

1     **Hybrid cross-linked chitosan/protonated-proline:glucose DES membranes with**  
2                     **superior pervaporation performance for ethanol dehydration**

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27 **Abstract**

28 This work explores a protonated L-proline:glucose (molar ratio 5:1) deep eutectic  
29 solvent (DES) in fabricating biopolymer membranes utilizing chitosan (CS). Initially, the  
30 miscibility of CS and DES to prepare homogeneous dense blend membranes has been  
31 investigated. Different techniques, such as scanning electron microscopy, contact angle  
32 (CA), atomic force microscopy (AFM), Fourier transformed infrared spectroscopy (FTIR)  
33 and swelling degree (uptake), were used to characterize the structure of the resulting  
34 membranes. Within the pervaporation performance for ethanol dehydration, Arrhenius  
35 and mass transfer analysis were analysed in detail. Interestingly, the addition of DESs  
36 provided superior performance to crosslinked CS: DES membranes compared with the  
37 ones lacking DES. Based on the morphology and properties observed, this new concept  
38 of CS-based membranes can be alternatively applied in other solvent separations  
39 requiring hydrophilic membranes.

40

41 **Keywords:** Proline:glucose, deep eutectic solvents; chitosan; water-ethanol; hydrophilic  
42 pervaporation.

43

44

45

## 46 1. Introduction

47 A current trend of research deals with the implementation of deep eutectic solvents  
48 (DESs), which are an emerging class of sustainable solvents, into new applications and  
49 processes. Some examples of applications are as coatings [1], eco-friendly media in  
50 reactors [2], extraction of biomolecules from natural products, [3], separation of heavy  
51 metal from complex mixtures, CO<sub>2</sub> capture [4], fuel desulfurization [5], assisting  
52 chromatographic techniques [6], biodiesel synthesis aided with enzymes [7], chemical  
53 and biochemical reactions [8], among others. The importance of DESs relies on their  
54 non-toxic character, low cost in synthesis, easy to use, biodegradable, environmentally-  
55 safe and reusable [9]. As for DES synthesis, these eutectic mixtures tend to be typically  
56 formed by linking a hydrogen bond acceptor (HBA), usually quaternary ammonium  
57 salts, and a hydrogen bond donor (HBD) [1,10]. As for membrane fabrication, DESs are  
58 initially utilized as additive agents in DES-supported membranes [11,12], since they can  
59 confer a synergistic effect in the separation features of polymer membranes. In fact,  
60 such performance improvement showed by DESs in membranes is ascribed to a  
61 facilitated diffusion and adsorption of molecules within the functional groups present in  
62 DESs [13–15]. Apart from their application as additives, DESs were proposed as pore-  
63 forming additives in phase inversion process via immersion precipitation for synthesizing  
64 membranes with asymmetrical patterns [16].

65 Very recently, our research group has synthesized and implemented a new DESs,  
66 based on an amino acid and an organosulfur solute, for fabricating dense chitosan (CS)  
67 membranes, which were subsequently applied into the pervaporation (PV) separation  
68 of methanol/MTBE mixtures [17]. CS was proposed in this study since it is the most



69 investigated biopolymer for PV membranes with high performance for the removal of  
70 water molecules from less polar or non-polar molecules [18,19], e.g., CS has shown  
71 interesting permeation rates and salt rejection in seawater desalination via PV [20]. It is  
72 worth mentioning that biopolymer-based membranes (including CS, sodium alginate,  
73 cellulose acetate, polylactic acid, among others) are a current scope of study according  
74 to the need of replacing chemically synthesized polymers [21,22]. Apart from the  
75 implementation of DES in biopolymer membranes, the fabrication of mixed matrix  
76 membranes (or nanocomposites) through the incorporation of nanomaterials is also a  
77 current trend in the field [23–25]. Unfortunately, there is still a big need in finding new  
78 DES to assist the fabrication of polymer membranes and improve somehow their  
79 physicochemical properties and thus separation performance. It is worth mentioning that  
80 the main challenge comprises the rapport of the eutectic mixture and organic phase  
81 (i.e., polymer) towards their compelling joining. Here, in this research, an original  
82 hydrophilic eutectic mixture, like protonated L-proline:glucose at molar ratio 5:1, was  
83 used for the unprecedented tailoring of cross-linked CS membranes to beaten the  
84 typical issues associated with the suitable distribution of the eutectic mixtures inside the  
85 biopolymer.

86 Strategically, the new DES owning hydrophilic character and soluble in water, such as  
87 protonated-L-proline:glucose under optimized molar ratio 5:1, has been eventually  
88 elaborated [26]. After this, the DES was blended with CS phase to fabricate a  
89 homogeneous dope solution, succeeded by an *in-situ* cross-linking via glutaraldehyde  
90 (GA). These final membranes were fully characterized and evaluated for practical  
91 separation application. PV experiments towards the removal of water from azeotropic



92 water-ethanol model mixtures demonstrated the membranes' appropriateness. Finally, a  
93 model based on the resistances-in-series model allowed us to characterize the mass  
94 transfer phenomenon.

95

## 96 **2. Materials and methods**

### 97 *2.1. Chemicals and supplies*

98 As for L-proline, this has been acquired with a purity of at least 98% from Sigma Aldrich.  
99 Glucose (pure, WarChem), hydrochloric acid (analytical reagent, POCH S.A.) and  
100 glutaraldehyde (at 25 wt.% concentration) were obtained and utilized lacking in  
101 additional treatment. The chitosan polymer has been purchased from Sigma Aldrich.

102

### 103 *2.2. Eutectic mixture preparation*

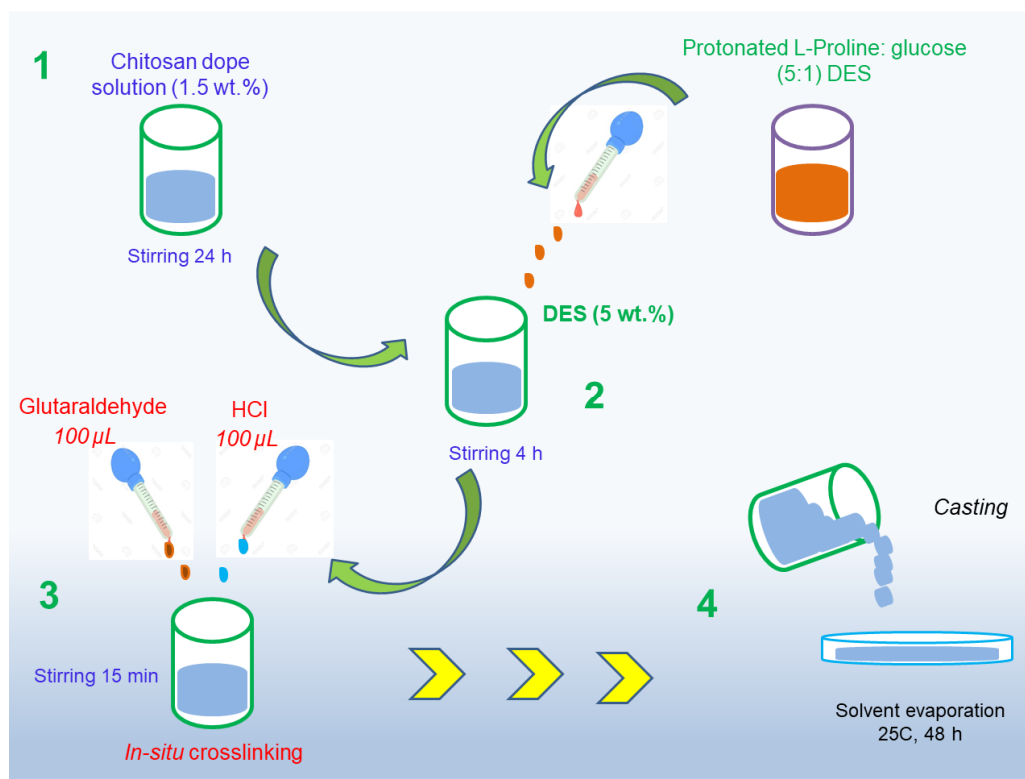
104 *A protonated-L-proline:glucose (5:1)* has been preliminarily prepared. Experimentally,  
105 10 g of L-proline and 86.86 mL of HCl 1M were continuously blended at given  
106 conditions (1000 rpm, 70 °C) up to results in a homogenous and translucent mixture.  
107 Next, glucose (3,13 g) was incorporated into the mixture. Residual water has been later  
108 eliminated via evaporation (BUCHI Rotavapor R-300, V-300 vacuum pump).

