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Breakthrough in a flat channel membrane microcontactor

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1 **Abstract**

2 In literature three different models describing the breakthrough pressure were identified: the Young-
3 Laplace model, the Kim-Hairrott-Zha model and the Franken et al. model. However, large differences
4 between experimental results and model are often reported and a comparative study is lacking. In
5 the present study, the different models were experimentally validated by measuring breakthrough
6 pressures in liquid/liquid systems. The average differences between model and experimental results
7 for the three models were respectively 37.5 %, 26.7 % and 32.2 %. The Kim-Harriott-Zha model
8 obtained the best results, however for the model it is advised that a solvent system with a low
9 contact angle is searched to determine the maximum correction angle. Therefore a fourth model was
10 proposed omitting this step and yielding an average deviation of 25.0 %.

11

12 **Keywords**

13 breakthrough pressure; critical entry pressure; membrane contactor; liquid-liquid extraction; parallel
14 flow

15

16 **1. Introduction**

17 Membrane contactors are interesting tools in separation processes, which have evolved the last two
18 decades into well accepted unit operations (Pabby and Sastre, 2013). The membrane immobilizes the
19 interface between two phases, liquid-liquid or gas-liquid, thereby allowing operation in parallel flow
20 without mixing or disrupting the flows. In this way liquid-liquid extraction can for instance be
21 performed, hence omitting a compulsory often slow phase separation step. A disadvantage of
22 classical liquid-liquid extraction is indeed the formation of stable emulsions, but also foaming,
23 unloading and flooding often poses problems (Gabelman and Hwang, 1999). Combining a membrane
24 with shallow channels, high mass transfer kinetics can be easily reached (Hereijgers et al., 2013),
25 requiring only a few minutes to obtain thermodynamic equilibrium. Kiani et al. (1984) and D’Ella et

26 al. (1986) demonstrated this in different membrane configurations, using both a flat membrane and
27 hollow fibers. Several applications have been reported, such as the removal of phenols out aqueous
28 waste streams (González-Muñoz et al., 2003). Using 1-decanol as solvent and a concentrated
29 aqueous NaOH solution as stripping solvent in a second membrane contactor, 99 % of the phenol
30 could be removed. Bocquet et al. (2006) extracted aroma compounds from aqueous solvents using n-
31 hexane and Dupuy et al. (2011a) extracted terpenes from lemon essential oil. For the recovery of
32 metal ions Maruyama et al. (2004) built a microfluidic channel with intermittent partition walls
33 instead of a membrane to pin the interface between the pillars, creating a stabilizing effect.

34 Supported liquid membrane (SLM) extraction is a special case of membrane extraction (Audunsson,
35 1986, Jönsson et al., 1993). In SLM the pores are filled with a wetting organic solvent and the
36 channels at both sides of the membrane contain water-based solvents at a different pH. Chargeable
37 solutes enter the contactor at a pH value at which they are uncharged, enabling transport through
38 the organic solvent. Once entered in the aqueous acceptor phase, the solutes become charged due
39 to a different pH, preventing them from back-diffusion. SLM is a technique primarily used in sample
40 preparation, where the acceptor phase often stands still, pre-concentrating the sample prior to
41 analysis. Additionally an electric field can be applied across the membrane to accelerate mass
42 transfer. Pedersen-Bjergaard and Rasmussen (2006) demonstrated this, by immersing a
43 polypropylene hollow fiber housing the acceptor solution and holding the organic solvent (typically 2-
44 nitrophenyl octyl ether) in the pores into the donor solution. The hollow fiber was mechanically
45 closed at one end preventing leakage of the acceptor solution into the donor solution. Placing an
46 electrode in each phase a recovery of 70 to 80 % was reached in typically 5 min only, extracting
47 various basic drug substances such as pethidine, nortriptyline, methadone, haloperidol and
48 loperamide.

49 Besides liquid-liquid extraction, membranes are also used as interface stabilizer in membrane
50 distillation modules or gas absorption modules. Using a hydrophobic membrane, the aqueous liquid
51 feed is fixed at the pore mouths, preventing it from entering or wetting the pores. Only vapor is

52 hence able to migrate through the pores. A cold aqueous liquid or surface at the other side of the
53 membrane can subsequently condense the vapor inside the module. Alternatively a sweeping gas or
54 vacuum can be used requiring however a large external condenser (Alkudhiri et al., 2012).

