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Highlights

Poly(3-hydroxybutyrate) membranes were selective in methanol/water separation
A novel technique was designed to determine liquid sorbed composition by polymers
Very low standard deviations were registered in sorption compositions results
Cluster formation and plasticization were verified through sorption and pervaporation
Separation factor increased with temperature in mixture pervaporation tests

1 # Sorption and pervaporation of methanol/water mixtures with poly(3-
2 hydroxybutyrate) membranes
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12
13 ## Abstract
14 In this contribution, poly(3-hydroxybutyrate) (PHB) membranes were evaluated in sorption and pervaporation
15 experiments for methanol/water separation. Single component sorption tests showed that PHB membranes have
16 higher affinity towards methanol than water: at 40ºC the sorption degree was 18.4 and 1.1% respectively. This was
17 in agreement with contact angle measurements, performed with both liquids, and Hansen solubility parameter. PHB
18 sorption degree in the whole methanol/water composition range and three temperature levels were determined,
19 showing an anomalous behavior (sigmoid like curves). A simple technique, named by us "Desorption by
20 Dissolution", was developed to determine sorbed mixture composition. It basically consists on dissolving the
21 polymer after sorption equilibrium in the mixture has been reached, to completely extract the mixture. Then,
22 chromatographic analysis is used to determine solution composition. It does not require adapting equipment or using
23 vacuum devices neither cold traps. When both components were present, methanol grams sorbed in the membrane
24 were always lower than the mixture in which they were immersed, while water sorption was enhanced due to
25 methanol presence. Very low standard deviation values were registered (< 0.84) confirming the technique reliability.
26 Single component fluxes and mass flux ratio in pervaporation increased with temperature: methanol flux was $3.5 \times$
27 10^{-5} kg m^{-2} s^{-1} at 25°C, whereas at 50°C exceeded 7×10^{-5} kg m^{-2} s^{-1}; water flux increased from 1.8×10^{-5} kg m^{-2} s^{-1} at
28 30°C to 2.2×10^{-5} kg m^{-2} s^{-1} at 50°C. Since permeances decreased, the increase in fluxes with temperature can be
29 attributed to the increase in vapor pressure driving forces. Mixture pervaporation results showed similar behavior,
30 highlighting the fact that separation factor increased with temperature as well: 3.5 at 30ºC and 3.8 at 50ºC.
31 Selectivities were higher than 12 for 10%wt water/methanol+water mixtures. Results were discussed in terms of
32 polymer crystallinity, solubility parameters, component size, activation energies and cluster formation.
33
34 *Key words: pervaporation; sorbed mixture composition; sorption selectivity; methanol/water mixture;
35 permeance; activation energy.*
36
37 ## Introduction
38
39 Pervaporation has been considered as an alternative energy-efficient method to separate azeotropic mixtures,
40 close boiling point liquids, isomeric or heat sensitive components, and to remove low concentration pollutants from
41 aqueous waste (Smitha et al., 2004). During pervaporation, separation takes place by preferential sorption and
42 diffusion of the desired component through a dense membrane.
43 Alcohols dehydration is one of the most studied pervaporation separations systems. Particularly, ethanol/water
44 and isopropanol/water mixtures have achieved a suitable development to be applied commercially. Large number of
45 publications and patents can be found in literature related to ethanol/water (Chapman et al., 2008) and
46 isopropanol/water (Kuila and Ray, 2013) separation, whereas the methanol/water is scarce (Pang et al., 2010)
47 opening up an interesting research field.
48 Most membranes with reasonable selectivity to separate ethanol/water mixtures, reach very low selectivity when
49 they are evaluated with methanol/water mixtures, mainly due to their small differences in molecular size and
50 membrane affinities. Although this mixture does not form an azeotrope, this separation is costly to achieve by
51 distillation because of the low relative volatility of methanol and water (Won et al., 2003), a challenge for
52 researchers, precisely because of the similarity of the components forming the mixture.
53 The main uses of methanol are related to the manufacture of other chemicals and fuels. It is mainly used in the
54 production of formaldehyde, acetic acid, methyl tert-butyl ether (MTBE) and as a basis for obtaining intermediate
55 products to be used in the synthesis of resins, foams and plastics. It is considered the most promising fuel for fuel
56 cells (Sridhar et al., 2005).
57 Table 1 summarizes the performance of several membranes for methanol-water separation under different
58 pervaporation operating conditions, reported in research articles since 2003 to date.
59
60 Table 1: Research papers that record the separation of methanol/water mixture by pervaporation, since 2003 to date.

Membrane	T (°C)	p_ℓ (kPa)	$w_{methanol}$	β_{ij}^{PV}	j (kg m^{-2}h^{-1}) (membrane	$j \times 10^5$ (kg m^{-2}s^{-1})	Authors

					(thickness, μm)		
PDMS and ZIF-71 Mixed matrix membranes: 10:0 10:1 10:2 10:3 10:4	50	NS	5%	5.3 6.1 7 8 7.7	0.486 (7) 0.469 (8) 0.611 (9) 0.458 (12) 0.417 (15)	13.5 13.0 17.0 12.7 11.6	(Li et al., 2014)
PPO composite membranes	70	NS	90%	27	1.3	36.1	(Fu et al., 2014)
(Vapor permeation) Sodium alginate/PVA (80/20) complexed with Ca ions and annealed 12h at 110ºC.	40 70 60 60 60 60	NS	80 80 95 90 80 60	∞ 46 83 135 160 30	0.017 0.07 0.018 0.025 0.04 0.06	0.5 1.9 0.5 0.7 1.1 1.7	(Bano et al., 2013)
ZIF-71 (using zinc acetate and 4,5-dichloroimidazole)	25	NS	5%	21.38	0.395	11	(Dong and Lin, 2013)
PA-6 asymetric	30 40 50 60	NS	90%	891 81 9 4.5	16.5 33.8 40 48	458.3 938.9 1111.1 1333.3	(El-Gendi and Abdallah, 2013)
PVA crosslinked with formaldehyde solution with TMSPEDA	30	NS	(20%v)	1.2-1.7	0.8 - 3.4	22.2 - 94.4	(Hu et al., 2013)
Sulfonated (5%) polyphenylsulfone	60	0.1	85%	11.1	0.033 (16)	0.92	(Tang et al., 2012)
SA/PVA complexed with divalent calcium ions	60	NS	80%	∞	0.025	0.7	(Mahmood et al., 2012)
PDMS/Silica nanocomposites membranes	30 40 50 60 30 30 30	0.1	4% 4% 4% 4% 1% 5% 10%	25 24 23 22 37 21 19	0.09 0.15 0.38 0.44 0.06 0.19 0.38	2.5 4.2 10.6 12.2 1.7 5.3 10.5	(Shirazi et al., 2012)
Chitosan	30	NS	4%	5	0.08 (100)	2.2	
Chitosan crosslinked with glutaraldehyde	30	NS	4%	4	0.11 (100)	3.0	(Zielińska et al., 2011)
PVA	NS	(Temperature gradient as diving force)	99% 97%	7 4.5	0.0016 (30) (water fluxes) 0.0054 (30)	0.044 (wáter fluxes) 0.15	(Sarkar et al., 2010)
Composite membr. PVA/ P(AA-Co-AN/SiO$_2$)	60	NS	98%	1534	0.58	16.1	(Pang et al., 2010)
PAI-PEI Hollow fiber	60	NS	85%	4.71	1.03	28.6	(Wang et al., 2009)
Supported hydroxyl sodalite	30 200	0.3	82%	∞	0.08 (1) 0.6 (1)	2.2 16.7	(Khajavi et al., 2009)
PPMS-CA	40	0.7-1.3	5%	5.1	1.36 (1-2)	37.8	(Luo et al., 2008)
PDMS-CA	40	0.7-1.3	5%	7	1.14 (1-2)	31.7	
PAA-co-AN nano SiO$_2$	60	1	98%	1458	0.32	8.9	(Liu et al., 2008)
PAA-co-AN nano SiO$_2$	70	1	70%	12	7.1	197.2	
DD3R zeolite membrane (Si/Al =980)	70	1	88%	5.5	2	55.6	(Kuhn et al., 2008)
Crosslinked PDMS	30	1	3%	1.8	0.56	15.5	(Mohammadi