109

### 110 *2.3. Membrane fabrication*

111 Overall protocol for membrane preparation is graphically described in **Figure 1**. All  
112 chitosan-based membranes have been fabricated using dense-film casting method. To  
113 formulate the dope solutions, the right quantity of CS (1.5 wt.%) was dissolved in 2 wt.%  
114 acetic acid in water. The polymeric dope mixtures were kept in agitation during a day.

115 After that, eutectic mixture L-proline:glucose (5 wt.%) has been then incorporated in  
116 dope mixtures. Importantly, 5 wt.% of eutectic mixture corresponds to the best ratio for  
117 the membranes, agreeing with previous studies [17,27]. The final solution was mixed  
118 during 4 h before the application of the *in-situ* cross-linking with GA, which was initially  
119 applied to confer a better chemical and solvent stability of the membranes, while  
120 ensuring the DES restraint into the polymer membrane [28]. The *in-situ* cross-linking  
121 has been performed using GA (100  $\mu$ L), followed by HCl (100  $\mu$ L). This final mixture was  
122 homogenized during 15 min, and then cast. Membrane samples were subjected to  
123 drying at 25 °C over 2 days. In general, the membranes' physical aspect has been  
124 found as typical homogeneous and continuous film phase with a thickness ca. 25  $\mu$ m.  
125 Finally, the final membranes were named as follows: cross-linked CS & cross-linked  
126 CS:L-proline:glucose, labelled as CS:PRO:GLU.



127

128 **Figure 1.** Preparation strategy of crosslinked chitosan membranes containing L-proline:  
129 glucose eutectic mixture.

130

#### 131 2.4. Membrane analysis and characterization

132 *Microscopy techniques: SEM and AFM:* Structure-morphological property was studied  
133 via FEI Quanta FEG 250 SEM microscope. The secondary electron detector was also  
134 utilized for the investigation, recording micrographs (at 5 kV accelerating voltage) in  
135 high vacuum mode. Preliminarily, the membrane samples were essentially coated via  
136 sputtering (gold layer ca. 10 nm), which was applied to balance the scarce surface  
137 conductivity. The respective micrographs were obtained at proper magnification.  
138 Regarding cross-section, membrane specimens were fractured by immersing in liquid  
139 N<sub>2</sub>. On the other hand, AFM studies were done using Nanosurf EasyScan 2 by contact  
140 mode using silicon tips (AppNano - SICON series) with 10nN constant force [29].

141 *FTIR analysis:* Membrane samples have been analysed via Nicolet iS10 spectrometer  
142 (from Thermo Fisher Scientific) presenting deuterated triglycine sulfate (DTGS)  
143 detector, along with a Golden Gate diamond ATR. Under resolution of 16 cm<sup>-1</sup>, spectra  
144 data was acquired in the range 4000–400 cm<sup>-1</sup>.

145 *Contact angle determination:* The surface CA determination has been done with  
146 ultrapure water. In this analysis, goniometer OCA15 (Data Physics) was utilized. The  
147 data were reported as the average and standard deviation (SD) of at least five assays.

148 *2.4.1. Uptake:* As for solvent uptake, which gives the solvent adsorption ability [30], has  
149 been investigated for pure ethanol and different water-ethanol mixtures ranging from 0-  
150 50 wt.% water in ethanol. Membrane sample (approximately 1×5 cm) was first weighed;



151 after this, it was then subjected to immersion in the binary solvent mixtures (at room  
152 temperature, 2 days). As documented in other investigations [31], the wet membrane  
153 pieces need to be fast cleaned to eliminate the possible residual solvent from surface.  
154 Right away, the weight of the samples was again determined (digital balance, Gibertini,  
155 Crystal 500, Italy). The uptake calculation was done accordingly [32]:

156

$$157 \quad Uptake (\%) = \frac{W_f - W_i}{W_f} \cdot 100 \quad \text{Eq. (1)}$$

158 where  $W_f$  and  $W_i$  are the weight values for wet samples after immersion and dry before  
159 immersion, respectively.

160

### 161 *2.5. Pervaporation separation performance*

162 PV tests have been done in a lab operation unit; the schematic illustration and  
163 additional information are observed in previous works [33]. In general, an azeotropic  
164 water-ethanol (10–90 wt.%, respectively) mixture was poured into a PV cell. The solvent  
165 temperature was controlled (20, 30, 40 and 50 °C) and kept constant utilizing a thermo  
166 digital circulating bath. At permeate side, the vacuum pressure was controlled at 1 mbar  
167 via CRVpro 4 vacuum pump (Welch Vacuum Products, USA).

168 Membrane samples with an active area of 5.3 cm<sup>2</sup> were located on a porous metal  
169 support at PV cell. Experimentally, permeating vapour was simultaneously condensed  
170 and collected by means of glass trap located inside a condenser containing liquid  
171 nitrogen. When steady-state was observed, the permeate samples were obtained from  
172 for 4 h running test and right away weighted to estimate the total permeate flux (J):





173 
$$J = \frac{Q}{A \cdot t} \quad \text{Eq. (2)}$$

174 where  $Q$  belong to the weight of the permeate (expressed in kg),  $A$  is the active  
175 membrane area ( $\text{m}^2$ ) while  $t$  is the testing time (h). The partial flux ( $J_i$ ) has been  
176 evaluated as the product of its respective weight fraction ( $y_i$ ) accordingly [34]:

177 
$$J_i = Y_i \cdot J \quad \text{Eq. (3)}$$

178

179 The separation factor ( $\alpha$ ) was estimated as follows [34]:

180 
$$\alpha = \frac{y_{water}/y_{ethanol}}{x_{water}/x_{ethanol}} \quad \text{Eq. (4)}$$

181 where  $y$  and  $x$  belong to the weight fraction of each compound present in permeate and  
182 feed, respectively. The permeate samples composition was analyzed using Autosystem  
183 XL gas chromatograph with flame ionisation detector (FID) and split/splitless injector  
184 (Perkin Elmer, USA). Separation was done using a 60,0 m x 0,32 mm ID x 1 um (DB-  
185 624) capillary column (Agilent, USA).

186 The  $J$  and  $\alpha$  data were given as the average of at least three tests to guarantee the  
187 results' accuracy.

## 188 2.6. Mass transfer analysis

189 To understand the mass transfer in the pervaporation system, the resistances-in-series  
190 theory has been used based on the solution-diffusion mechanism [35]. Considering the  
191 solution-diffusion model, a mass transfer flux of a component  $i$  can be denoted as a  
192 function of an overall mass transfer coefficient and a driving force, as follows:

193 
$$J_i = K_{overall,i}(P_i^\circ \gamma_i x_i - P_p y_i) \quad \text{Eq. (5)}$$

194 Where,  $K_{overall,i}$  denotes the total mass transfer coefficient for the component  $i$ ,  $P_i^\circ$  is the



195 vapour pressure for the component  $i$ ,  $\gamma_i$  is the activity coefficient of the component  $i$ ,  $P_p$   
 196 is the total pressure at the permeate side,  $x_i$  is the molar fraction of the component  $i$  at  
 197 the liquid side, and  $y_i$  is the molar fraction of the component  $i$  at permeate side. In a  
 198 pervaporation system, the permeate side is under vacuum pressure so that the total  
 199 pressure at the permeate side can be neglected, and Eq. (5) can be rewritten and  
 200 simplified as follows:

$$201 \quad J_i = K_{overall,i} \cdot (P_i^\circ \cdot \gamma_i \cdot x_i) \quad \text{Eq. (6)}$$

202 According to García et al. [36] and Arregoitia-Sarabia et. al. [35], overall mass transfer  
 203 coefficient can be described as the combination for individual resistances

$$204 \quad \frac{1}{K_{overall,i}} = \frac{1}{K_{L,i}} + \frac{1}{K_{m,i}} = \frac{P_i^{sat} \gamma_i}{k_{L,i} \rho} + \frac{\delta}{P_i} \quad \text{Eq. (7)}$$

205 where  $k_{L,i}$  is the mass transfer coefficient for the component  $i$  at the liquid side,  $\rho$  is the  
 206 density of the liquid feed,  $\delta$  is the membrane thickness, and  $P_i$  is the permeability of the  
 207 membrane for the component  $i$ .