55 Membrane distillation is applied for several applications such as desalination (Banat and Simandl,
56 1998), removal of heavy metals (Zolotarev et al., 1994) and treatment of organic polluted aqueous
57 waste streams (El-Abbassi et al., 2011). For gas absorption one side of the membrane is contacted
58 with liquid and the other side with gas. Mavroudi et al. (2006) examined in this way the mass transfer
59 resistance of CO₂ absorption using a hollow fiber.

60 Critical in all these membrane operations is the stability of the parallel flow profile, which is the
61 purpose of the membrane. By capillary action the interface between both phases should be pinned
62 preferably at the pore mouth. If the interface is pinned inside the pores, the membrane is partially
63 wetted, and has as a consequence a negative impact on the mass transfer in gas-liquid absorption.
64 Wang et al. (2005) reported a reduction of as much as 20 % of the global mass transfer coefficient
65 even if the pores are only 5 % wetted. When the operation conditions are not carefully selected, the
66 pressure difference across the membrane can become excessive. At that moment one of the phases
67 will flow through the pores and disperse in the other phase, making phase separation again
68 necessary and the membrane irrelevant. This phenomenon is called breakthrough. However, the
69 operation conditions or pressure difference across the membrane at which this occurs are often
70 differently defined in the literature and no comparative study is performed.

71 In the present paper, the validity of different models describing the breakthrough pressure is
72 examined by experimentally measuring breakthrough pressures, focusing on liquid-liquid extraction
73 systems.

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78 **2. Breakthrough pressure models**

79 Based on the pressure profile of both phases two situations can be defined. In the first situation the
80 pressure of the non-wetting phase is higher than the pressure of the wetting phase. In this classical
81 situation the non-wetting phase will not enter the pores by capillary forces, holding the interface at
82 the pore mouth. At the breakthrough pressure, also called the critical entry pressure, the non-
83 wetting phase will penetrate through the pores and disperse in the wetting phase. To calculate this
84 breakthrough pressure the Young-Laplace law (Eq. 1) is most often used in the literature (Alkhudhiri
85 et al., 2012, García-Payo et al., 2000, Bougie and Illiuta, 2013, Saffarini et al., 2013, Dupuy et al.,
86 2011b, Lawson and Lloyd, 1997):

$$\Delta P_b = \frac{-2\gamma\beta\cos\theta}{r} \quad (1)$$

87 with γ the interfacial tension between the two immiscible liquids in liquid-liquid operation. In gas-
88 liquid operations γ is replaced by the surface tension σ . The influence of the pore shape is
89 represented by β . The Young-Laplace law is defined for cylindrical pores and therefore β is often
90 lacking, as a value of 1 is assumed in that case. For irregular shapes a value between 0 and 1 is found.
91 θ is the contact angle between liquid 1, liquid 2 or gas phase and the membrane material and r is the
92 maximum pore radius.

93 Instead of correcting the Young-Laplace equation using the β -coefficient, Kim and Harriott (1987)
94 proposed a different model (Eq. 2). They noticed that some membranes have a fibrous structure like
95 paper or a mat of glass wool and that the pores are the irregular spaces between the adjacent fibers.
96 Therefore Kim and Harriott (1987) assumed it is more accurate to describe the pores as a donut-like
97 geometry, resulting in the following model (Eq. 2) to describe the breakthrough pressure.

98

$$\Delta P_b = - \frac{2\gamma \cos(\theta - \alpha)}{r \left(1 + \frac{R}{r} (1 - \cos \alpha) \right)} \quad (2)$$

99 with γ the interfacial or surface tension, θ the contact angle, r the smallest pore radius along the pore
 100 passage holding the largest pore bottleneck, R the radius of the fibers of the membrane forming the
 101 pores (Fig.2) and α the correction angle for the pore shape which can be calculated from the contact
 102 angle. Setting the derivative of (Eq. 2) to zero yields the following equation (Eq. 4), from which α can
 103 be calculated:

$$\frac{d(\Delta P_b)}{d\alpha} = 0 \quad (3)$$

$$\sin(\theta - \alpha) = \frac{\frac{R}{r} \sin \theta}{1 + \frac{R}{r}} \quad (4)$$