2

	T	p_ℓ	$w_{metanol}$	β_{ij}^{PV}	j	ℓ	
– CA support							et al., 2005)
A type Zeolite (Mitsui)	60	0.7	89.9%	10000	0.46 (10-30)	12.8	
T type Zeolite (Mitsui)	60	0.7	90.2%	100	0.27 (10-30)	7.5	(Sommer and Melin, 2005b)
Amorphous Silica (ECN)	60	1.1	89.6%	10	1.87 (0.2)	51.9	
Amorphous Silica (Pervatech)	60	1.3	89.5%	20	0.39 (0.2)	10.8	
T type Zeolite (Mitsui)	90	2	90%	2240	1.5	41.6	(Sommer and Melin, 2005a)
Amorphous Silica (ECN)	90	2	90%	55	2.2	61.1	
PERVAP® 2201 (Sulzer Chemtech)	60	1	10%	3	1.6	44.4	(Van Baelen et al., 2005)
Ge-ZSM-5	30	0.5	5%	36	0.5	13.9	(Li et al., 2003)
Crosslinked Chitosan Membr.	45	0.3	83.9%	5.3	0.49 (26.2)	13.6	(Won et al., 2003)
Tubular Membr. Pervatech+Silica	51	0.8-1	85%	7	0.7 (0.1)	19.4	(ten Elshof et al., 2003)
B-ZSM-5 monolith supports	30	1	5%	8.5-12	0.21-0.12	5.8 – 3.3	(Bowen et al., 2003)

61 T: feed mixture temperature, p_ℓ: permeate pressure, $w_{metanol:}$ %wt methanol in feed, β_{ij}^{PV}: separation factor, j: total flux, ℓ:
62 membrane selective layer thickness, PDMS: polydimethylsiloxane, ZFI: zeolite imidazolate frameworks, PPO: poly(2,6-
63 dimethyl-1,4-phenylene oxide), PVA: poly(vinyl alcohol), PA: polyamide, TMSPEDA: N-3-(trimethoxysilyl) propyl
64 ethylendiamine, SA: Sodium alginate, AA: acrylic acid, AN: acrylonitrile, PAI: polyamide-imide, PEI: polyetherimide, PPMS:
65 polyphenylmethylsiloxane, CA: cellulose acetate microfiltration membranes as support, Ge-ZSM-5: Germanium-substituted
66 Zeolite membranes, B-ZSM-5: Boron-substituted Zeolite membranes, NS: not specified.

68 The involved phenomena in pervaporation is described by the well known sorption-diffusion model, in which
69 selective sorption becomes a fundamental parameter to characterize a membrane. Regarding sorption experiments,
70 when a polymer is contacted with a vapor or liquid mixture, mixture composition in the polymer under equilibrium
71 conditions will generally differ from the contacting composition, mainly caused by a selective sorption phenomenon
72 within the polymeric matrix. Relation of vapor or liquid composition with the corresponding polymer mixture
73 sorbed values, is useful to study and predict polymer behavior for different applications such as membrane
74 separation processes (Baker, 2004; Heintz et al., 1991; Mulder, 1991), film packaging (Barr et al., 2000), sensor
75 development (Adhiri and Majumdar, 2004), among others.

76 The most widely used technique to determine sorbed mixture composition into a polymer matrix, consist of
77 introducing the polymer film in the desired liquid mixture and when the sorption equilibrium is reached, film is
78 removed, wiped carefully with tissue paper and immediately placed in a device for desorbing the liquid by vacuum
79 and heat. Produced vapors are collected in another container, cooled with liquid nitrogen, and the composition is
80 determined by gas chromatography or another technique. Most authors use this technique (Bhat and Pangarkar,
81 2000; Cunha et al., 2002; Kao et al., 2002; Luo et al., 2007; Ma et al., 2008; Niang and Luo, 2001; Peng et al., 2006;
82 Wolinska-Grabczyk, 2006) and some others have done minor modifications, such as carrying out the desorption in
83 the pervaporation system itself, instead of using an additional device (Kondolot Solak et al., 2008).

84 Despite being the most common technique, it has some drawbacks:

85 - Total desorption of the liquid sorbed by the membrane cannot be guaranteed. Some authors weigh the
86 membrane along the desorption stage, ending the experiment when the membrane reaches its initial dry weight.
87 This leads to considerable error due to successive stages of weighing and also causes long desorption times.

88 - To collect enough liquid volume, it is necessary to work with large membrane samples, that requires more time
89 for sorption and desorption steps, and even to place the membrane in the desorption device. Consequently, it
90 leads to increasing component evaporation and accuracy loss, especially when working with very volatile
91 substances.

92 - It is noteworthy that many authors report to weigh the membrane, before carrying out the desorption
93 experiment, to establish the total sorption degree. So, in the whole process, the solvents can be evaporated from
94 the membrane before desorption process begins. Under these conditions, is very likely that composition of the
95 mixture in the membrane differs from the corresponding equilibrium value.

96 Recently, some new interesting alternative techniques to determine liquid mixture composition in polymeric
97 films were reported. Kamaruddin and Koros (Kamaruddin and Koros, 2000) studied methanol/MTBE mixtures
98 sorption in a glassy polyimide. They extracted the organics from the polymer with a 5 wt % N,N-dimethyl
99 acetamide (DMAc) water solution. Since DMAc is a swelling polyimide agent, desorption of organics from the
100 glassy polymer must have been facilitated. Organic extract composition was analyzed with gas chromatography
101 head-space analysis. Hauser et al. (Hauser et al., 1989) have reported the desorption of water containing organic

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102 mixtures from polyvinylalcohol, using carbon tetrachloride followed by desorbate analysis with infrared
103 spectroscopy. Awkal et al. (Awkal et al., 2006) have reported a new technique based on in situ desorption in a [1]H
104 NMR tube for determining the sorption selectivity of a series of new poly(urethane-imide)s and Clèment et al.
105 (Clément et al., 2007) have designed a desorption apparatus which consist of a desorption mini-oven coupled with
106 an on-line chromatograph.
107 In this contribution we present a simple technique, named by us as "Desorption by Dissolution", that does not
108 require adapting equipment and there is no need of vacuum devices and liquid nitrogen. Moreover it is suitable for
109 analyzing polymers with low sorption degree and after sorption equilibrium is reached by the polymer, subsequent
110 steps depend only on polymer dissolution time which is much easier to perform than desorption. With this technique
111 it is possible to perform quick and reliable determination of membrane sorption selectivity thus providing valuable
112 information for pervaporation process.
113 Sorption and pervaporation tests were performed with poly(3-hydroxybutyrate) (PHB) membranes and
114 methanol/water mixtures. PHB is an intracellular polyester synthesized by certain bacteria as a carbon and energy
115 storage compound. It was previously characterized (thermal behavior and crystallinity degree) and evaluated for
116 methanol/MTBE separation by pervaporation by our research group with promising results (Villegas et al., 2011).
117 Within these, highlight the fact that both flux and separation factor increase with feed mixture temperature. That is
118 why we have decided to continue evaluating the performance in pervaporation of this membrane material for the
119 separation of other mixtures of interest.