208 The mass transfer coefficient has been calculated using the following correlation based  
 209 on the work of Johnson et. al. [37]:

$$210 \quad Sh = \frac{k_{L,i} \cdot d_{pervaporation\ cell}}{D_{sol}} = 0,0924 \cdot \left[ \frac{\mu}{\rho \cdot D_{AB}} \right]^{0,5} \cdot \left[ \frac{R \cdot d^2 \cdot \rho}{\mu} \right]^{0,71} \quad \text{Eq. (8)}$$

211 where  $d_{pervaporation\ cell}$  is the diameter of pervaporation vessel,  $D_{AB}$  represents the  
 212 diffusion coefficient,  $\mu$  regards the viscosity of the mixture,  $d$  is the diameter of propeller,  
 213 and  $R$  is the revolution per second of the propeller.

214 Finally, the membrane selectivity ( $S_{i,j}$ ) and pervaporation separation index (PSI) are  
 215 determined as follow:

$$216 \quad S_{i,j} = \frac{P_i}{P_j} \quad \text{Eq. (9)}$$

217 
$$PSI = J(S_{i,j} - 1) \quad \text{Eq. (10)}$$

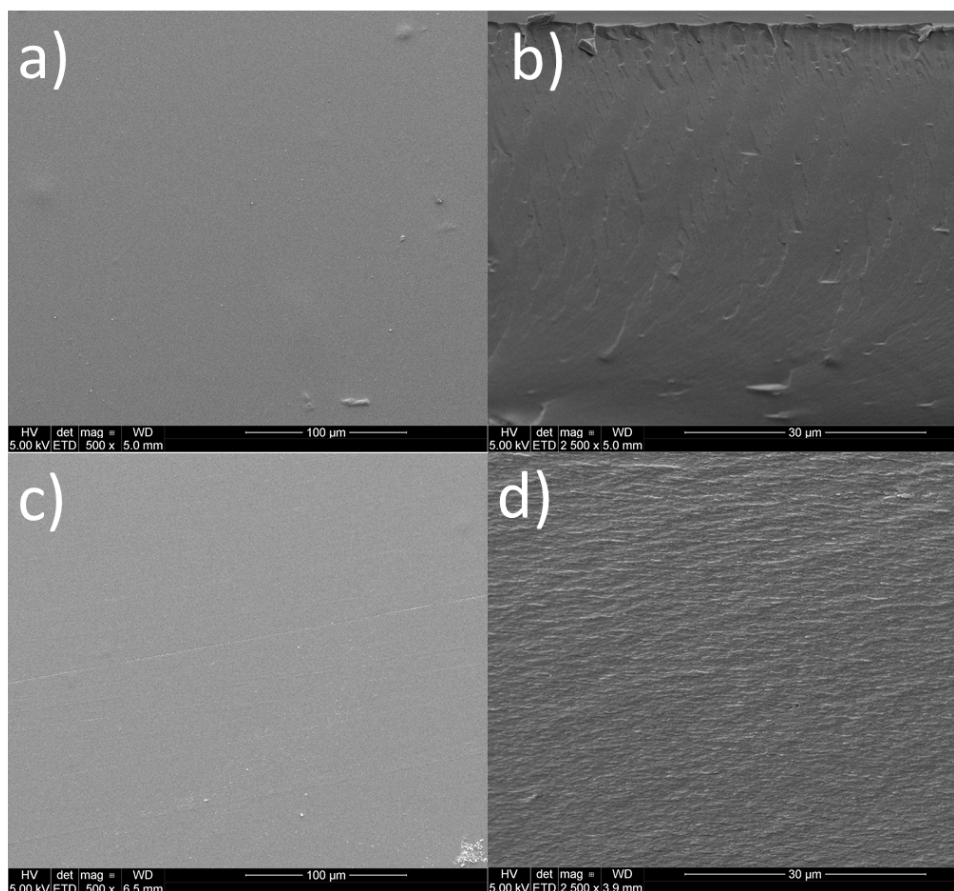
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### 219 **3. Results and discussion**

#### 220 3.1. *Structure-morphological analysis.*

221 As for prepared membranes either with/without DES, they exhibited a convincing flat  
222 and smoothie surface with no apparent defects. It was visibly clear that there is no sign  
223 of being plastically deformed, this latter is characteristic of dense polymeric membranes  
224 [38]. For pristine CS membrane, cross-section view (**Figure 2b**) showed clear crater-like  
225 structure. This is typically observed when deforming via freeze-fracture. Additionally,  
226 this typical structure has been also observed in other pristine biopolymer membranes  
227 (like chitosan) [28,39]. Referring to CS:PRO:GLU membrane (**Figure 2d**), it also  
228 showed a homogeneous dense structure lacking in pores or pinholes between the  
229 organic phase and eutectic mixture. Essentially, the obtained morphology is considered  
230 as convincing proof of exceptional blending/miscibility among the hydrophilic eutectic  
231 mixture and CS, this has been reported in precedented studies, e.g., in  
232 polymer/polyethylene glycol blend membranes [40,41].

233



234

235 **Figure 2.** SEM surface and cross-section micrographs of the fabricated CS and L-  
 236 proline:glucose membranes. (a, b) cross-linked chitosan and (c, d) cross-linked  
 237 chitosan:L-proline:glucose (CS:PRO:GLU).  
 238

239 Herein, the incorporation of this eutectic mixture has interestingly contributed to obtain a  
 240 compact but less smooth morphology. As mentioned previously, it has been  
 241 documented that DESs can act as pore former additive to prepare of porous  
 242 membranes [16,42]. In this case, our scope is proposed to physically merge and  
 243 enmesh the chosen hydrophilic solvent in the hybrid membrane for potentialize its  
 244 separation effect once maintained in the membrane structure. Our hypothesis relies on

245 the tremendously success of DESs for the extraction of low molecular weight molecules  
246 based on their property to tremendously generate H-bonds by means of dipole-dipole  
247 and coulombic forces, among other solute-solvent complexing synergy [43,44].

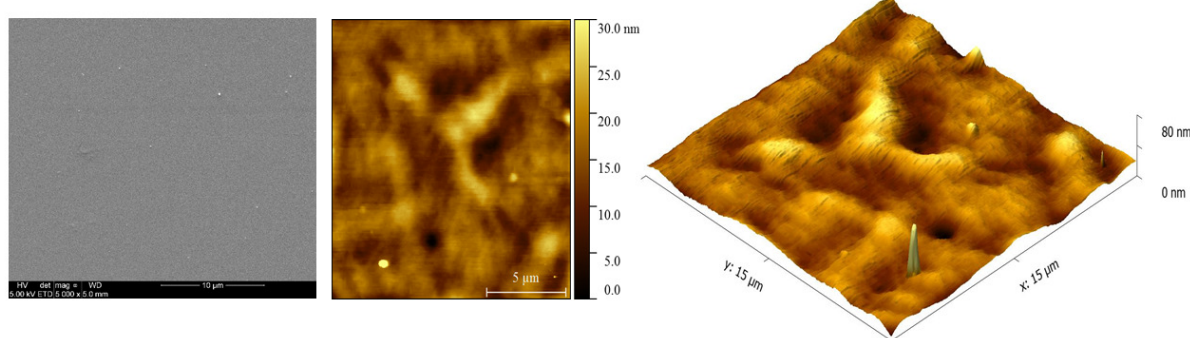
248 The eventual success of obtaining homogeneous dense membranes, with convincing  
249 evidence of non-DES encapsulation, is due to the synergy of CS at linking some agents  
250 thanks to its functional groups. In other words, the lack of functional groups among both  
251 phases (i.e., polymer and DES) will consequently lead to not enough interacting  
252 properties and consequently minimal miscible features [45]. These latter properties  
253 become relevant when dealing with the merging of inorganic/organic dispersing agents  
254 into polymers, where potential presence of functional groups or chemically  
255 functionalized nanosized materials eventually achieves good synergy and contact at the  
256 interface among polymer and filler [46].