104 For air-liquid systems the model yields adequate correlations but for liquid-liquid system deviations
 105 are large and unsatisfactory (Kim and Harriott, 1987), unfortunately no explanation for these
 106 observations is given. Zha et al. (1992) proposed a similar model as (Eq. 2) by studying SLM systems
 107 and introduced a restriction for the correction angle α . Its absolute value can never be higher than
 108 the maximum correction angle α_m . An estimate of α_m is obtained by measuring the breakthrough
 109 pressure with a solvent system with a low contact angle. Zha et al. (1992) used a 25 % aqueous
 110 ethanol solution and air as the second phase to measure this and proceeded as follows. r and R/r are
 111 estimated from nonlinear regression using (Eq. 2) by measuring the breakthrough pressure and the
 112 contact angle for a range of different solvent systems. Knowing this, α_m is estimated from (Eq. 2)
 113 using the breakthrough pressure for the 25 % aqueous ethanol/air system. If the absolute value of
 114 the correction angle from (Eq. 4) is larger than α_m , α_m should be used in (Eq. 2) to calculate the
 115 breakthrough pressure. Zha et al. (1992) tested this model for three different membranes: Durapore
 116 HVHP ($d_{\text{pore, max, manufacturer}} = 1.6 \mu\text{m}$, $d_{\text{pore, max, fit}} = 1.30 \mu\text{m}$), Celgard 2500 ($d_{\text{pore, max, manufacturer}} = \text{not given}$,
 117 $d_{\text{pore, max, fit}} = 0.34 \mu\text{m}$) and Accurel 2E-PP ($d_{\text{pore, max, manufacturer}} = 0.81 \mu\text{m}$, $d_{\text{pore, max, fit}} = 0.80 \mu\text{m}$) and

118 concluded that the fitted maximal pore sizes were in agreement with those provided by the
 119 manufacturers. Zha et al. (1992) also pointed out that r and R can be estimated from SEM pictures of
 120 the membrane. Caution should however be taken as the pore shape is often irregular making it
 121 difficult to correctly estimate the pore size from a SEM picture.
 122 Franken et al. (1988) also studied the model of Kim and Harriott (1987) and proposed that this model
 123 is only valid when the pore edges are “rounded”. However, when the pores of the membrane are
 124 “sharp-edged” the denominator of (Eq. 2), which can be seen as a hydraulic radius, has to be
 125 modified (Eq. 5):

$$\Delta P = - \frac{2 \gamma \cos (\theta - \alpha)}{R \cos \alpha} \quad (5)$$

126 The breakthrough pressure is reached when the meniscus has to overcome the narrowest point in
 127 the pore. This ‘sharp-edged’ barrier is overcome when ΔP equals (Eq. 6):

$$\Delta P_b = - \frac{2 \gamma \cos (\theta + \alpha_m)}{r} \quad (6)$$

128 At the sharp-edged barrier, $R \cos \alpha$ equals r as the pore is then at its narrowest point. However, as
 129 indicated by Franken et al. (1988) most of the membranes have rounded pores and the sharp-edged
 130 structure is only obtained with special production processes (e.g. thermal inversion with slow
 131 cooling).

132 From all the models it is clear that the interfacial tension, the contact angle and the pore radius and
 133 morphology are the deciding factors that determine the breakthrough pressure. However, it is not
 134 clear which model is most suitable to predict the breakthrough pressure under common conditions.

135 In the first situation the pressure of the non-wetting phase was higher than that of the wetting
 136 phase. In the second situation the pressure of the wetting phase is higher than that of the non-
 137 wetting phase. This is always an undesirable state as breakthrough will always occur. This is logical
 138 since there is no capillary action anymore holding back the liquid.

139

140 3. Material and Methods

141 3.1 Chemicals

142 The water used throughout the experiments was prepared in the laboratory (Milli-Q-gradient,
143 Millipore, Bedford, MA, USA). Methyl isobutyl keton (MIBK) was purchased from Acros Organics and
144 the remaining chemicals used were purchased from Sigma-Aldrich. All chemicals were of analytical
145 reagent grade.

146

147 3.2 Breakthrough pressure

148 The breakthrough pressure was determined for 5 different water/organic solvent systems (n-
149 heptane, 1-octanol, ethyl acetate, MIBK and toluene) and two different flat sheet membranes (Table
150 1).

