

1 **The impact of toluene and xylene on the performance of cellulose triacetate membranes**
2 **for natural gas sweetening**

3 Authors: H. T. Lu¹, Liu. Liang¹, S. Kanehashi², C. A. Scholes¹, S. E. Kentish^{1,*}

4 ¹*Department of Chemical Engineering, The University of Melbourne, Parkville, VIC3010*
5 *Australia*

6 ²*Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16*
7 *Nakacho, Koganei, Tokyo 184-8588 Japan*

8 **Abstract**

9 The presence of condensable aromatic hydrocarbons in raw natural gas streams creates a
10 significant challenge for acid gas removal through membrane separation. In this work, the
11 impact of toluene and xylene on the gas separation performance of cellulose triacetate (CTA)
12 membranes was studied. When operating at low CO₂ partial pressures (0.75 Bar), both toluene
13 and xylene reduced the permeation of CO₂ at low vapour activities, due to competitive sorption
14 and the pore-filling or anti-plasticisation effect. Conversely, at vapour activities greater than
15 0.5, toluene caused membrane plasticisation, possibly coupled with a decrease in crystallinity.
16 On the other hand, when operating at 7.5 Bar CO₂ pressure, plasticisation was observed at a
17 lower vapour activity of 0.3 for both toluene and xylene. This study shows that two penetrants
18 can influence the plasticisation behaviour in a co-operative manner that cannot be described by
19 a simple additive model. The study also shows that the permeabilities of toluene and xylene
20 are comparable with that of methane.

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23 Keywords: Cellulose triacetate; BTEX; methane; carbon dioxide.

24 * Corresponding author: Tel: +61 3 8344 6682; fax: +61 3 8344 4153

25 E-mail address: sandraek@unimelb.edu.au (S.E. Kentish)

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1. Introduction

Natural gas will become the second largest energy resource globally within the next few decades [1, 2]. Raw natural gas contains condensable hydrocarbons, acid gases and impurities that require pre-treatment to meet consumer specifications and for pipeline transport. A range of separation technologies have been commercialised for natural gas processing, with membrane gas separation commercially proven for natural gas sweetening (acidic gas removal). Cellulose triacetate (CTA) membranes are the market leaders for gas sweetening membranes, because of their low cost, durability and competitive gas separation performance [3, 4].

Condensable aromatic hydrocarbons, known as BTEX (Benzene, Toluene, Ethylbenzene and Xylene) are present in raw natural gas at concentrations ranging from 200 to 3000 ppm, dependent on the natural gas source [5, 6]. The presence of these hydrocarbons presents significant challenges. Firstly, they are toxic and thus not readily vented with the waste acid gases. Secondly, they can freeze during cryogenic separation [7]. The presence of BTEX in natural gas can also alter the gas separation performance of polymeric membranes, by competing for sorption sites with the acid gases, by blocking the gas transport pathways through the polymeric matrix or by plasticising the polymeric matrix [8]. Toluene has been shown to reduce the CO₂ permeability and CO₂/CH₄ selectivity in polyimides [9-12] and amorphous perfluoropolymers [13]. Polyimide membranes have also been reported to be plasticised by toluene, resulting in a significant decline in CO₂/CH₄ selectivity [10, 14].

Studies of the impact of BTEX on cellulose acetate based membranes are limited and focus mainly on H₂/CH₄ separation [6, 15, 16]. Wensley and King show that the presence of toluene (up to 2.5 kPa) or benzene (up to 8.8 kPa) reduces H₂ and CH₄ permeabilities by 10 – 15% but the H₂/CH₄ selectivity is increased by 10% [6, 15]. Cellulose acetate membranes used in the Cosmo Oil Refinery (Japan) for hydrogen separation were stable over a three year operating period in 1.8 – 5.2 kPa BTX but the gas permeability declined around 20% in the presence of the BTX [16].

The kinetic diameter and critical temperature of H₂ (2.89 Å and 33.2 K [17]) is much smaller than CO₂ (3.3 Å and 304.2 K [17]) and hence the impact of BTEX on CO₂/CH₄ separation may be quite different. Schell et al. [6] report a 10% decrease in CO₂ and CH₄ permeability in cellulose acetate membranes in the presence of 5.4 kPa BTX within a 6% CO₂ balance CH₄ gas mixture. The permeability of BTEX through cellulose acetate membranes is generally reported to be lower than methane [15] but no numerical data has been reported. To the best knowledge of the authors, there are no reports of plasticisation of cellulose acetate membranes by BTEX.

Given the significance of these aromatic hydrocarbons and the lack of literature, we present in this work a detailed study of the effect of toluene and xylene on the separation of CO₂ and CH₄ when using CTA membranes. The hydrocarbons are exposed to the CTA membrane over a range of vapor pressures representative of the BTEX concentrations that are experienced in

1 natural gas processing. The solubility and permeability of toluene and xylene within the
2 membranes are also reported.