257 CS itself presents a large number of  $\text{NH}_2$  and OH terminal domains, which makes the  
258 biopolymer an exceptional polymer for polymer blend formation [19]. While specific  
259 DESs should also possess functional groups to synergistically interact with CS  
260 conferring specific properties to the final membrane. Here, it is quite possible that this  
261 hydrophilic DES (PRO: GLU), presenting various functional groups (e.g., amino,  
262 hydroxyl, oxygen and carbonyl containing groups), could interconnect with CS. Clearly,  
263 the surface micrograph of the blend membranes proves a smooth, continuous and  
264 defect-free surfaces with lack of any pinholes. In literature, other DES, such as choline  
265 chloride-malonic acid, was able to turn the flat surface of chitosan films to a non-  
266 homogenous morphology while keeping a compact pattern [47]. In this study, we also  
267 confirm a smoother surface by adding the DES agent into CS, as observed in **Figure 3**.

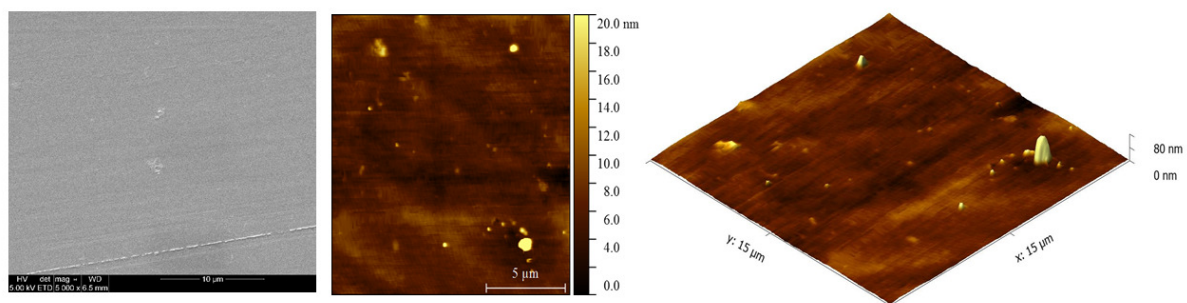


268 It is worth mentioning that the DES-free crosslinked CS membrane displayed an  
269 average root mean square roughness of  $S_q=4.0\pm0.5$  nm, where the incorporation of  
270 DES slightly lowered such value to  $S_q=3.0\pm0.5$  nm. Certainly, upon the nature of the  
271 eutectic mixture, the exaggerated load of the DES may promote a rough structure of the  
272 final eutectic-chitosan blend membranes [48].

### Crosslinked CS membrane



### Crosslinked CS PRO:GLU (5:1)



273  
274 **Figure 3.** AFM surface and 3D images (15 × 15 μm) of pristine CS and CS:PRO:GLU  
275 membranes.

276 It is worth mentioning that the blending of DES into CS membrane may influence the  
277 mechanical and thermal properties of the resultant membranes. In a previous work, it  
278 has been stated that eutectic mixtures (e.g., based on L-proline:sulfolane) worsened  
279 specific mechanical properties, such as Young's modulus and tensile strength, but such

280 an effect was compensate due to the *in situ* cross-linking [17]. DESs tend to decrease  
281 the intermolecular interactions in the CS network, causing the co-called plasticization.  
282 The incorporation of plasticizers (like DES) in CS, in fact, produces a transition from a  
283 rigid to a softer material with elastic properties [49]. Aside from this effect, DES has  
284 been demonstrated to affect the thermal stability of the CS membranes in terms of glass  
285 transition temperature ( $T_g$ ), e.g., DES-modified CS films exhibited a lower  $T_g$  in  
286 comparison with bare CS membranes. Eventually, this can be ascribed to eutectic  
287 mixture decomposition. Interestingly,  $T_g$  values decreased proportionally as the DES  
288 content increased. According to Jakubowska et al. [47], DES concentration increment  
289 results in a decrease in temperature at which decomposition starts.

290

### 291 3.2. FTIR and water CA characterization

292 As seen in **Figure 4**, the FTIR data essentially confirms the effective merging of the  
293 hydrophilic PRO:GLU solvent and the biopolymeric phase. Full spectrum data show a  
294 firm and vast patterning with asymmetry ranged approximately  $3350\text{-}3450\text{ cm}^{-1}$ , which a  
295 consequence of overlaying the O-H and N-H stretching oscillations of terminal groups  
296 connected by H-bonds. Typically, CS spectrum exhibits a various absorption patterns  
297 around  $1650\text{ cm}^{-1}$  (which corresponds to C=O stretching of possible CO=NH<sub>2</sub> terminal  
298 group),  $1520\text{ cm}^{-1}$  (which corresponds to N-H wagging of non-acetylated  
299 2-aminoglucose) and ca.  $1580\text{ cm}^{-1}$  (which corresponds to N-H wagging of CO=NH<sub>2</sub>  
300 terminal), which evidenced by other reports [50]. Apart from that, absorption patterning  
301 located  $\sim 1150\text{ cm}^{-1}$  refer to a skew-symmetric stretching for C-O-C links,  $1060\text{ cm}^{-1}$  and  
302  $1050\text{ cm}^{-1}$ , ascribed to possibly skeletal frequencies comprising a typical C-O



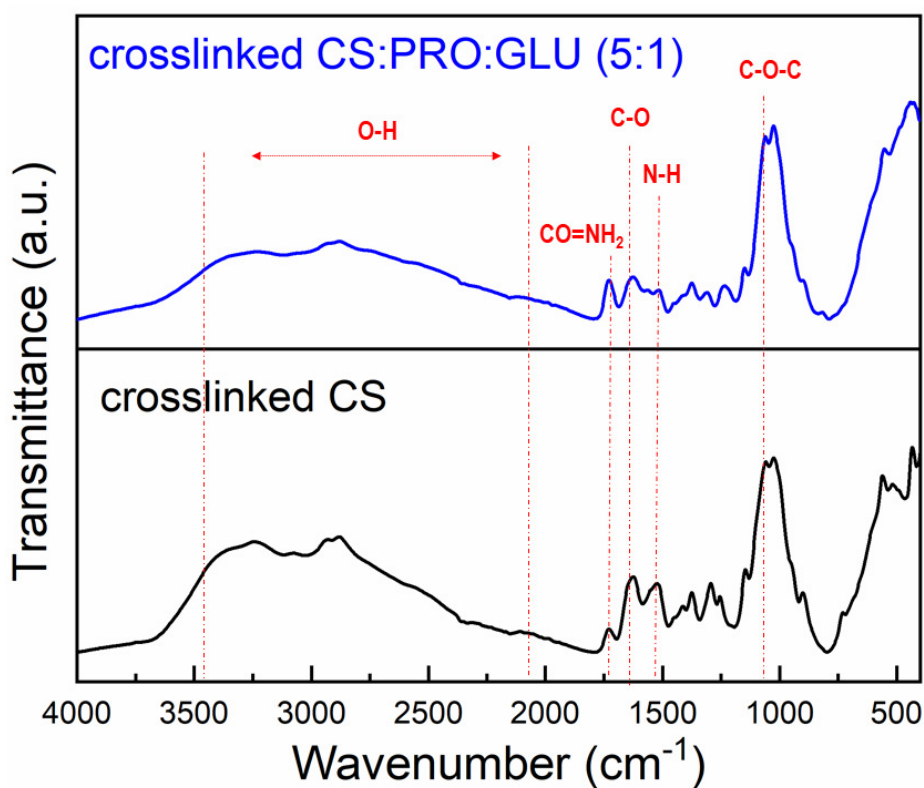
303 conjunction. Concerning to the DES, the amino acid (L-proline) owns an extra  $\text{-NH}_2$   
304 terminal, identified as an  $\text{RR}'\text{C}=\text{NR}''$ . Hence, proline is also identified as an imino acid.  
305 As proline's three-carbon R-grouping tends to be merged to the alpha-nitrogen terminal,  
306 this molecule presents a restrained rigid-ring with rotational behaviour [26]. In the case  
307 of glucose, it is a monosaccharide presenting six carbon atoms and an aldehyde group.  
308 Considering the typical structure of any DES, both molecules (HBA and HBD) are  
309 structurally well attached via electrostatic interaction (i.e., H-bonds) to form a final  
310 eutectic system [51], this latter interaction is apparently observable with a firm shifting  
311 and oscillation for the peak ranged from  $3750\text{-}1950\text{ cm}^{-1}$  [52]. When this PRO:GLU  
312 eutectic system is fused in the CS, this results in modest but clear motion on the usual  
313 polymer patterning. This latter interaction reveals an exceptional attraction between  
314 phases and is translated to affinity. Clear motions, together with the classic behaviour of  
315 the patterning, in the range of  $3650\text{-}3100\text{ cm}^{-1}$ , must also be noted showing an  
316 overlying of the spectra, which are ascribed to O—H, N—H and C—O oscillations in  
317 chemical functionalities of the eutectic mixture and polymer. Jakubowska et al. [47]  
318 have also reported similar molecular interactions when prepared and characterized  
319 chitosan/DES hybrid materials. Importantly, the resulting reticulated flat films containing  
320 glutaraldehyde commonly demonstrate clear absorption increment among  $1600\text{-}1650$   
321  $\text{cm}^{-1}$  thanks to N=C bonds [53,54]. The widening at  $1550$ ,  $1740$  and  $2850\text{ cm}^{-1}$  refers to  
322 the free aldehyde chain and raised C-H length, respectively. Aliphatic  $\text{-NH}_2$  terminals  
323 decay directly proportional as the peak  $1150\text{ cm}^{-1}$  decreases. Alternatively, DES have  
324 been identified as potential cross-linker agents for CS. Especially, eutectic mixtures  
325 containing carboxyl groups are able to interact with the  $\text{NH}_2$  groups of CS creating an