151

152 **Table 1: Specifications of the examined membranes provided by the manufacturer.**

| Material | Manufacturer | Porosity (%) | Thickness (μm) | Pore Size (nm) |
|---------------|----------------|--------------|--------------------------------|------------------|
| PTFE | Frisenette Aps | 68.0 | 70 | 100 ^a |
| Polypropylene | Celgard | 55 | 25 | 64 ^b |

153 **a: Measured by the bubble point test method**

154 **b: Measured by the water intrusion test method**

155

156 The membrane was clamped between two aluminum bodies with a channel of 13 mm wide, 90 mm
157 long and 100 μm deep. Pillars of 1 mm in an equilateral triangle pattern with a spacing of 2 mm were
158 defined inside the channel to support the membrane, resulting in a membrane area of 12 cm^2
159 (Hereijgers et al., 2012, 2013). Rinsing with methanol was first performed in both channels at a flow
160 rate of 5 mL/min with an HPLC pump (Shimadzu) to remove all the air. Using syringe pumps (kd

161 Scientific) water and the organic solvent were fed into the membrane microcontactor (MMC) at a
 162 flow rate of 50 $\mu\text{L}/\text{min}$ (Fig. 1a). Using a backpressure regulation valve at the outlet of the MMC, the
 163 pressure at the non-wetting side of the membrane was gradually increased until breakthrough was
 164 observed. The pressures at both inlets and outlets were monitored using 4 pressure transducers
 165 (Gefran, model no. TK-N-1-E-B01D-H-V). Once breakthrough was observed the pressure difference at
 166 that moment across the membrane revealed the critical pressure. Every breakthrough pressure was
 167 measured three times. In order to check if the design of the MMC or the flow of the liquids has an
 168 influence on the breakthrough pressure, the breakthrough pressure for the 5 solvent systems was
 169 also measured for the PTFE membrane using a sample holder and a pressurized vessel (Fig. 1b). A
 170 pre-cut piece of the PTFE membrane (72 mm^2) was clamped between two aluminum bodies. The
 171 organic wetting solvent was applied on top and water the non-wetting solvent was allowed to flow
 172 for a few minutes underneath the membrane to remove all the air bubbles. Once all the air was
 173 removed this exit was closed and the pressure was gradually increased using a pressure regulator
 174 until breakthrough was visually observed. This was repeated three times.
 175 The different models and set-ups were compared by calculating the average difference between the
 176 measured breakthrough pressure and the one predicted by the model as follows (Eq. 7).

$$\varepsilon = \frac{100\%}{n} \sum_{j=1}^n \frac{|\Delta P_{b,j,m} - \Delta P_{b,j,c}|}{\Delta P_{b,j,m}} \quad (7)$$

177 with ε the average difference and n the number of measurements.

178

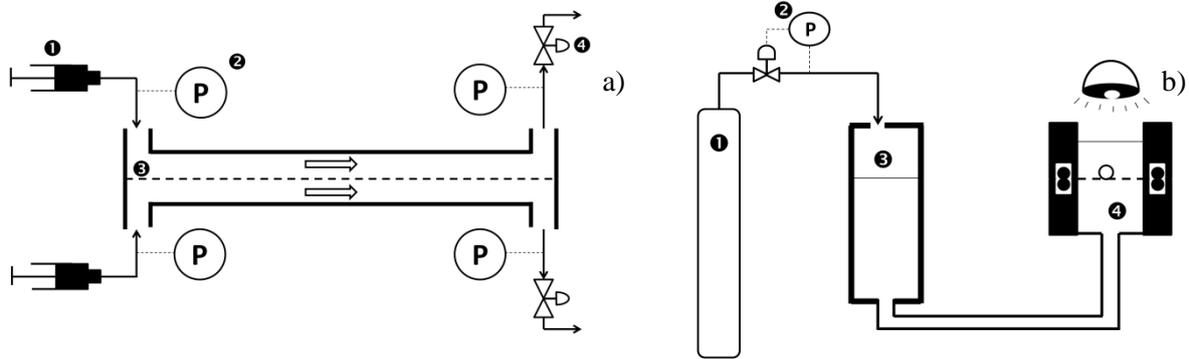
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182

183 Fig. 1: Schematic drawing of the set-ups to measure the breakthrough pressure. a) MMC set-up: ❶ syringe
 184 pump, ❷ pressure transducer, ❸ MMC, ❹ backpressure regulation valve b) Sample holder set-up: ❶
 185 nitrogen gas bottle, ❷ pressure controller, ❸ pressurized vessel, ❹ sample holder.



