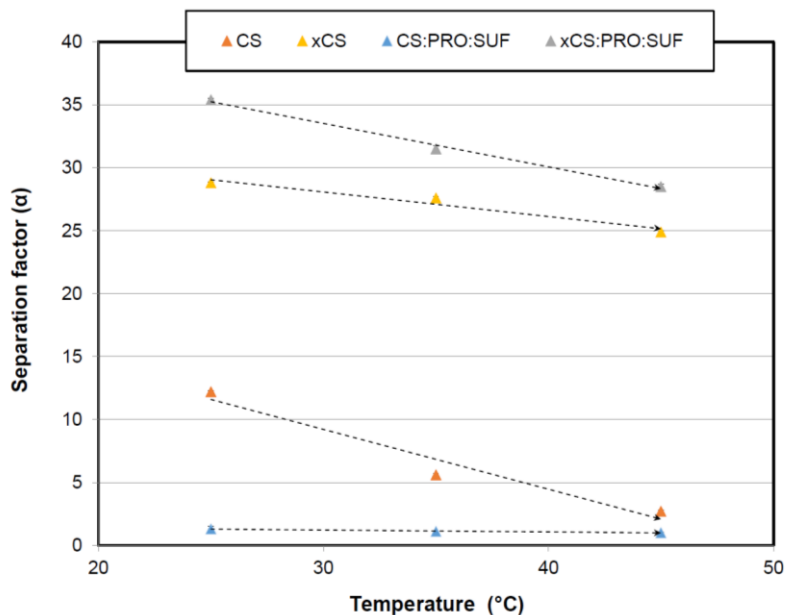
383 **Table 3.** Apparent activation energies for total permeate, MeOH and MTBE partial
 384 fluxes of the CS-DES membranes.

385

Membrane	Activation energy values (kJ/mol)		
	Total	Methanol	MTBE
CS	8.05	5.12	20.44
xCS	12.46	13.34	15.66
CS:PRO:SUF	8.64	10.79	7.70
xCS:PRO:SUF	5.38	0.49	12.63

386

387 Regarding the selectivity, the separation factor in pristine CS membrane decreases as a
 388 function of the temperature (see **Figure 4**). Importantly, such selectivity was improved by
 389 incorporating the DES with the aid of in situ cross-linking, reaching a value up to 35 (at
 390 25°C). In general, high separation factors and lower permeation rates were, in fact,
 391 obtained at the lowest temperatures for all membranes. This agrees with the free volume
 392 theory, which establishes that thermal motion of polymer chains in the amorphous regions
 393 induces a free volume increase. As temperature increases, the frequency and amplitude
 394 of the chain jumping (i.e., thermal agitation) increases, and consequently, the free volume
 395 becomes larger [43]. Even if the kinetic diameters of MeOH and MTBE substantially differ
 396 (3.6 and 6.2 Å, respectively), the thermal motion of the polymeric chains facilitates also
 397 the diffusion of larger molecules (like MTBE) across the membrane conducting to a
 398 decrease in the separation factor. Additionally, the separation factor decrease agrees with
 399 the fact that activation energy values for MTBE were larger than for MeOH.



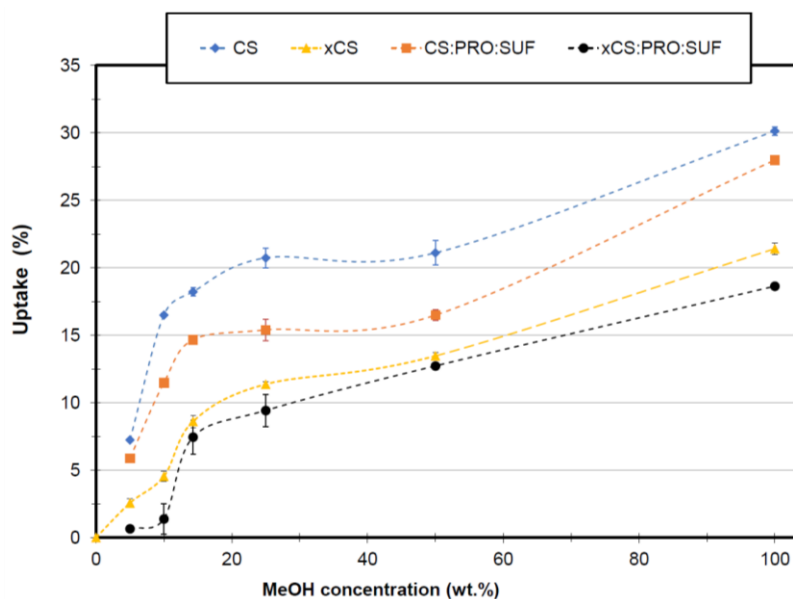
400
 401 **Figure 4.** Effect of feed temperature on the separation factor (feed composition:
 402 14.3 wt.% MeOH; 85.7 wt.% MTBE, pressure: 0.05 mbar). The curves are only guides to
 403 the eye.