326 amide connection [48]. Such an amide connection has been also been observed in CS  
327 membranes blended with choline chloride -citric acid [52]. Interestingly, the blending of  
328 choline chloride-urea DES into the CS structure was able to create the saccharide ring  
329 (C–O–C) between DES and CS, proving the formation of a resilient solid biopolymer  
330 membrane without adding cross-linking mediator [55].

331



332

333 **Figure 4.** Spectrum data from FTIR measurement for pristine crosslinked chitosan and  
334 its eutectic mixture-based blend membrane.

335

336

337 A relevant point to highlight during the addition of this hydrophilic DES in membranes

338 regards its remarkable response on either hydrophilic or hydrophobic nature of the  
339 membrane. The DES-free cross-linked chitosan flat membrane revealed angle values  
340 of ca. 70° (see **Figure 5**), which agrees with outcomes published previously, e.g., angle  
341 values of chitosan nearly 74-88° [50,56]. In principle, the nature (either hydrophilic or  
342 hydrophobic) of the biopolymer indeed stands on its degree of deacetylation, e.g., large  
343 deacetylation gives as a result exceptional hydrophilicity in membranes due to many  
344 NH<sub>2</sub> terminals tend to be available in the biopolymer [57], this becomes relevant since  
345 hydrophilicity is needed for enhanced water adsorption over a membrane interface [58].  
346 Hydrophilic nature of chitosan follows from its polar hydrophilic terminals, including -NH<sub>2</sub>  
347 and -OH; unfortunately, this polar nature is compromised when applying cross-linking.  
348 However, the addition of the PRO: GLU DES in the CS contributed to an enhanced  
349 hydrophilicity translated to lower CA values of ca. 50°. This gives an idea that the polar  
350 groups given by the DES have a meaningful influence at improving the hydrophilic  
351 nature of the membrane. Importantly, glucose is classified as polar since hydroxyl  
352 groups presents high affinity to hydrogen bonds and effective electronegativity.

353

354

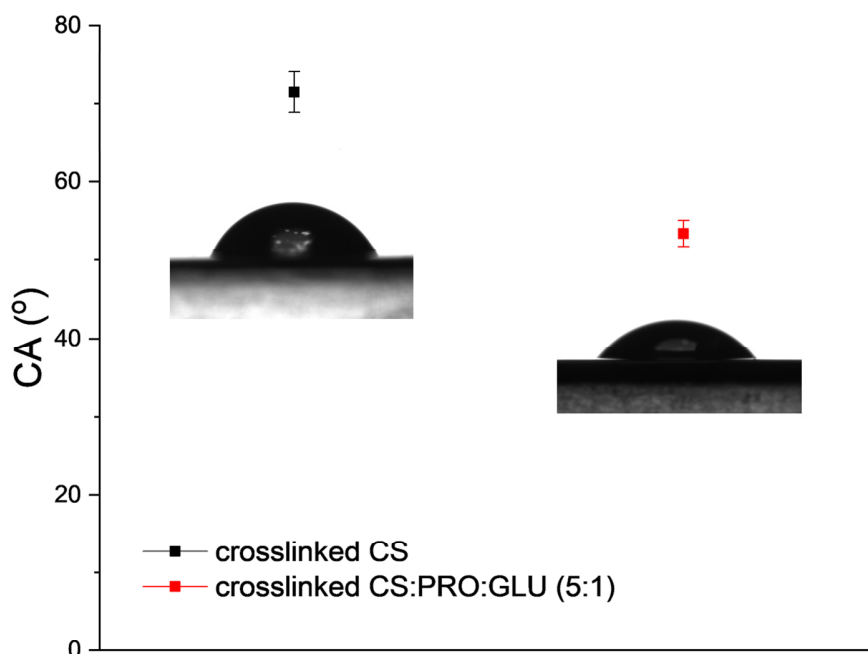
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361 **Figure 5.** CA values pristine crosslinked CS and CS:PRO: GLU membranes.

362

363 3.3. *Pervaporation testing*

364 3.3.1. *Operating temperature dependence of permeation and separation factor.*

365 PV data for all assayed membranes are reported in **Table S1**. **Figure 6** shows the

366 influence of the feed temperature on the total permeation flux, in which a permeation

367 increase was noted in the range of 20-50 °C in pristine cross-linked and its blend with