186

187 3.3 Contact angle

188 The contact angles were measured with the sessile drop method (KrüssKR DSA30). A piece of the
 189 membrane was clamped and submerged in the wetting liquid in a cuvette and a 5 μL droplet of the
 190 non-wetting liquid was dispensed, using an automated syringe of 10 μL . Once the droplet rested onto
 191 the membrane a picture was taken sideways from which the contact angle was determined.

192

193 4. Results

194 4.1 Study of the breakthrough models

195 The contact angle and breakthrough pressures were first measured for different solvents for the
 196 PTFE and PP membranes (see table 2). The interfacial tension value was taken from literature (North,
 197 1999). The breakthrough pressure of n-heptane and toluene could not be determined for the
 198 polypropylene membrane, because the pressure to be measured lied above the maximum operating
 199 pressure of 10 bar of the used pressure transducers. These results were used to calculate the
 200 breakthrough pressures ($\Delta P_{b,c}$) for the different models in order to check their validity. The free
 201 parameters of each model were fitted by the sum of least squared values.

202 **Table 2: Contact angle and breakthrough pressure results measured using the MMC set-up (Fig. 1a).**

| | PTFE membrane | | | PP membrane | |
|---------------|------------------------------|------------------------|-----------------|------------------------|-----------------|
| | γ (mN/m) ^a | $\Delta P_{b,m}$ (bar) | θ (°) | $\Delta P_{b,m}$ (bar) | θ (°) |
| n-Heptane | 51 | 3.03 ± 0.14 | 128.4 ± 2.5 | OR ^b | / |
| 1-Octanol | 8.52 | 0.59 ± 0.12 | 133.6 ± 3.5 | 4.17 ± 0.09 | 123.8 ± 5.1 |
| MIBK | 15.7 | 0.74 ± 0.01 | 138.6 ± 4.2 | 4.24 ± 0.28 | 105.9 ± 5.6 |
| Ethyl Acetate | 6.79 | 0.52 ± 0.02 | 133.5 ± 1.5 | 1.19 ± 0.05 | 127.9 ± 4.0 |
| Toluene | 36.1 | 2.58 ± 0.07 | 123.1 ± 2.9 | OR ^b | / |