4 **2. Experimental**

5 *2.1. Membrane fabrication*

6 The cellulose triacetate (CTA) polymer utilised in this study was kindly supplied by Cellulose
7 Company – Daicel Corporation (Japan). The degree of acetylation of the polymer is reported
8 as 61.6%.

9 Dense membrane fabrication followed a typical solvent casting method as described in our
10 previous publications [18, 19]. A 1 wt% solution was prepared by dissolving the dried CTA
11 powder into dichloromethane (ChemSupply, Australia). The solution was filtered and cast into
12 glass petri dishes, which were then kept covered for solvent evaporation. After 24 hours, the
13 membranes were peeled from the petri dishes and annealed in a vacuum oven for 24 hours at
14 35°C, followed by a further 24 hours at 100°C. The annealed CTA membranes were kept in a
15 desiccator for 14 days prior to utilisation in sorption and permeation studies to minimise the
16 impact of the initial physical aging of the glassy membranes [20, 21]. The membrane thickness
17 was measured by a micrometer and was in the range of 65 – 75 µm. The membrane density
18 and crystallinity were 1.297 ± 0.003 (g/cm³) and 56 ± 5 (%) respectively [19].

19

20 Thin film composite (TFC) membranes were also fabricated by a spin coating method that is
21 also well described in the literature [18, 22, 23]. A 4 wt% CTA in dichloromethane solution
22 was coated onto a porous hydrophilic polytetrafluoroethylene (PTFE) membrane with 0.2 µm
23 nominal pore size (Omnipore™, Merck Millipore, Australia). The PTFE support was initially
24 wetted by water to minimise the penetration of solution into the pores [23]. The spinning rate
25 was 1500 rpm in 20 s. The membrane thickness was determined by Scanning Electron
26 Microscopy (FEI Quanta 200 ESEM FEG).and was in the range of 10 – 15 µm.

27 *2.2. Sorption measurements*

28 The sorption of toluene (>99.5% purity, ChemSupply, Australia) and xylene (>99.0% purity,
29 ChemSupply Australia) in CTA was studied by immersing dense membrane samples into the
30 hydrocarbon liquid at 35°C. The mass of the dried membrane (m_o) was initially weighed by a
31 XS205 DualRange balance (Mettler Toledo, Australia) with maximum 0.02% error. After
32 immersing into the hydrocarbon solution for a specified time (t), the membrane was removed,
33 the excess liquid droplets were wiped from the membrane surfaces and the mass uptake (m_t)
34 recorded by weighing. The membrane was determined to be at equilibrium (m_∞) when the mass
35 change was less than 0.1 wt% over a 24 hour timespan. The hydrocarbon uptake was calculated
36 via Equation 1.

$$37 \text{ Hydrocarbon uptake (\%)} = \frac{m_t - m_o}{m_o} \times 100 \quad (1)$$

38 The sorption kinetics is described here by a simple heuristic equation (Equation 2) [24, 25],
39 where k is a constant and n is an exponent that characterises the type of diffusion occurring.
40 For Fickian diffusion, $n = 0.5$ and the k constant can be related to the diffusion coefficient. A

1 value of n greater than 0.5 is indicative of non-Fickian polymer relaxation, through
2 plasticisation or changes in crystallinity. In particular, when $n = 1.0$, 'Case II diffusion' is said
3 to occur [26-28], when a region of non-Fickian swelling moves through the polymer as a
4 function of time. In this case, the k constant is proportional to the velocity of the advancing
5 relaxation front [29].

$$6 \quad \frac{m_t - m_o}{m_\infty - m_o} = kt^n \quad (2)$$

7 A gravimetric sorption analyser, GHP – FS, equipped with a Cahn D-200 microbalance (VTI
8 Scientific Instruments, USA) as described previously [30], was utilised to determine the
9 solubility of toluene and xylene vapour. Equilibrium at each vapour pressure increment was
10 determined as a mass change of less than 0.003 wt% over 15 minutes (toluene) and 90 minutes
11 (xylene), respectively.

12 The solubility of CO₂ and CH₄ in CTA was determined using a high pressure gravimetric
13 sorption analyser (Belsorp, MicrotracBel Corporation, Japan). The membrane sample was
14 installed into the sample chamber and the chamber was evacuated overnight. The experiment
15 gas was then fed into the chamber with incremental increases in gas pressure from 50 kPa to
16 38000 kPa absolute pressure. Some sorption data for toluene and xylene vapour was also
17 collected using this second sorption analyser. Sorption equilibrium at each pressure increment
18 was determined as a mass change of less than 0.2 µg over two hours, following which the mass
19 of swollen membrane was recorded.