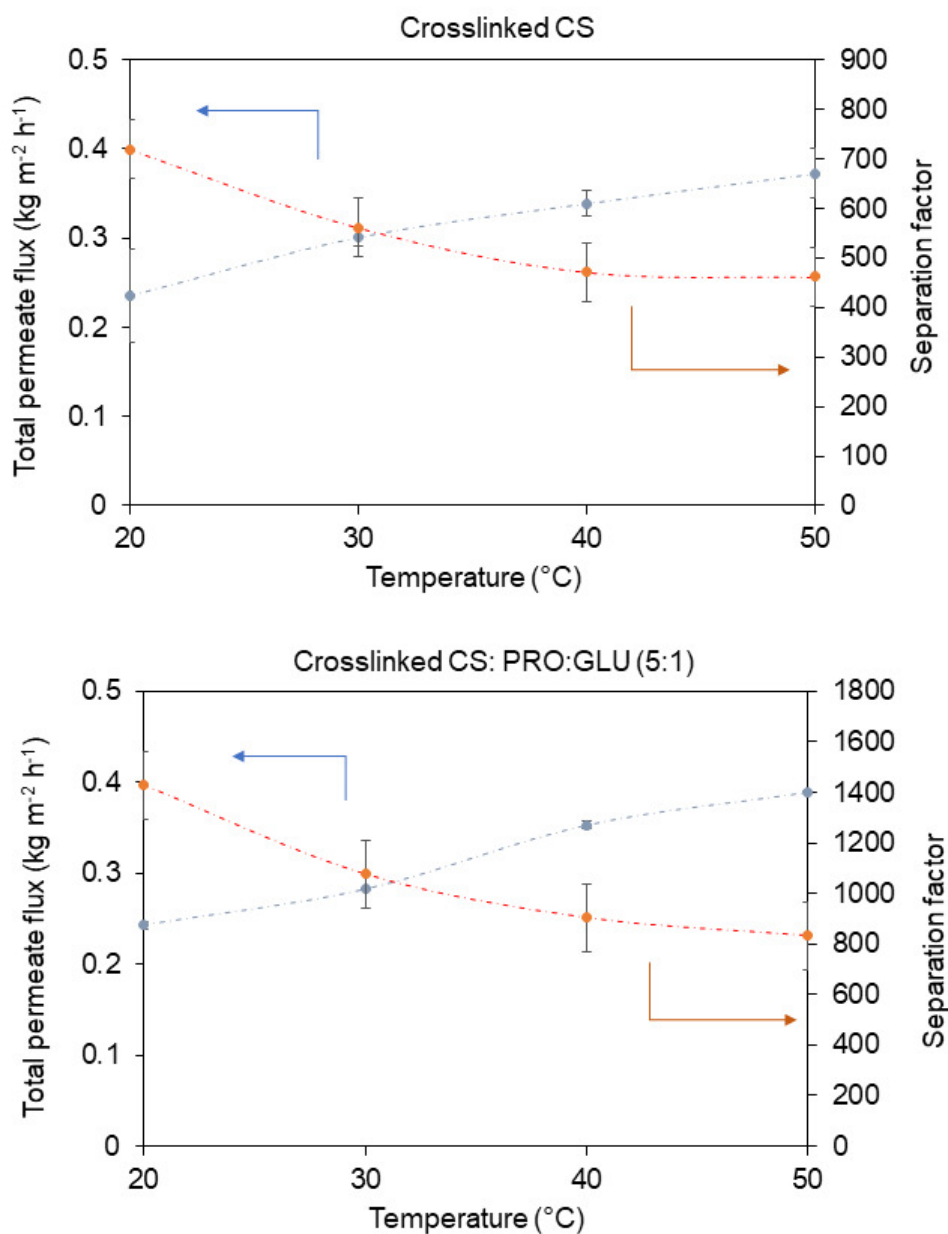
368 PRO: GLU DES. It is actually traditional behaviour for polymers as their chains tend to

369 present improved flexibility under high temperature, which consequently contribute to

370 enhanced solvents' sorption. This consequently increases the transport of molecules

371 across the intermolecular distances of polymer membranes [59].

372



373

374 **Figure 6.** Permeation and separation factor behaviour in respect to operating

375 temperature (10/90 wt.% H<sub>2</sub>O/EtOH, pressure: 1 mbar). The semi continuous loops are

376

only guiding.

377

378 Essentially, an influence of temperature on overall flux was further analysed by means  
379 of the Arrhenius equation, as denoted in Eq. 11.

380

$$381 \quad J = J_o \cdot \exp\left(-\frac{E_{app}}{R \cdot T}\right) \quad \text{Eq. (11)}$$

382 In theory,  $J_o$  refers to the pre-exponential element, while  $E_{app}$  corresponds to the  
383 apparent activation energy for the transport. The product  $R \cdot T$  expresses the typical  
384 term of energy. By applying mathematical logarithms in previous Eq. (11),  $E_{app}$  is  
385 determined directly from the straight line proving a compelling relationship between  
386 flux and temperature; it means, an increment in overall flux occurs with temperature  
387 increase. As **Table 1** reports, it is noted that water displays lower  $E_{app}$  values (ca.  
388 5.07 kJ mol<sup>-1</sup>) in respect to ethanol (~10.27 kJ mol<sup>-1</sup>) in crosslinked CS membrane,  
389 confirming the water affinity of chitosan. On the other hand, the eutectic solvent  
390 blending slightly increased the  $E_{app}$  in water molecules approximately 5.57 kJ mol<sup>-1</sup> for  
391 the hybrid CS:PRO:GLU membrane, however,  $E_{app}$  value for ethanol has been more  
392 impacted by DES incorporation. Particularly, the  $E_{app}$  keeps unchanged towards  
393 water in respect to ethanol ranging from 20 to 50 °C. It is important to point out that  
394 the temperature increment impact mainly the water permeation, and it is greatly  
395 restricted the permeating ethanol; this is supported by Almeida et al. [60], who  
396 documented an improved water solubility in CS films containing DES, in which the  
397 water solubility increased when increasing the DES content. In this study, the  
398 existence of this hydrophilic PRO: GLU increases the energy demanded for the



399 permeating solvent to be transported over the membrane interface, which is more  
400 prominent for ethanol. This latter aspect is in agreement with the DES hydrophilicity,  
401 which favours for the selective properties for the more polar compounds (like water)  
402 [61].

403

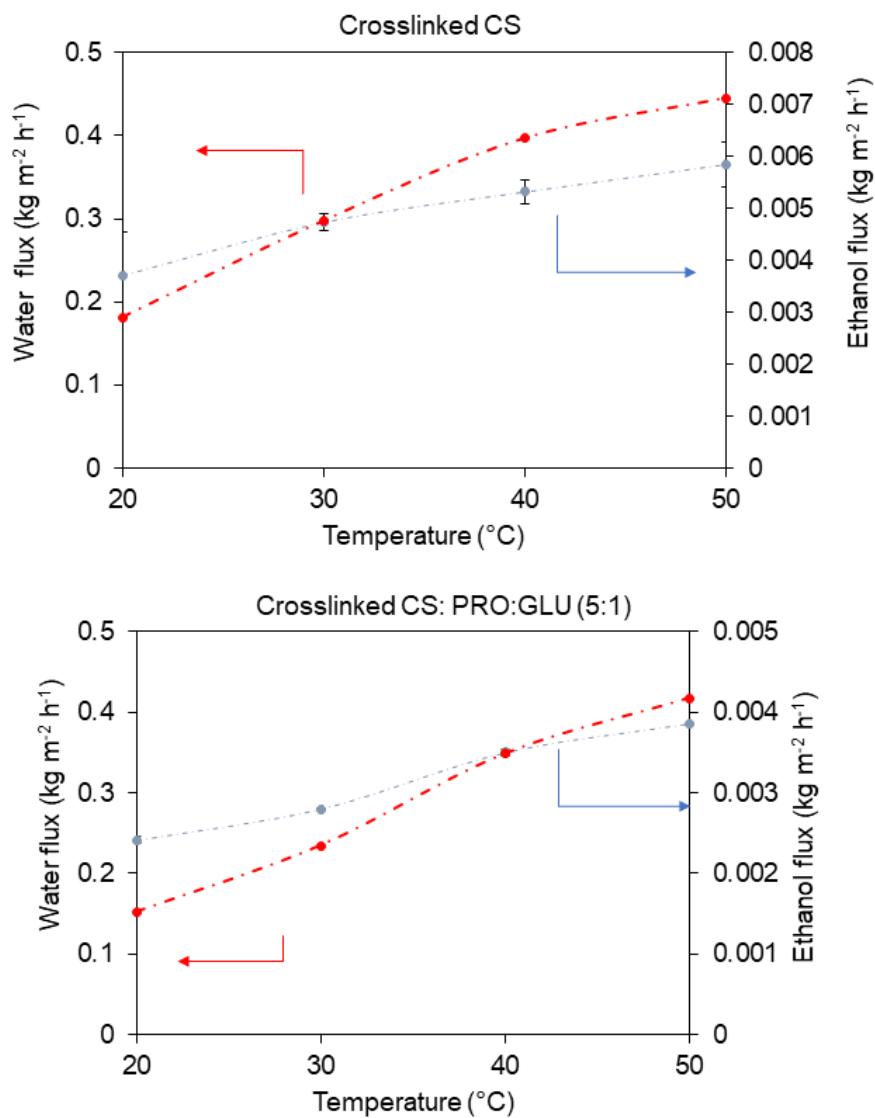
404 **Table 1.** Apparent activation energy values for overall flux, and single water and ethanol  
405 across prepared hybrid materials.