203 **a: North (1999)**

204 **b: Out of detection range (> 10bar)**

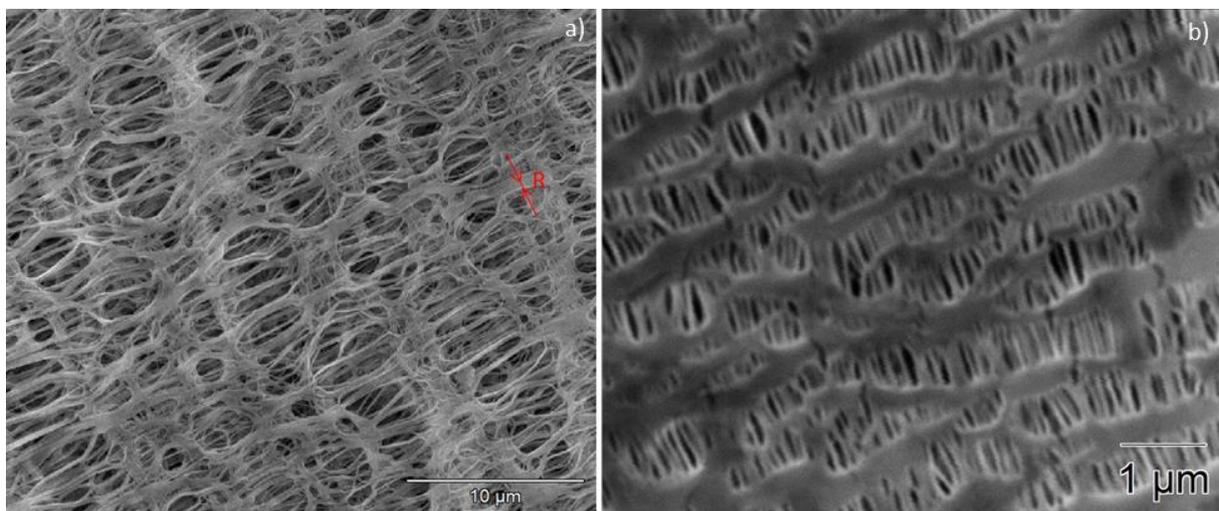
205

206 The first examined model was the Young-Laplace model (Fig. 3a) (Eq. 1). β was obtained by fitting for
 207 the PTFE and PP membrane, resulting respectively in values of 0.51 and 2.36. As β should
 208 theoretically lie between 0 and 1, this was clearly not the case for the PP membrane. A possible
 209 explanation is that the given pore size by the manufacturer was underestimated. For the Young-
 210 Laplace model, the average difference between the calculated and measured breakthrough pressure
 211 was 37.5 %. The second model (Eq. 2) that was evaluated was the one described by Kim-Harriott
 212 (1987) and Zha et al. (1992) (Fig. 3b). As stated by Zha et al. (1992), α_m is best determined with a
 213 solvent system where the contact angle is low (referred to as advancing contact angle in Zha et al.,
 214 (1992)), as the importance of α increases with a decreasing contact angle. Zha et al. (1992) used an
 215 air-25 % ethanol mixture with contact angles equal or below 100 °. As for the PTFE membrane, all the
 216 contact angles were more than 20 ° higher it can be assumed that α_m was not reached. Nonetheless
 217 with toluene-water giving the smallest contact angle, its α_m equaled to -56.9 ° which is in absolute
 218 terms larger than all the α obtained for the other solvent systems justifying the made assumption.
 219 For the PP membrane α_m equaled to -27.7 ° determined out of the MIBK-water system. r and R/r
 220 determined by the best fit with R/r restricted to be non-negative for the PTFE membrane were

221 respectively 319 nm and 0.0 and for the PP membrane 43 nm and 1.7 and the average deviation
222 equaled 26.7 %. The Kim-Harriott-Zha model resulted in a better relation than the Young-Laplace
223 model, which is not completely surprising as two fitting parameters instead of one were used. The
224 best fit R/r value for the PTFE membrane was zero. When looking at the SEM picture of the
225 membrane (Fig. 2a) R/r should indeed be very small as the membrane consists of very thin
226 overlapping and cross-linked fibers. For the PP membrane (Fig 2b) it was more difficult to see if the
227 R/r value corresponds to the observed geometry as there is a large spread in R.

228

229 **Fig. 2: SEM pictures of the PTFE membrane (a) and PP membrane (b). An example of R (Eq. 2) is given in (a).**



230

231

232 The third model evaluated was that described by Franken et al. (1988) (Fig. 3c) (Eq. 6). Just as the
233 two previous models the fitting parameter in this case α_m was determined by a best fit, which was
234 equal to 124.1 ° and 48.8 ° for the PTFE and PP membrane respectively. The average deviation was
235 equal to 32.2 %. As this model is only valid when the pores have sharp edges which are not common
236 (Franken et al., 1988), it is not surprising that it results in a fit of poorer quality. Observing the SEM
237 pictures of the two tested membranes (Fig. 2) it was clear that the pores are indeed rounded and not
238 sharp-edged.

239 From the three models the Kim-Harriot-Zha model turned out to give the best fit, using two fitting
240 parameters only. Looking at the Young-Laplace and the Franken model, one could state that the