404
 405 It is important to mention that *in situ* cross-linking was required at this specific case. As
 406 can be seen in **Table 2**, the direct incorporation of DES into CS led to a loss of the
 407 selective properties of the membrane. To date, it has been documented that DES addition
 408 tends to increase the free volume in polymer matrices. According to Jakubowska et al.
 409 [41], a possible expansion of the free volumes fosters the polymeric chain translation,
 410 which, if from one side can enhance the stabilization of films at elastic flow regime
 411 (improving the elongation at break properties), from the other side it can lower the
 412 selective performance of the membrane.

413 Finally, the determination of the uptake properties of the studied membranes is reported
 414 in **Figure 5**. It can be seen that all membranes display low uptake values, e.g., lower

415 than 7%, for low MeOH concentrations (up to 10 wt.%). However, the increase of MeOH
416 concentration in the feed mixture, led to a higher swelling of the membranes. The addition
417 of DES caused a decrease in the solvent uptake ability of the membranes. This may
418 support Jakubowska's hypothesis [41] that DES provides stabilization of the CS
419 membranes. Of course, the uptake was substantially suppressed when cross-linking was
420 applied since such a protocol makes polymer membranes more resistant to the solvent
421 mixtures due to a higher restriction of polymer chains mobility [44]. It is well known that
422 PV membranes which are less susceptible to swelling are preferred to guarantee more
423 stable performance when separating organic/organic feed solutions. To point out, the
424 membranes also exhibited, to some extent, stable mechanical properties since the
425 properties did not change strongly after use in PV testing (see **Table 1**).

426



427

428 **Figure 5.** Uptake of CS-DES membranes at different MeOH concentrations (at 30 °C).

429

The curves are only guides to the eye.

430

431 3.3.2. Performance comparison of CS-DES membranes with literature

432 As in all membrane-based technologies, it is clear that the PV performance of either
433 polymer and composite membranes is strongly influenced by several factors, including
434 membrane properties (such as membrane material, nature, structure) and operating
435 conditions (such as feed concentration, temperature, driving force, flow rate, etc.) [45].

436 To some extent, the membrane structure depends on the membrane preparation protocol
437 used [46]. Therefore, since most of the research has been carried out at different
438 operating conditions, it is challenging to provide a fair comparison of PV data among
439 different studies [47]. In this work, we tentatively compare the performance of different
440 membranes (pristine, blend and composites) at close operating conditions, as enlisted in

441 **Table 4.** The main bridle of hydrophilic polymers (like CS) is related to their high swelling
442 tendency which may limit the mechanical properties and stability of the membranes
443 prepared with them. If a membrane is swollen, there is a lack of efficient separation
444 performance due to the polymer chains mobility. Therefore, many efforts have been done
445 to improve the physicochemical properties of CS, by using several approaches such as
446 the blending with polymers, agents and inorganic nanomaterials.

447 In this work, the best performance, in terms of selectivity, was obtained for the
448 xCS:PRO:SUF membrane, which exhibited a separation factor of 35.4 (at 25 °C). Such a
449 value corresponds to 3-fold higher separation factor compared with pristine CS
450 membrane; unfortunately, the permeation flux was compromised. When compared with
451 literature, our xCS:PRO:SUF membranes showed better selectivity than other polymers,
452 such as modified polyether ether ketone (PEEKWC), poly(vinyl alcohol) (PVA), acrylic



453 acid plasma polymerized poly(3-hydroxybutyrate), and composite membranes (GO-
 454 polyimide, polyamide filled with Al₂O₃) (see **Table 4**). Definitely, the permeation rate could
 455 be improved by handling the operating temperature but it may affect the selective
 456 properties.

457 On the contrary, xCS:PRO:SUF membranes did not show a competitive selectivity in
 458 comparison to cellulose acetate/polyvinyl pyrrolidone (PVP), PVA/cellulose acetate
 459 blend, cross-linked PVA, cellulose acetate filled with HZSM5 membranes, among other
 460 composites. At this point, it is confirmed that these membranes (i.e., xCS:PRO:SUF) are
 461 still limited by their selective-permeable trade-off.