Hybrid formulation	$E_{app}$ (kJ mol <sup>-1</sup> )		
	Overall	Water	Ethanol
Crosslinked chitosan	5.15	5.07	10.27
Crosslinked CS:PRO:GLU	5.63	5.57	11.76

406

407 When dealing with selective affinity,  $\alpha$  parameter in pure CS membrane decayed when  
408 the temperature decreased, as seen in **Figure 6**. Promisingly, separation factor was  
409 substantially enhanced via DES incorporation observing data of ca. 1,427 (at 20 °C).  
410 Obviously, large  $\alpha$  parameters with lower permeating yield were indeed recorded at the  
411 minimal testing temperature. It somehow in accordance to the polymer “free-volume”  
412 theory, as it declares a thermal movement in chains specifically at amorphous localities  
413 boosting an increment in free-volume. It is known that as temperature raises, the  
414 frequency and magnitude of the chain swing increases provoking a free volume  
415 increment [62]. Although the kinetic diameters of water and ethanol are substantially  
416 different (2.6 and 4.3 Armstrong, respectively), the thermal movement in polymer chains

417 can indeed facilitate the diffusivity for bigger solvent molecules (like ethanol) over a  
418 membrane interface compromising the separation factor. In addition to this, hydrophilic  
419 eutectic mixtures have demonstrated to break the intermolecular structure of CS and  
420 thus open the network structure, allowing the permeation of solvent molecules [48,60].



421  
422 **Figure 7.** Water and ethanol flux in respect to operating temperature (10/90 wt.%  
423 H<sub>2</sub>O/EtOH). The semi continuous loops are only guiding.  
424



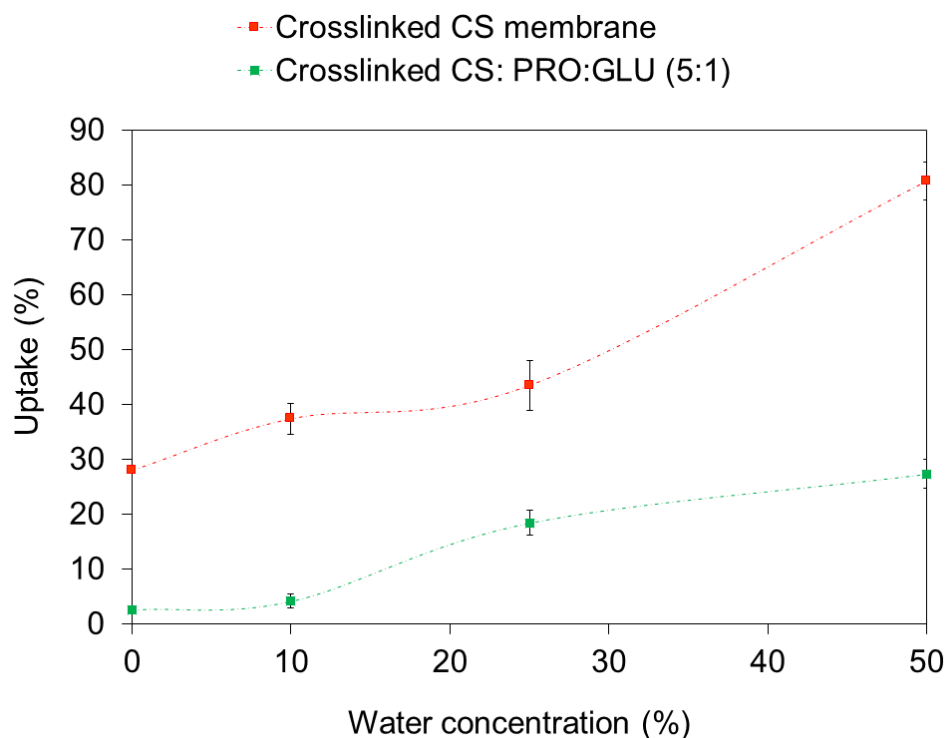
425 Very recently, Jakubowska et al. [47] have reported that the DES addition promotes the  
426 free volume increment in polymeric matrices. This is ascribed to the enlargement of  
427 free-volume fostering the chain motion, which can produce a decrement for the  
428 membrane's selective efficiency. However, an application regarding this hydrophilic  
429 PRO: GLU DES did not affect the selective properties of CS membrane. Interestingly,  
430 both parameters, such as permeation rate and selectivity, were significantly improved.  
431 As shown in **Figure 7**, DES preferentially promoted the passage of water molecules  
432 over the polymeric phase while concurrently hindering a possible ethanol permeation. At  
433 this point, the polarity of the solvents becomes relevant for their own transport and  
434 extraction from complex systems [63].

435 The analysis for the solvent uptake in the developed membranes is represented in  
436 **Figure 8**. It is clearly observed how both membranes show low solvent uptake when  
437 there is a minimal concentration of water in the ethanolic solutions. Experimentally, a  
438 water concentration increment of the feeding solvent mixture resulted in a higher  
439 membrane swelling in a water concentration from 10 to 50 wt.%. Surprisingly, the  
440 incorporation of PRO: GLU DES provoked a decrement in terms of solvent uptake  
441 performance compared with the pristine CS. This latter phenomenon supports  
442 Jakubowska's findings [47] in which a DES confers stability in chitosan membranes.  
443 The uptake is generally expected to be restricted once a crosslinking protocol is  
444 implemented as this treatment provides resistance to polymer materials against polar  
445 solvents thanks to an enhanced stricture in mobility of chains [64]. Swelling  
446 phenomenon is adequately identified as one of the primary bottlenecks of hydrophilic-  
447 based polymer materials when separating polar molecules [20]. Therefore, less prone to





448 be swollen membranes are preferentially needed to acquire a stable separation during  
449 long-term testing.



450

451 **Figure 8.** Solvent uptake of CS-eutectic solvent membranes under various water  
452 percentage in ethanol (at room temperature). The semi continuous loops are only  
453 guiding.

454

455 *3.3.2. PV data comparability of cross-linked CS: PRO:GLU membranes with other*  
456 *studies*

457 As for PV testing, it is obvious that the PV separation efficiency of both hybrid and  
458 polymer materials is primarily dependent on distinct factors, such as membrane  
459 properties (e.g., material type, physiochemical and intrinsic properties, structure, etc.),  
460 along with operating parameters including feed composition, operating temperature,

461 pressure gradient, etc. [34]. Especially, the membrane structure is somehow dictated by  
462 the applied membrane preparation strategy [65], while most PV evaluation of  
463 membranes has been experimented at different feed concentration and operating  
464 parameters. This makes particularly tough to give a fairer comparability among  
465 pervaporation results from various works [66]. In our research, we eventually make a  
466 comparison of performance outcomes among distinct membrane concepts either  
467 unmodified polymer, blends, composites or inorganic tested under close operational  
468 parameters, as reported in **Table 2**. Here, the outstanding selectivity, expressed as  
469 separation factor, for crosslinked CS:PRO:GLU membrane was found at 20 °C  
470 (approximately 1,427), which represents almost 2-folds bigger  $\alpha$  value in comparison to  
471 unmodified crosslinked chitosan. In addition to this, the highest permeation rates were  
472 acquired at the highest tested temperature (at 50 °C) in both membranes while showing  
473 a decrement in selectivity. The membrane containing the DES showed a slight  
474 improvement in permeation (see **Table S1**). When compared with other reports,  
475 crosslinked CS:PRO:GLU membranes exhibited better selectivity than other composite  
476 membranes, such as crosslinked PVA-filled GO, CS-filled H-ZSM-5, polyimide (PI)-filled  
477 ZIF-8, CS-filled titanium dioxide ( $\text{TiO}_2$ ), PI-filled MSS-1, crosslinked PVA-filled ZIF-8-  
478  $\text{NH}_2$ , among others (see **Table 2**). Depending on the used inorganic fillers filled into the  
479 polymer membranes, the aforementioned composites can offer higher permeation rates  
480 than our findings. Unfortunately, crosslinked CS:PRO:GLU membranes did not  
481 overcome the exceptional selectivity of crosslinked sodium alginate-filled beta zeolite  
482 and NaP1 zeolite membranes with unprecedented separation factor values. It is worth  
483 pointing out that these membranes (i.e., crosslinked CS:PRO:GLU) are overcoming the



484 selective-permeable trade-off of the pristine CS membranes.