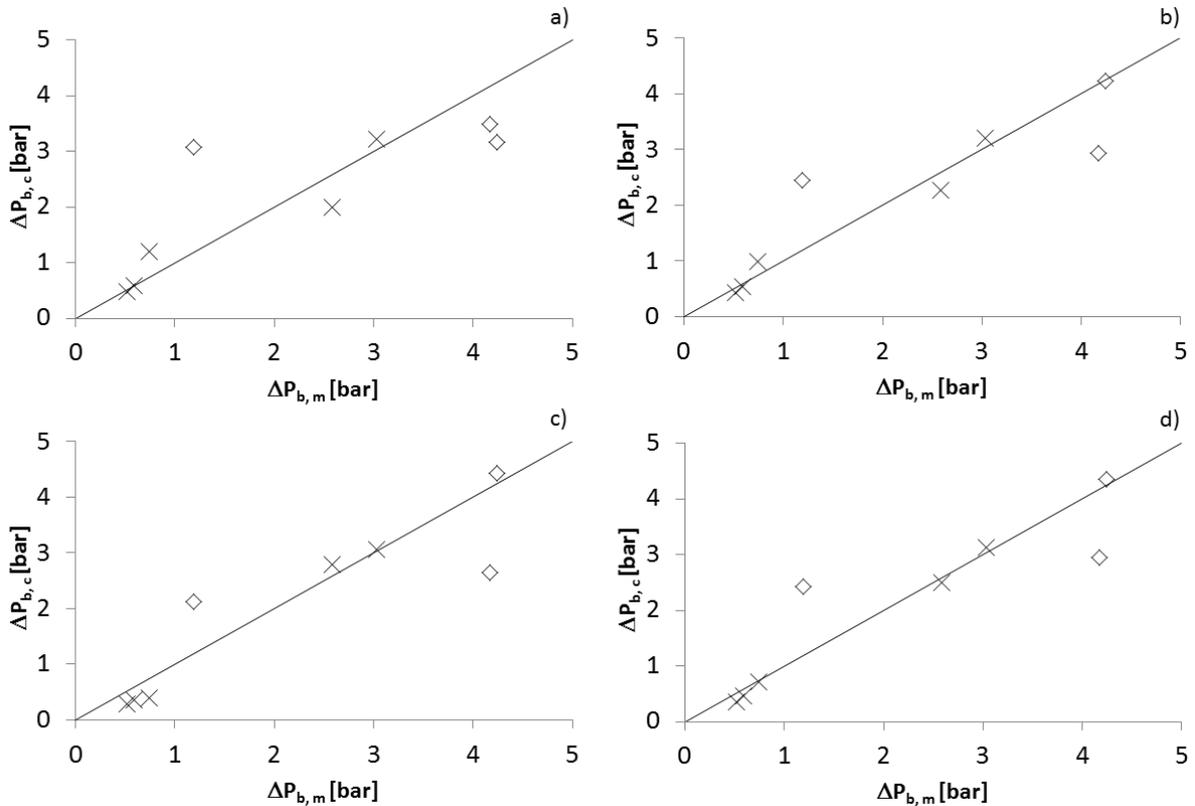
241 fitting parameters compensate for the pore shape. Combining both parameters a fourth model (Eq.
 242 8) could be composed:

$$\Delta P_b = -\frac{2\gamma\beta\cos(\theta + \alpha)}{r} \quad (8)$$

243 Using both an α - and β -parameter an average deviation of 25.0 % was obtained (Fig. 3d). This is an
 244 improvement of around 10 % compared to the Young-Laplace and Franken model, and a slight
 245 improvement compared to the Kim-Harriot-Zha model, but which requires a system with a low
 246 contact angle to determine α_m . β was 0.5 and 1.2 for the PTFE and PP-membrane respectively and α
 247 was 105.9 ° and 30.1 °.

248

249 **Fig. 3: The measured breakthrough pressure vs. the calculated breakthrough pressure with the respective models:**
 250 **a) Model of Young-Laplace, b) Model of Kim-Harriott-Zha, c) Model of Franken et al., d) Fourth model combining α**
 251 **and β (Eq. 8) (× PTFE, ◇ PP). The solid line corresponds to the values expected according to the model.**



252

253

254 **4.2 Influence of operating conditions**

255 In order to verify whether it was correct to measure the breakthrough pressure with the MMC
 256 module the breakthrough pressure was also measured using a second set-up (Fig. 1b, Table 3). Using
 257 a pressure vessel the pressure can be increased until breakthrough is observed in such a way that
 258 there was no movement of the liquids. Besides the normal pressure difference across the membrane
 259 during flow, there is also a tangential stress exerted by the friction of the flowing fluids (Berthier et
 260 al., 2009). This raised the question whether it influences the breakthrough pressure, however as
 261 reported by Berthier et al. (2009) it is expected to be negligible.

262 The breakthrough pressures of both set-ups are depicted in Fig. 4 with an average difference of 2.4 %
 263 between the two methods. It is thus possible to predict the breakthrough pressure in future MMC
 264 experiments by measuring the breakthrough pressures of a few solvent systems using the same
 265 MMC set-up and there is hence no need for building a second set-up.