462
 463 **Table 4.** Comparison of CS-DES membrane performance with some pure polymeric
 464 and mixed matrix membranes at close MeOH-MTBE azeotropic conditions.

Membrane material	Filler loading:	MeOH Concentration	Operating conditions	J (kg m ⁻² h ⁻¹)	Separation factor (α)	Reference:
xCS:PRO:SUF	-	14.3 wt.% MeOH	25 °C, 0.05 mbar	0.008	35.4	This work
GO-polyimide	4 wt. %	14.3 wt.% MeOH	45 °C, 0.05 mbar	0.091	9.0	(Castro-Muñoz et al., 2019)
PEEKWC	-	15 wt.% MeOH	40 °C, 6.1 mbar	0.068	10	[49]
PVA	-	30 wt.% MeOH	45 °C, 15 mbar	0.900	25	[50]

Poly(lactic acid)	-	15 wt.% MeOH	30 °C, 6 mbar	0.620	5	[51]
Poly(lactic acid)	-	14.3 wt.% MeOH	40 °C, 6.1 mbar	0.090	75	[52]
Cellulose acetate-PVP blend	-	20 wt.% MeOH	45 °C, 3 mbar	0.225	340	[53]
PVA-cellulose acetate blend	-	15 wt.% MeOH	45 °C, 17 mbar	796*	1427	[54]
Acrylic acid plasma polymerized poly(3-hydroxybutyrate)	-	20 wt.% MeOH	45 °C, 1.3 mbar	11*	3	[55]
Cross-linked PVA	-	20 wt.% MeOH	50 °C, 0.4 mbar	0.036	1230	[56]
Cross-linked PAMHEMA	-	11 wt.% MeOH	50 °C, 1.33 mbar	0.140	150	[57]
Polyamide filled with Al ₂ O ₃	10 wt.%	50 wt.% MeOH	30 °C	15*	20	[58]
cellulose acetate filled with HZSM5	0.5 wt.%	20 wt.% MeOH	40 °C, 3.3 mbar	4.2*	150	[59]
Sulfonated polyarylethersulfone with cardo filled with [Cu ₂ (bdc) ₂ (bpy)] _n	30 wt.%	15 wt.% MeOH	40 °C, 6 mbar	0.28	2300	[60]
cellulose acetate filled with ZnO	10 wt.%	31 wt.% MeOH	40 °C, 5 mbar	2*	400	[61]
Sulfonated polyarylethersulfone with cardo filled with MIL-53(Al)-SO ₃ H	15 wt.%	15 wt.% MeOH	40 °C, 6 mbar	0.368	1990	[62]
CS	-	30 wt.% MeOH	50 °C	0.120	7	[63]

465 * Normalized flux by thickness.

4. Concluding remarks and future perspectives

In this work, dense CS-hydrophilic L-proline:sulfolane membranes have been, for the first time, successfully prepared and characterized. By fully mapping the structure of the membranes, this study demonstrated complete miscibility and embodiment of the proposed novel hydrophilic DESs (PRO:SUF) into the polymer phase. Importantly, since we have used environmentally friendly materials (such as CS, water, organic DES), these membranes can be considered as pioneering work in manufacturing more sustainable dense bio-based membranes.

After preliminarily testing in MeOH-MTBE separation using PV process, this new concept of membranes (xCS:PRO:SUF) presents a 3-fold higher separation efficiency than the pristine CS. As an outlook, the future works can focus on improving the permeation rates of the membranes in order to make them more attractive for other PV separations. In fact, thanks to their ability in forming H-bonding interactions, DESs may promote an enhanced separation of other polar molecules from azeotropic mixtures [27]. Moreover, the novel membranes, due to their dense nature, can be also interesting to be tested in gas separation applications.

Finally, in view of making the entire fabrication process fully sustainable, GA can be replaced with a more benign cross-linker such as genipin.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Science Centre, Warsaw, Poland – decision no. UMO-2018/30/E/ST8/00642. Financial support from Polish National Agency for Academic Exchange (NAWA) under Ulam Programme



489 (Agreement No. PPN/U LM/2020/1/00005/U/00001) is gratefully acknowledged. R.
490 Castro-Muñoz also acknowledges the School of Engineering and Science and the
491 FEMSA-Biotechnology Center at Tecnológico de Monterrey for their support through the
492 Bioprocess (0020209113) Focus Group. The authors also acknowledged Emilia Gontarek
493 for her indispensable support for FTIR and contact angle measurements.

494

495 **Conflict of Interest**

496 The authors declare no conflict of interest.

497

498 **References**

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