2. Experimental

2.1. Materials
124 Powder PHB (Mw ~ 524.000 g/mol) was kindly provided by BIOCYCLE®, PHB Industrial S.A. (Brazil).
125 Methanol was provided by Merck (Germany) and chloroform, by Cicarelli (Argentina). All chemicals were of
126 analytical grade and used without further purification.

2.2. Membrane synthesis
129 PHB polymeric membranes were prepared as described in (Villegas et al., 2011) by casting a chloroform
130 solution (6 wt./v%) in glass Petri dishes. After primary crystallization, where there exists a fast spherulitic growth, a
131 period of slower crystallization takes place called Secondary Crystallization that occurs once the spherulite surfaces
132 have impinged on each other (IUPAC, 1997). That is why after solvent evaporation at room temperature,
133 membranes were stored for three weeks in a dry atmosphere to complete secondary crystallization of the amorphous
134 phase (de Koning and Lemstra, 1993; de Koning et al., 1994; El-Hadi et al., 2002), since PHB is slow to reach
135 crystallization equilibrium (Gunaratne et al., 2004).

2.3. Contact Angle
138 Contact angle (Θ) measurements were performed by the sessile drop method at room temperature, using a
139 goniometer (Standard Goniometer with DROPimage standard, model 200, Ramé-Hart Instrument Co., USA). A
140 drop of liquid (water or methanol) (10 μL) was placed onto the polymer surface by a micro syringe. The drop image
141 was recorded by the video camera and digitalized. The drop shape was solved numerically and fitted using a
142 mathematical soft provided by the manufacturer. Five readings were taken on different parts of each film. Average
143 of contact angle values and standard deviation were calculated.

2.4. Liquid sorption
146 PHB membranes were dried in an oven at 45ºC and then under vacuum for 2 days. They were weighed and
147 immersed in methanol/water mixtures with different compositions at three temperature levels. After sorption
148 equilibrium was reached, the membranes were removed, wiped carefully with tissue paper, and weighed
149 immediately. The first measurement was performed after a week and repeated several times to guarantee
150 equilibrium sorption has been reached. Sorption degree (%S) of the membrane is defined by the following equation:

151 $$\%S = \frac{m_w - m_d}{m_d} \times 100 \qquad (1)$$

152 m_d denotes the mass of the dried membrane and m_w the mass of the membrane after sorption equilibrium. All
153 experiments were repeated four times and the results averaged. The calculated mean standard deviation was less
154 than 1.6%. For pure substances sorption, sorbed mass ratio (θ) was also calculated for each temperature as
155 expressed in eq. (2).

156 $$\theta = \frac{\%S_i}{\%S_j} \qquad (2)$$

157 subscript i denotes the component with the highest sorption degree and j with the lowest.

2.5. New technique to determine sorbed mixture composition

2.5.1 Technique steps

4

162   The technique designed to determine composition of the mixture sorbed in a given material, has been named
163 "Desorption by Dissolution (DxD)" and basically consists on dissolving the polymer, after sorption equilibrium in
164 the mixture has been reached, to completely extract the sorbed mixture. Although this idea is not novel (it could be
165 thought as a special liquid-solid extraction case where the extraction solvent can dissolve the polymeric membrane),
166 it has never been applied to determine sorbed mixture composition in polymers. The developed procedure can be
167 described by the following steps:

168 1. Immerse dried membranes samples (2×5 cm^2) into an appropriate amount of liquid mixture of interest, using
169   hermetic recipients, and keep them at a specific temperature until sorption equilibrium is reached. This period of
170   time should be previously determined as the time needed to reach constant weigh of the sorbed membrane,
171   parameter that depends on temperature, polymer and mixture under study (Section 2.4). The amount of liquid
172   mixture should be such that liquid phase composition does not change significantly due to membrane sorption.

173 2. Prepare test tubes with caps and place a given volume of a suitable polymer solvent to ensure complete
174   membrane dissolution. A test tube for each sorbed membrane is needed and for each run, at least three repetition
175   tests should be performed to compare obtained values and to establish standard deviations.

176 3. Remove sorbed membranes from liquid mixtures, wipe them carefully between tissue papers and introduce them
177   immediately in the test tubes containing the membrane solvent. Make sure that they are hermetically sealed.

178 4. Maintain the tubes at a suitable temperature to achieve membrane dissolution (usually it should be heated to
179   accelerate the dissolution step and according to Van Krevelen (Krevelen, 1990), the dissolution is better
180   promoted close to the solvent boiling temperature).

181 5. Once the obtained homogeneous solution reaches again room temperature, use gas chromatography or other
182   appropriate technique to determine the sorbed solution composition. In the case of chromatography, three peaks
183   will be detected: two of them corresponding to the mixture of interest and the third one to the solvent.

184   Concentrations reported in this contribution were obtained with a Buck Scientific Gas Chromatograph (GC),
185 Model 310, with thermal conductivity detector, (USA) equipped with a Porapack Q column. Results were always
186 the average of four experiments for each system. Standard deviation is presented for each experimental data.

187   To verify that the dissolved polymer did not affect the chromatographic analysis, a solution was prepared with a
188 known composition of a mixture of interest, and the membrane solvent was add. This solution was divided into two
189 test tubes. A membrane piece was introduced and dissolved in one of them. Solutions of both tubes were analyzed
190 trough chromatography and the spectrums were equal.

191   The same procedure was performed with two other solutions at different mixture compositions, confirming that
192 the polymer presence did not affect the results. Furthermore, the chromatograph calibration curve was done again
193 when the measurements were finished, to analyze if the chromatographic column has suffered any kind of soiling by
194 the polymer and no changes were observed. The average weight of the dry membranes used in these experiments is
195 0.16 g, membranes that are dissolved in 3 cm^3 of solvent. The injections in the chromatograph were of 8 microliters,
196 so 4.3×10^{-4} g of polymer are introduced in each injection. We can guarantee that more than 10000 injections can be
197 done without even notice that there is some polymer inside the column. Furthermore, the polymer is not driven by
198 the carrier within the chromatograph, and it remains in the injection zone where the solvent evaporates almost
199 instantly upon entering the column at high temperature. Anyway, if the reader is still concerned about the
200 chromatographic column, we can suggest the following things that are very easy to implement:

201   a) Using a syringe with a syringe filter, like the ones that are used very often to clarify small-volume
202 sample solutions prior to HPLC, suck out the liquid consisting on polymer, solvent and binary mixture, to remove
203 the polymer. There are plenty of commercial filters, and one with a PTFE membrane is recommended due to its
204 chemical resistance. Use this polymer free filtered liquid for injection into the GC.