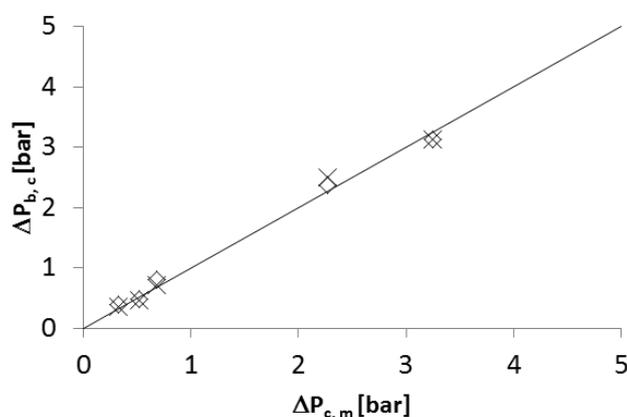
266

267 **Table 3: Breakthrough pressure results measured using the sample holder set-up.**

| | n-Heptane | 1-Octanol | MIBK | Ethyl Acetate | Toluene |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\Delta P_{b,m}$ (bar) | 3.25 ± 0.10 | 0.52 ± 0.02 | 0.68 ± 0.01 | 0.33 ± 0.04 | 2.27 ± 0.04 |

268

269 **Fig. 4: The measured breakthrough pressures vs. the calculated breakthrough pressure according to the modified**
 270 **Young-Laplace model (Eq. 8) for the PTFE membrane using the MMC set-up (×) and the sample holder set-up (◇).**



271

272 Comparing the four models the preference is given to the fourth proposed model (Eq. 8) as it gives
273 the best correlation and no special solvent system is required to obtain the fitting parameters as
274 well. Once they are known it is only necessary to measure the contact angle to have a reasonable
275 estimation of the breakthrough pressure, this is important when one wants to operate the system for
276 a longer period of time (Prasad and Sirkar, 1990). By continuously monitoring the trans-membrane
277 pressure, process parameters such as back pressure or flow rates can be regulated, ensuring a stable
278 operation.

279 It was observed from the SEM pictures (Fig. 2) that both membranes have a large pore size
280 distribution which cannot be neglected. Knowing that the maximum pore size has a big influence on
281 the breakthrough pressure, further improvement is possible here. Van Rijn (2004) produced such a
282 membrane for microfiltration using an etching step after laser interference or deep UV lithographic
283 definition of the pores. Fully cylindrical pores with pore sizes as small as 100 nm and thicknesses
284 beneath 1 μ m were demonstrated. For this membrane, the Laplace model can be used, due to the
285 cylindrical and smooth pore shapes. Using supporting beams, the maximum allowed transmembrane
286 pressure upon rupture was estimated to be 2 bar, which allows for high liquid velocities. Even though
287 the kinetics of extraction is reduced by the relatively low overall porosity (25%, Van Rijn (2004)) of
288 the membrane, due to the presence of these support beams and the thickness of the walls in
289 between the pores (in order to guarantee mechanical stability), the potential of this membrane
290 format cannot be underestimated. The membrane thickness of 1 μ m yields a negligible mass transfer
291 resistance and with state-of-the art micromachining techniques wafer sizes of 30 cm diameter can be
292 achieved. The high cost will however probably prevent a widespread implementation on the short
293 term. Also taking fouling into consideration, which becomes of greater importance at reducing pore
294 sizes, it can be expected that the average user will stick to disordered membranes, which can be
295 easily produced with maximal pore sizes with sub-micron dimensions, for which the models studied
296 in this paper are of high significance.

297

298 **5. Conclusions**

299 Three different models from the literature describing the breakthrough pressure were compared
300 using experimentally measured breakthrough pressures for a set of liquid/liquid combinations and
301 two different membranes (PTFE and PP). The Young-Laplace and the Franken et al. model gave an
302 average deviation of 37.5 % and 32.2 % while the Kim-Harriott-Zha model produced an average
303 deviation of 26.7 %. A disadvantage of this latter model is that a search for a solvent system with low
304 contact angle is advised to find α_m . For this reason, the fitting parameters α and β from the Young-
305 Laplace and Franken et al. model were combined into a fourth model to take the pore shape better
306 into account, on the one hand yielding a slightly better fit of 25.0 %, but more importantly on the
307 other hand avoiding a search of α_m .

308

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