485

486 **Table 2.** Comparison of crosslinked CS: PRO: GLU membrane performance with some  
 487 composites and inorganic membranes tested with similar water-ethanol mixtures.

Membrane concept	Filler content:	Water %	Testing conditions	J (kg m <sup>-2</sup> h <sup>-1</sup> )	Separation factor	Reference:
Crosslinked CS:PRO:GLU	-	10 wt. %	20 °C, 1 mbar	0.242	1,425	This work
Crosslinked CS:PRO:GLU		10 wt. %	50 °C, 1 mbar	0.389	831.7	This work
Crosslinked PVA- GO	1 wt. %	10 wt. %	40 °C, 3 mbar	0.137	263	[67]
CS-filled H-ZSM-5	8 wt. %	10 wt. %	80 °C, 10 mbar	0.230	152	[68]
Crosslinked sodium alginate-filled beta zeolite	10 wt. %	10 wt. %	30 °C, 0.6 mbar	0.130	1,600	[69]
Polyimide-filled ZIF-8	12 wt. %	10 wt. %	42 °C, 44 mbar	0.260	300	[70]
CS-filled TiO <sub>2</sub>	6 wt. %	10 wt. %	80 °C, 50 mbar	0.340	196	[71]

Polyimide-filled MSS-1	12 wt.%	10 wt.%	42 °C, 44 mbar	0.310	190	[70]
Crosslinked CS-filled silica	5 wt.%	10 wt.%	70 °C, 10 mbar	0.410	919	[72]
Crosslinked PVA-filled ZIF-8- NH <sub>2</sub>	7.5 wt.%	15 wt.%	40 °C, 1 mbar	0.120	200	[73]
NaP1 zeolite membranes	-	10 wt.%	75 °C, 4 mbar	0.45	200 000	[74]
PVA composite membrane	-	10 wt.%	60 °C, 5 mbar	0.140	170	[75]
PVA composite membrane (PERVAP 2201, Sulzer Chemtech)	-	10 wt.%	60 °C, 10 mbar	0.100	100	[76]

488

489

490 **3.4. Mass transfer performance**

491

492 Through the mass transfer model developed for the pervaporation process, and  
 493 equations 7 and 8, mass transfer resistances can be determined for the different  
 494 membranes, which are shown in **Table 3**.

495 **Table 3.** Mass transfer resistance distribution

496

	T (°C)	Crosslinked CS			Crosslinked CS:PRO:GLU		
		$R_{liq} \left(\frac{s}{m}\right) \cdot 10^4$	$R_{membrane} \left(\frac{s}{m}\right)$	$R_{overall} \left(\frac{s}{m}\right) \cdot 10^8$	$R_{liq} \left(\frac{s}{m}\right) \cdot 10^4$	$R_{membrane} \left(\frac{s}{m}\right) \cdot 10^8$	$R_{overall} \left(\frac{s}{m}\right) \cdot 10^8$
Water	20	0.799	0.155	0.155	0.799	0.149	0.149
	30	1,37	0.222	0.222	1,39	0.219	0.219
	40	2,26	0.346	0.346	2,32	0.329	0.329
	50	3,60	0.529	0.529	3,72	0.502	0.502
Ethanol	20	1,07	58.3	58.3	1.07	113	113
	30	1,79	64.4	64.4	1.81	132	132
	40	2,90	82.3	82.3	2.96	153	153
	50	4,52	120	120	4.68	209	209

497

498

499 **Table 3** shows how the transport stage in the membrane corresponds to the one that  
 500 presents the greatest resistance to mass transfer for the two membranes under study,  
 501 as well as for water and ethanol, reaching approximately 99% of the total resistance

502 distribution of them. On the other hand, despite the great importance of the resistance  
 503 value to mass transfer of the membrane, differences in behavior can be observed when  
 504 comparing the same membrane with water and ethanol, at the same temperature. It is  
 505 seen that in crosslinked CS membrane, the resistance for ethanol transport is two  
 506 orders of magnitude bigger compared to water, and as for the membrane modified with  
 507 DES, a difference of 3 orders of magnitude is obtained, which implies that the  
 508 modification by including DES improves the separation performance, fulfilling the task of  
 509 obtaining a membrane with a greater hydrophilic character, offering approximately twice  
 510 the resistance to ethanol than the crosslinked CS membrane, whereas for water, the  
 511 resistances are similar.

512 To compare the performance of membrane modification with DES, it is necessary to  
 513 compare the selectivity factors, this information is presented in **Table 4**.

514 **Table 4.** Water/ethanol selectivity for the different membranes.

T (°C)	Crosslinked CS		Crosslinked CS:PRO:GLU	
	$S_{W/E}$	$PSI \left( \frac{kg}{m^2h} \right)$	$S_{W/E}$	$PSI \left( \frac{kg}{m^2h} \right)$
20	375	87	756	183
30	290	87	600	181
40	238	80	464	163
50	228	85	416	162

515

516

517 Regarding the selectivity factors that both membranes present, it is observed how the  
518 incorporation of proline-glucose as DES allows a greater selectivity towards water,  
519 mainly because they prevent the passage of ethanol molecules through the membrane,  
520 which explains the increase in the resistance of the membrane to ethanol doubling its  
521 value respect to the resistance towards ethanol in the Crosslinked CS membrane. The  
522 addition of PRO:GLU DES to the membrane allows the PSI of the membrane to improve  
523 more than double in comparison with the crosslinked CS membrane, even the  
524 membrane performance is greater than that reported in the literature for the water-  
525 ethanol system [67].

526 Finally, the increase in temperature results in selectivity decrement of the Crosslinked  
527 CS:PRO:GLU membrane, being the temperature at 20°C the one that presents the best  
528 performance, which is corroborated by the PSI value presented by the membrane.

529

530

531

532

533





#### 534 4. Conclusions and future research

535 This research reveals the fabrication and characterization, for the first time, of dense  
536 crosslinked CS-hydrophilic protonated-L-proline: glucose. The membranes present a  
537 compelling miscible properties and integration of the original hydrophilic eutectic mixture  
538 (PRO:GLU) along the organic biopolymer interface. In general, it was utilized eco-  
539 friendly items (including biopolymer, water as primary solvent, “green” eutectic mixture),  
540 making the developed hybrid materials as good candidates for fabricating sustainable  
541 and eco-friendly dense membranes.

542 For water-ethanol pervaporation separation, these hybrid membranes offer a 2-fold  
543 improved pervaporation yield than the DES-free crosslinked chitosan and slight  
544 enhancement in permeation. As a perspective, the forthcoming research must be  
545 emphasized on enhancing the permeation yield and membranes’ selective properties  
546 when incorporating inorganic phases like nanomaterials. By smartly selecting the  
547 hydrophilic nanostructured materials (such as graphene oxide, MXene, UiO-66 MOF),  
548 the resultant mixed matrix membranes based on CS may offer unprecedented permeation  
549 rates while improving the selective properties as well [23,67]. Also, these membranes  
550 can be assayed in other attractive PV separation applications, such as methanol/MTBE  
551 [77], water/isopropanol [78], water/hydrazine hydrate [79], requiring hydrophilic  
552 membranes. Due to their interesting capability to form H-bonding intermolecular forces,  
553 DESs could foster an outperforming extraction of some other polar solvents present in  
554 azeotropic systems [17,43]. Variety of available DESs, as well as high potential for new  
555 developments in this field, tries to design new DES-based membranes having tailored  
556 selectivity. Lately, visualizing a possible preparation protocol in a more sustainable way,



557 the crosslinker agent (i.e., glutaraldehyde) could be substituted by another less harmful  
558 substance. Here, green substances, such as cinnamaldehyde [80], genipin [81], could  
559 be an alternative.

560

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569

### 570 **Conflict of Interest**

571 The authors declare no conflict of interest.

572

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