205   b) Use a pre-column before the chromatographic column. It consists on a 5 to 10 cm in length column filled
206 with a material with no separation purposes. It will serve to retain the polymer micrograms after each injection. If
207 there is a decrease in the flow rate of carrier gas (which does not occur until after approximately 10000 injections),
208 change the pre-column section for a new one.

209   With this technique it is possible to calculate the Sorption Separation Factor $\left(\beta_{ij}^s\right)$ (called Sorption Selectivity or
210 Solubility Selectivity by some authors), calculated in similar fashion as in pervaporation, but in this particular case,
211 it relates the sorbed composition in the membrane, with the mixture composition of the liquid where the membrane
212 was immersed.

213    $$\beta_{ij}^s = \frac{x_{im}/x_{jm}}{x_{io}/x_{jo}} \qquad (3)$$

214   x_i and x_j denote components i and j mole fractions, and the subscripts o and m, feed and sorbed mixture in
215 the membrane, respectively. According to the solution-diffusion model, the selectivity of a membrane is factored
216 into a product of solubility selectivity and diffusivity selectivity $\left(\beta_{ij}^D\right)$ (Xu et al., 2003) which can be calculated,
217 taking into account the pervaporation separation factor $\left(\beta_{ij}^{PV}\right)$, by the following:

218    $$\beta_{ij}^D = \frac{\beta_{ij}^{PV}}{\beta_{ij}^S} \qquad (4)$$

5

219   The Concentration Ratio $\left(\psi_i^s\right)$, called by some authors Enrichment Factor, can also be determined, among other
220   relevant factors and parameters for mathematical modeling.

221    $$\psi_i^s = \frac{x_{im}}{x_{io}} \qquad (5)$$

222

223   *2.5.2 Advantages*
224   — This technique ensures total desorption, since the membrane is dissolved, with no need to weigh it
225   continuously to verify that total desorption has been achieved. It should be noted that, despite working with a
226   crosslinked polymer, the technique is equally applicable. It is known that crosslinks prevent the liquid molecules
227   from penetrating the polymer (Carraher, 2003). Therefore, they neither allow entry of the solvent into the polymer
228   matrix nor the permeant mixture, so it does not matter if these segments remain undissolved. However, the not
229   crosslinked and amorphous regions, responsible of transport properties, will always be dissolved. On the other hand,
230   a membrane with an excessive degree of crosslinking, loses the sense of being applied in separation processes
231   because they are practically impermeable.
232   — There is no need to adapt equipments, such as vacuum pumps or special devices, or even use cold trap
233   lines, to perform sorption experiments. Only sensible concentration instruments are needed to ensure reliable results.
234   — It is not necessary to use a large amount of membrane since usual chromatographic sensibility ensures
235   sorbed component detection, even when polymer presents low sorption degrees.
236   — The same procedure can be used for multicomponent mixtures or adapted easily for vapor sorption.

237
238   *2.6. Pervaporation*
239   Pervaporation experiments, as described in (Villegas et al., 2011), were carried out in a standard permeation
240   stainless steel circular cell, using a flat sheet membrane with an effective transport area of 2.83×10^{-3} m². The
241   membrane was supported on a filter paper over a porous sintered steel disk. The feed solution was maintained at the
242   desired temperature with a thermo-circulator water bath being fed directly to the membrane side of the cell through a
243   peristaltic pump. The permeate side was kept at a constant pressure of 130 Pa by a vacuum pump and the vapor from
244   the permeate side was collected in cold traps with liquid nitrogen. To guarantee uninterrupted operation, two cold
245   traps were used in parallel, and a third one was used for pump protection. At the end of each run, the pump
246   protection cold trap showed no traces of condensed liquid (i.e. the permeate was completely condensed in the first
247   one). Total permeation flux was determined by measuring the weight collected in the first cold trap every hour at
248   steady state conditions. Compositions of both, permeate collected and the feed, were determined by thermal
249   conductivity gas chromatography (Buck Scientific Gas Chromatograph, Model 310, with thermal conductivity
250   detector, (USA) equipped with a Porapack Q column). Pervaporation experiments with single components and
251   methanol/water mixtures were performed at 30, 40 and 50ºC. Pervaporation performance of the membrane was
252   evaluated on the basis of flux (j_i, kg m⁻² s⁻¹), pervaporation separation factor (β_{ij}^{PV}) and the flux ratio (φ) to
253   estimate an ideal selectivity for pure substance pervaporation.

254    $$j_i = \frac{Q_i}{A.t} \qquad (6)$$

255    $$\beta_{ij}^{PV} = \frac{x_{i\ell}/x_{j\ell}}{x_{io}/x_{jo}} \qquad (7)$$

256    $$\varphi = \frac{j_i}{j_j} \qquad (8)$$

257   Q_i denotes the weight of permeate i collected within time t, A the membrane effective area, x_i and x_j are the molar
258   fractions of components i and j, and subscripts o and ℓ denote feed and permeate sides, respectively. According to
259   Wijmans (Wijmans, 2003) and Baker et al's (Baker et al., 2010) suggestions, evaluation of the membrane
260   performance using permeances (P_i^G/ℓ, expressed in gpu= 1×10^{-6} cm³(STP) cm⁻² s⁻¹ cmHg⁻¹) and corresponding
261   selectivities (α_{ij}) were also calculated from Eqs 9-12.

262    $$\frac{P_i^G}{\ell} = \frac{j_i}{(f_{io} - p_{i\ell})} \qquad (9)$$

263    $$\alpha_{ij} = \frac{P_i^G}{P_j^G} \qquad (10)$$

264   where P_i^G denotes the gas based permeability, ℓ is the membrane thickness, f_{io} is the feed side fugacity and $p_{i\ell}$ the
265   partial pressure of a component i on the permeate side of the membrane, calculated as:

266    $$f_{io} = \gamma_{io}^L x_{io} p_{io}^{sat} \qquad (11)$$

267    $$p_{i\ell} = x_{i\ell} p_\ell \qquad (12)$$

6

268 and γ_{io}^{L} is the activity coefficient of component i in the liquid feed, p_{io}^{sat} the pure component i vapor pressure and
269 p_{ℓ} the total pressure in the permeate side. Activity coefficients were estimated using the Wilson equation and the
270 parameters reported by Park et al. (Park et al., 2002). The molar volume of pure-liquid compound at each
271 temperature needed in the Wilson equation was calculated with the Component Plus Program (ProSim S.A.) and
272 p_{io}^{sat} with the Antoine equation. These experiments were repeated eight times for each set of conditions and the
273 results averaged. The mean standard deviation calculated was less than 8%.
274
275
276 **3. Results and discussion**
277
278 *3.1 – Pure substances sorption*
279 Figure 1 shows sorption results of methanol and water in PHB membranes at different temperatures. It is
280 observed that the membrane sorbs preferably methanol, *%S* increasing with increasing temperature, as expected for
281 liquid sorption. Sorbed water percentage is much smaller and has a very slight increase with rising temperature. That
282 is why the sorbed mass ratio of methanol to water ($\theta_{methanol/water}$) increases with temperature, reaching a value of 16
283 at 40 º C.
284
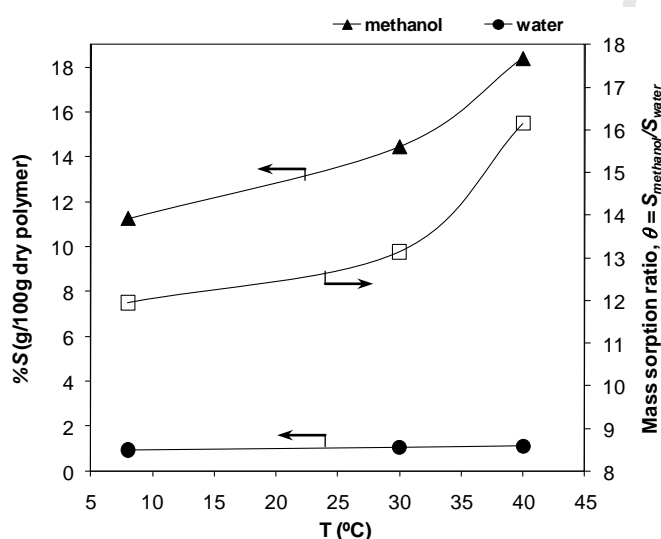
285
286 Figure 1: Effect of temperature on single water and methanol sorption in membranes PHB.
287
288 These results agree with those predicted by the Hansen theory and the contact angle measurements of both
289 solvents in the PHB membranes (Table 2). According to Hansen (Hansen, 2004), the solubility of a polymer is
290 characterized in a three dimensional space by a spherical solubility region, which center is defined by the polymer
291 solubility parameters, and the sphere radius is called the interaction radius (R_o). To determine if a solute lies within
292 the solubility sphere of a polymer and therefore dissolves the polymer, its distance to the polymer center should be
293 lower than the interaction radius for the polymer. The distance between solute and the center of the solubility sphere
294 ($\Delta\delta_{(s-p)}$) is calculated as:

295 $$\Delta\delta_{(s-p)} = \left[4\,({}^{s}\delta_{d} - {}^{p}\delta_{d})^{2} + ({}^{s}\delta_{p} - {}^{p}\delta_{p})^{2} + ({}^{s}\delta_{h} - {}^{p}\delta_{h})^{2} \right]^{1/2} \qquad (13)$$

296 where ${}^{s}\delta$ and ${}^{p}\delta$ are the Hansen parameters for solvent and polymer, respectively. Subscripts refer to atomic-
297 nonpolar interactions (*d*), molecular-dipolar interactions (*p*), and molecular-hydrogen bonding interactions (*h*).
298 Terada and Marchessault (Terada and Marchessault, 1999) determined the solubility parameters (Table 2) and
299 the interaction radius ($R_o = 8.5$) for the amorphous PHB. As can be seen, $\Delta\delta_{(methanol-PHB)} > R_o$ for both solvents but
300 methanol is nearest, which suggest more affinity to the alcohol.
301
302 Table 2: Solubility parameters (δ, MPa$^{1/2}$), contact angle (Θ), kinetic diameter (Φ_k) and molar volume (υ).

	δ_d	δ_p	δ_h	[2]$\Delta\delta_{(s-p)}$	[3]Θ	Φ_k (nm)	[4]υ (cm^3/mol-g)
[1]PHB	15.5	9.0	8.6	—	—	—	—
Methanol	15.1[a]	12.3[a]	22.3[a]	14.1	23.7 ± 0.3	0.39[c]	40.73
Water	15.5[b]	16.0[b]	42.3[b]	34.4	64.1 ± 1.2	0.27[d]	18.07

303 [1] Data from (Terada and Marchessault, 1999); [2]$\Delta\delta_{(s-p)}$ calculated from eq. 13; [3] this contribution; [4] Perry's Chemical Eng.
304 Handbook (Perry and Green, 1999); [a] Data from (Ma et al., 2008); [b] Data from (Shao and Huang, 2007); [c] Data from (Sano et al.,
305 1995); [d]Data from (van Gemert and Petrus Cuperus, 1995);.

7

306
307   According to surface chemistry theory, the contact angle between solutions and a film can be used to judge the
308 interaction between organic and membrane as well. Smaller contact angle indicates more liquid-solid affinity. As
309 can be seen in Table 2, methanol/PHB contact angle (Θ) is much smaller than water/PHB. Therefore, both methods
310 agreed in pointing out to a higher methanol-polymer affinity (smaller $\Delta\delta_{(s-p)}$ and Θ), endorsing the results of pure
311 liquids sorption.
312
313 *3.2 – Pure substances pervaporation*
314   Pervaporation results working individually with methanol and water are shown in Figure 2.a. Methanol fluxes
315 exceed water ones at all tested temperatures. The methanol flux increase with temperature is very sharp and almost
316 linear, taking values close to 3.5×10^{-5} kg m^{-2} s^{-1} at 25 ° C, whereas at 50 ° C exceeds 7×10^{-5} kg m^{-2} s^{-1}. On the other
317 hand, water flux is maintained near 2×10^{-5} kg m^{-2} s^{-1}, rising slightly with increasing temperature. As result, the flux
318 ratios indicate the preference for methanol permeation and an increasing mass flux ratio (φ) with temperature.
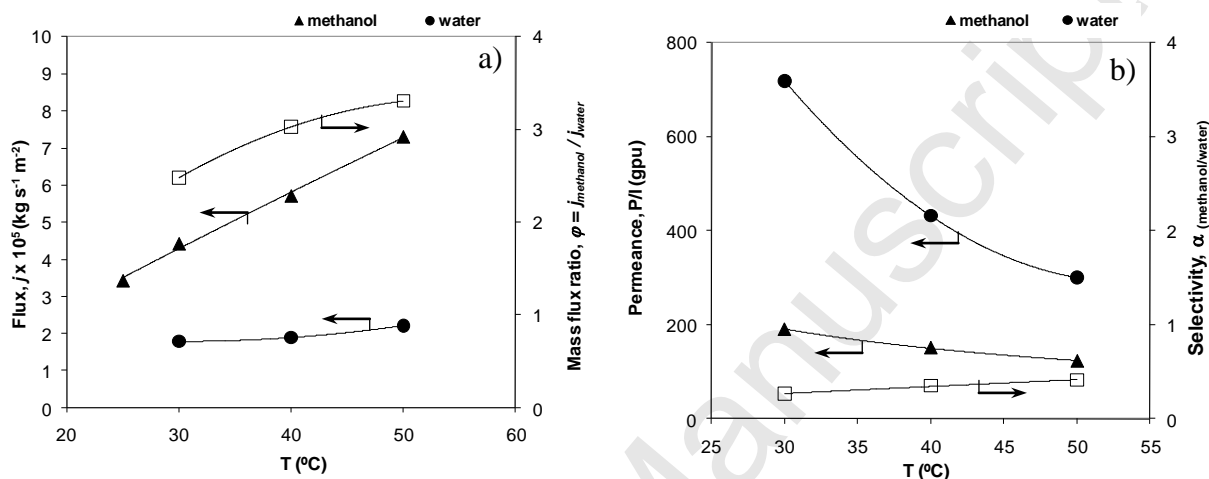
319
320
321 Figure 2: Effect of feed temperature in single methanol and water pervaporation tests in PHB membranes, a) flux
322 and mass flux ratio; b) permeance and selectivity.
323
324   The permeation behavior reflects the sorption results obtained for pure compounds, following the same trend, i.e.
325 a low sorption, low permeation and slight temperature effect for water, while the opposite behavior occurs for
326 methanol.
327   Segmental polymer mobility and consequently its free volume, increase with temperature, leading to a faster
328 permeant molecular transport. At the same time, the driving force for mass transport also increases since it depends
329 upon the vapor pressure of each pure compound. To avoid this latter effect, gas-based permeance results are plotted
330 as a function of temperature in Figure 2.b. As can be seen, permeances decreased as temperature increased but
331 selectivity increase. Therefore, the increase in fluxes with temperature can be attributed to the increase in the vapor
332 pressure driving forces. Notice that selectivity in Fig. 2.b is lower than one because water permeances are higher
333 than methanol's. This is due to pure methanol vapor pressure is approximately five times higher than that of water
334 in this temperature range, that is, a driving force five times higher for methanol, giving high fluxes but low
335 permeances.
336
337 *3.3 – Pervaporation of a 10%wt water/(methanol+water) mixture*
338   Results of pure components sorption and pervaporation tests indicated that methanol should be the component
339 that preferably permeates the membrane in methanol-water mixture separation by pervaporation. However, tests for
340 a 10% wt/wt methanol/(water + methanol) feed mixture at 50 °C, resulted in an average total flux of 2×10^{-5} kg s^{-1}
341 m^{-2} and an average separation factor of 0.85, which corresponds to a composition in the permeate 8.5% wt/wt
342 methanol. This separation factor value lower than one means that when both compounds are present in the feed
343 mixture, water permeates the membrane preferably. This phenomenon will be understood and explained in section
344 3.5 with the results from DxD technique.
345   Therefore, a mixture with a lower proportion of water (10% wt/wt water in the mixture) was prepared and used
346 as feed mixture for pervaporation tests (i.e. membrane for dehydration of alcohols). The results of these experiments
347 are presented in Figure 3. The feed mixture temperature slightly affects permeate fluxes, increasing with increasing
348 temperature (Fig 3.a). A mild increase in separation factor with temperature was recorded as well and
349 $\beta^{PV}_{water/methanol}$ was between 3.5 and 3.8. Although this simultaneous increase does not correspond to usual behavior
350 of polymeric membranes, the PHB presented the same behavior against methanol-MTBE mixtures studied by our
351 research group, information that was reported in a previous paper (Villegas et al., 2011). This demonstrates that the

8

352 effects of swelling and plasticization that cause decreased selective ability in membranes separation processes are
353 less pronounced as the temperature increases, due to the high degree of crystallinity of PHB membranes.
354   In Figure 3.b, fluxes were normalized with respect to the driving force to make comparison independent of
355 operational parameters. As can be seen, permeances of both components decreased as temperature increased.
356 Therefore, the rise in both fluxes with temperature was due to the increasing driving force.
357   The flux of each component decreased when working with the mixture compared with the pure component
358 fluxes (Figure 2.a vs. Figure 3.a), since the driving force for transport also decreased because it is a mixture. When
359 this information is traduced in permeances, water preferably permeates the membrane and the values are higher than
360 for pure water (Figure 2.b vs Figure 3.b) while methanol's are lower. Methanol presence enhances water permeation
361 due to its higher affinity towards the membrane material, as was discussed in section 3.1, plasticizing the polymeric
362 matrix. Moreover, the lower size of water molecules in relation to methanol's (Table 2) allows water to permeate in
363 the plasticized material reaching high selectivity values ($\alpha_{water/methanol} \cong 13$).
364
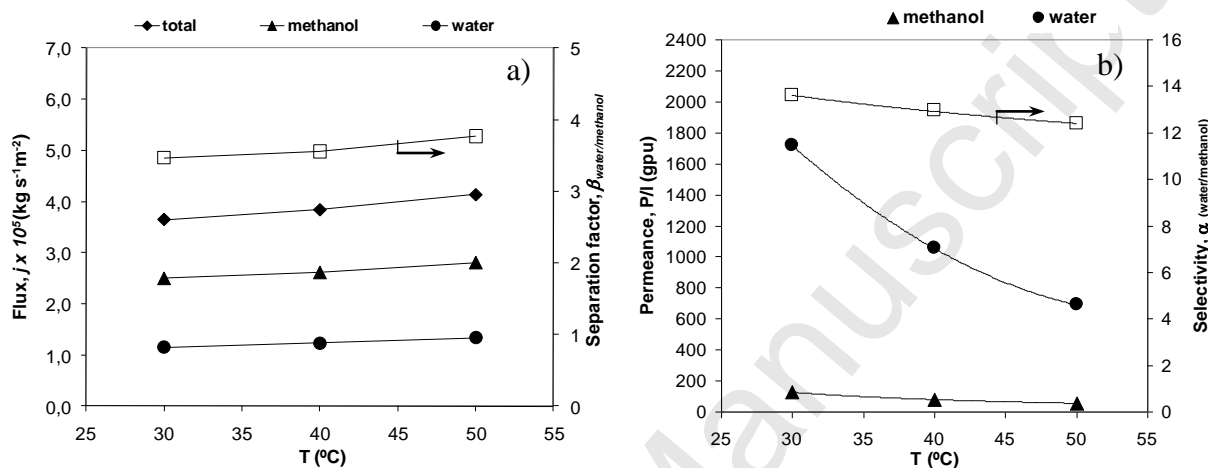
365
366 Figure 3: Effect of feed temperature in pervaporation tests for 10%wt/wt water/(water+methanol) mixtures in PHB
367 membranes, a) flux and separation factor; b) permeance and selectivity.
368
369 *3.4 – Effect of feed composition and temperature on sorption*
370   The effect of feed composition on sorption degree (*%S*) at different temperatures is shown in Figure 4. As
371 expected, the %S increased with temperature for each composition, reaching 18% for pure methanol (right axis) at
372 40 °C. For pure water, sorption values are very low (1%) and they are practically indifferent to temperature.
373   For each isotherm, an increase in the sorption degree was observed for the membranes as methanol concentration
374 increased in the mixture in which they were immersed. This increase in %S does not follow an ideal behavior,
375 indicated by dotted lines in the figure for each temperature.
376   At low temperatures (8°C) the *%S* is lower than ideal in the whole composition range. Furthermore, the *%S*
377 increases linearly up to a concentration of 50%wt. When this concentration is exceeded, a change in slope is
378 observed but a linear trend is noticed as well.
379   At higher temperatures, when the methanol concentration is low, the *% S* is less than ideal. When methanol
380 concentration is increased (compound with higher affinity to the polymer) this behavior is reversed. For the 30ºC
381 and 40ºC isotherms, the sorption degree exceeds the predicted value for an ideal system at 70 %wt and 55%wt in
382 methanol (approximately) respectively. These sigmoid shapes correspond to an anomalous behavior and indicate
383 strong interactions between the mixture components. We will go back to this subject in the next section (3.5).
384

9
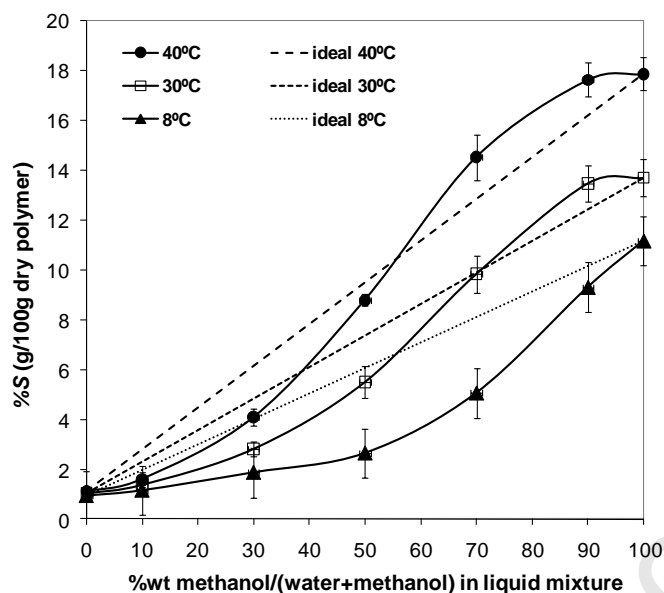
Figure 4: Effect of feed composition on sorption degree at different temperatures. Ideal behavior is represented with dotted lines for each temperature. Bars represent standard deviation.

3.5 – Sorbed mixture composition

Figure 5 shows the results of mixture composition sorbed by the PHB membrane, when they were immersed in methanol/water mixtures at different compositions and 30°C, determined by the "Desorption by dissolution" technique proposed in this contribution.
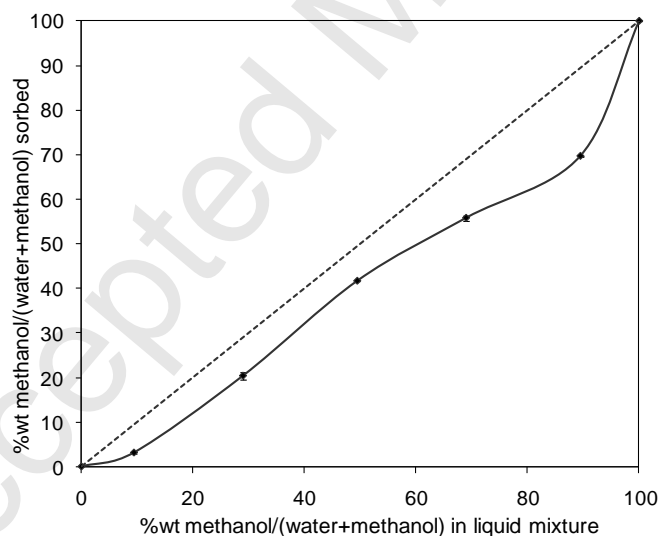

Figure 5: Liquid mixture composition sorbed by the PHB membranes at 30 °C, depending on the composition of the mixture in which they were immersed. Bars represent standard deviation but they are too small to be seen. Ideal behavior is represented with a dotted line.

Methanol concentration in the membranes was lower than the mixture in which they were immersed for the whole composition range. This can be attributed to the fact that the hydrogen bonding between water–alcohol pairs is much stronger than water–water and alcohol–alcohol pairs, causing water molecules to cluster around alcohol molecules (Krishna and van Baten, 2010). This explains the obtained pervaporation results for a 10% wt methanol (section 3.3), where methanol/water separation factors were lower than one. For this concentration, methanol composition in the membrane is only 3% wt. Furthermore, also affects the fact that the mobility of molecules is significantly lowered due to this cluster formation (Krishna and van Baten, 2010).

These data are easier to analyze if, for each mixture composition, the sorbed grams of methanol and water are graphed, taking into account information presented in Figure 4 and 5, resulting in Figure 6. It is observed that increasing methanol concentration in the mixture, increases methanol grams sorbed but most notorious is the increase of sorbed water grams, achieving a maximum value near 70%wt in methanol. This means that the presence

10

412 of alcohol contributes favorably in water sorption, reaching values four times higher than those corresponding to
413 pure water (left axis). Taking into account the polymer-solvent affinity mentioned in section 3.1, it can be assumed
414 that methanol acted as plasticizer and water penetrated the PHB together with methanol forming cluster structures,
415 increasing water sorption in the polymer.
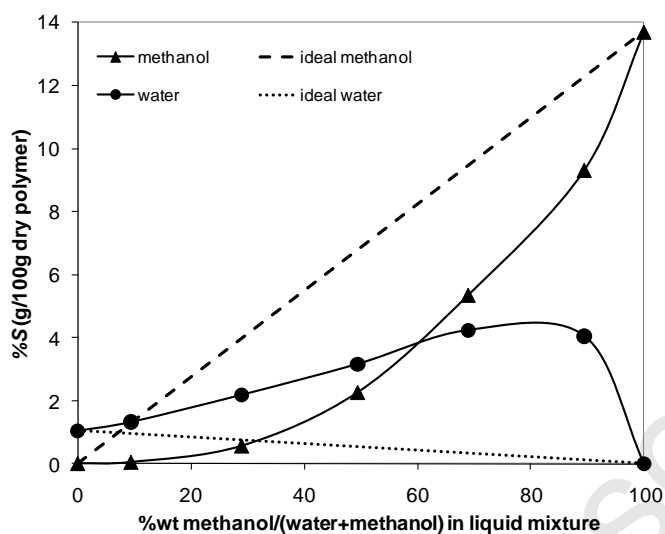
416
417 Figure 6: Grams of water and methanol sorbed by PHB membranes at 30°C, depending on the composition of the
418 mixture in which they were immersed. Ideal behavior is represented with dotted lines for each substance.
419
420

421   The sorption separation factor is greater than one for all compositions, indicating the preference to water sorption
422 when both components are present. Furthermore, this factor takes high values for mixtures that are in the extremes
423 of the range of composition, i.e. highly concentrated solutions in water or in methanol, showing a minimum value
424 close to 35%wt methanol. For the particular case of the 10%wt water mixture, separation factors were determined
425 through sorption and pervaporation tests: $\beta^S_{water/methanol}$= 3.69; $\beta^{PV}_{water/methanol}$= 3.47. Using Eq. (4), the diffusion
426 separation factor resulted $\beta^D_{water/methanol}$= 0.94. The sorption separation factor describes the sorption equilibrium
427 between liquid feed and the membrane immediately adjacent to it, while the diffusivity selectivity calculated from
428 Eq. (4) represents an average of the diffusivity characteristics across the membrane (Xu et al., 2003).
429 The preferential sorption of water in the membrane when methanol is present, together with the smaller molecular
430 size of water in comparison to methanol (kinetic diameter or molar volume in Table 2), pointed out to a membrane
431 with much higher selectivity than that obtained in pervaporation, effect attributed to cluster formation and confirmed
432 through DxD technique.
433
434 *3.6 – Activation energies*
435   Activation energy analysis completes the interpretation of temperature effects. To estimate the activation
436 energies of component *i* for liquid sorption (ΔHm_i = enthalpy of mixture), diffusion (Ed_i), and pervaporation (E_i)
437 processes, Arrhenius type relationships were assumed. Since E_i includes the effect of temperature on pervaporation
438 driving force, permeation activation energy (Ep_i) is more suitable to analyze the influence of temperature on
439 membrane permeation behavior (Feng and Huang, 1996). Activation energies, obtained from the logarithmic plots
440 with reciprocal temperatures, are presented in Table 3 and the equations are summarized in Villegas et al. (Villegas
441 et al., 2011).
442   High activation energy values implied a more sensitive behavior with temperature changes. Ep_i values were
443 negative for both compounds, indicating that the vapor sorption contribution (exothermic process) was more
444 important than the diffusion contribution on temperature dependence ($|\Delta Hs_i|>|Ed_i|$), since $Ep_i = Ed_i + \Delta Hs_i$. Thus,
445 the membrane permeability coefficient decreased as temperature increased. Temperature increase promoted
446 methanol diffusion to a greater extent than water ($Ed_{water}|<|Ed_{methanol}|$) and the methanol flux was more sensitive to
447 temperature changes than water.
448
449 Table 3: Enthalpy of mixture (ΔHm_i), Enthalpy of vaporization (ΔHv_i), Enthalpy of dissolution (ΔHs_i) and
450 activation energies for pervaporation (E_i), diffusion (Ed_i) and permeation (Ep_i) for pure compounds in PHB
451 membranes.

(kJ/mol)	Pure Components	
	Methanol	Water
ΔHm_i	10,63	3,77
E_i	23,49	8,67

11

Ed_i	12,85	4,90
ΔHv_i	38,02	43,87
ΔHs_i	-27,39	-40,10
Ep_i	-14,86	-35,20

452
453   Furthermore, the two components of the activation energy for pervaporation: enthalpy of mixing and activation
454 energy for diffusion, are much higher for methanol than water, highlighting that the effect of temperature for alcohol
455 is stronger.
456
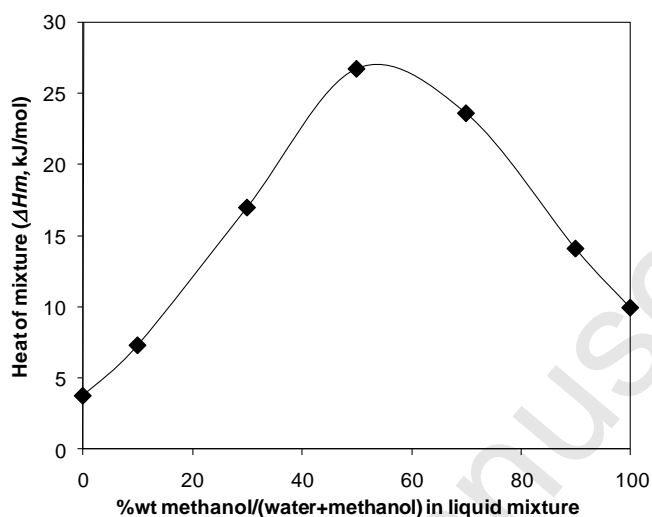
457
458 Figure 7: Enthalpy of mixture at different methanol-water compositions in PHB membranes
459

460   For binary mixtures, sorption results also followed an Arrhenius type behavior. Enthalpy of mixture, at different
461 compositions, obtained from sorption experiments are shown in Figure 7. The presence of a second component
462 increases ΔHm values compared with the pure ones, reflecting a strong molecular interaction between methanol-
463 water molecules, with a maximum value near 50%wt. This supports the hypothesis mentioned about cluster
464 formation.
465

466 **4. Conclusions**
467 Biodegradable poly(3-hydroxybutyrate) membranes were evaluated in sorption and pervaporation experiments for
468 methanol/water separation. A simple and reliable technique, named "Desorption by Dissolution", was developed and
469 successfully implemented to determine sorbed mixture composition in polymeric matrices. This technique also
470 helped to explain why pervaporation results sometimes are different than those predicted through total sorption
471 degree and liquid-solid affinity techniques. Single component fluxes and separation factors in pervaporation
472 increased with temperature while permeances decreased. Mixture pervaporation results showed similar behavior,
473 highlighting the fact that separation factors increased with temperature as well. Temperature influence on flux and
474 selectivity were well interpreted when membrane permeance was analyzed in terms of solvent-polymer and solvent-
475 solvent interactions and activation energies for single components and mixtures. Cluster formation and plasticization
476 were evidenced and verified through the Desorption by Dissolution technique and pervaporation results.
477

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List of symbols, abbreviations and units

Symbol	Abbreviation
T	Temperature [ºC]
p_ℓ	Permeate total pressure [kPa]
$w_{methanol}$	%wt methanol in feed [%]
β_{ij}^{PV}	(Pervaporation) separation factor
β_{ij}^{s}	Sorption Selectivity, Solubility Selectivity or Sorption Separation Factor
β_{ij}^{D}	Diffusion selectivity
ℓ	Membrane selective layer thickness [µm]
j	Total Flux [kg m^{-2}h^{-1}]
$\%S$	Sorption degree [g/100g dry polymer]
m_d	Mass of the dried membrane [g]
m_w	Mass of the membrane after sorption equilibrium [g]
θ	Sorbed mass ratio
x_i	Mole fraction of component i
x_j	Mole fraction of component j
ψ_i^{s}	Concentration Ratio or Enrichment Factor
Θ	Contact angle [º]
φ	Flux ratio
Q_i	Weight of permeate I [kg]
t	Time [s]
A	Membrane effective area [m^2]
P_i^{G}/ℓ	Permeance [gpu= 1×10^{-6} cm^3(STP) cm^{-2} s^{-1} cmHg^{-1}]
α_{ij}	Selectivitiy
f_{io}	Fugacity of component i in the feed side [kPa]
$p_{i\ell}$	Partial pressure of component i in the permeate side [kPa]
γ_{io}^{L}	Activity coefficient of component i in the liquid feed
p_{io}^{sat}	Pure component i vapor pressure [kPa]
$^{s}\delta$	Hansen parameters for solvent [MPa$^{1/2}$]
$^{p}\delta$	Hansen parameters for polymer [MPa$^{1/2}$]
$\Delta\delta_{(s-p)}$	Distance between solute and the center of the solubility sphere
Φ_k	Kinetic diameter [nm]
υ	Molar volume [cm^3/mol-g]
ΔHm_i	Enthalpy of mixing [kJ/mol]
ΔHv_i	Enthalpy of vaporization [kJ/mol]
ΔHs_i	Enthalpy of dissolution [kJ/mol]
E_i	Activation energies for pervaporation [kJ/mol]
Ed_i	Activation energies for diffusion [kJ/mol]
Ep_i	Activation energies for permeation [kJ/mol]
Subscripts	
o	Feed side
m	Membrane
i	Component i
j	Component j
ℓ	Permeate side
d	Atomic-nonpolar interactions
p	Molecular-dipolar interactions
h	Hydrogen bonding interactions