20 *2.3. Permeability measurements*

21 The permeabilities of gas mixtures was measured by a variable volume constant pressure
22 (VVCP) gas permeation apparatus. The hydrocarbon vapour was introduced into the feed gas
23 via a bubbling arrangement, as reported previously [13, 31, 32]. Either 10% CO₂ in balance
24 CH₄ mixed gas (99.999% purity, Coregas, Australia) or pure CO₂ (99.9% purity, BOC,
25 Australia) at 7.5 bar was introduced to the bubbler to carry the hydrocarbon vapour to the feed
26 side of the membrane holder. The permeate stream was swept by helium (99.99% purity,
27 Coregas, Australia) at 1 bar absolute pressure to a gas chromatograph equipped with a thermal
28 conductivity detector (490 micro GC, Agilent technologies, Australia) for concentration
29 analysis. The hydrocarbon activity was regulated by changing the temperature of the bubbler
30 [31]. The GC was calibrated against five different partial pressures of toluene and xylene by
31 passing helium directly through the bubbler and to the GC. The xylene utilised in this study
32 was composed of 86 mol% of the *p*- and *m*-xylene isomers as determined by the gas
33 chromatography trace. In addition, the GC was also calibrated against pure CO₂, pure CH₄
34 (99.95% purity, Coregas, Australia) and the 10% CO₂ in balance CH₄ gas mixture.

35

3. Results and discussion

3.1. Solubility of toluene and xylene in Cellulose Triacetate

Both xylene and toluene absorb initially into CTA in a manner that is linear with time (Figure 1). The calculated exponent n (Equation 1) for toluene and xylene during this initial period was 0.99 ± 0.04 and 0.98 ± 0.03 , respectively. As discussed above, this is typical of Non-Fickian Case II polymer relaxation processes [26-28]. Such behaviour has been reported in several hydrocarbon – glassy polymers system such as toluene – poly(vinyl chloride) [33], toluene - polystyrene [34] and dichloromethane – cellulose acetate [35]. It should be noted that while the sorption behaviour observed here occurred over many hours, it is expected to occur much more rapidly in industrial membrane systems where the active layer is much thinner ($<1\mu\text{m}$) [21, 42].

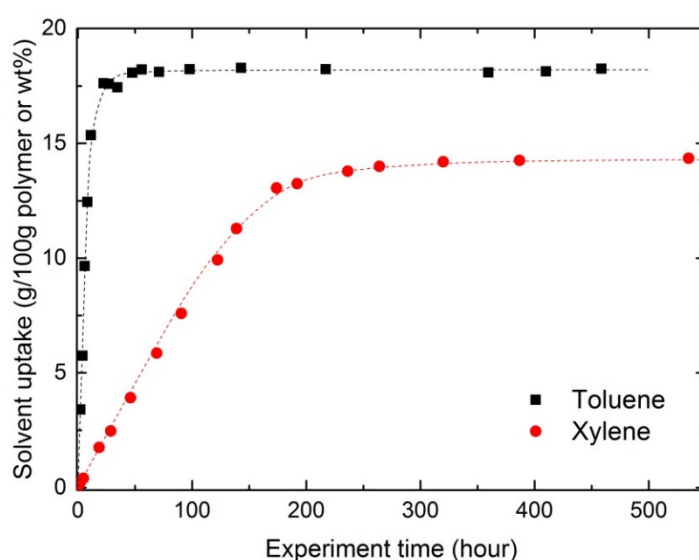


Figure 1 The sorption of liquid toluene and xylene into a cellulose triacetate membrane ($62 \pm 2\mu\text{m}$ thickness) at 35°C . The dashed lines are added to guide the eye.

The sorption rate of toluene is greater than xylene at the same CTA membrane thickness (Figure 1) because of the smaller kinetic diameter of toluene (Table 1). This is also evident from the greater value of the k constant calculated from Equation 1 for toluene ($0.00143 \pm 0.0004 \text{ s}^{-1}$) versus xylene ($0.000127 \pm 0.00002 \text{ s}^{-1}$). On a molar basis, the equilibrium solubility of xylene is slightly greater than toluene (Table 1), due to its higher critical temperature. [36-38].

1 **Table 1**

2 The properties of penetrants and their solubility in CTA membranes

	Toluene	Xylene	CH ₄	CO ₂
Molecular Weight (g/mol)	92.14	106.16	16.04	44.01
Kinetic diameter (Å) [17, 39-41]	5.85	5.85 (<i>o</i> -xylene) 6.80 (<i>p</i> - & <i>m</i> -xylene)	3.80	3.30
Critical temperature (K) [41, 42]	384	411 – 417	191	304
Solubility	wt % ¹	19.0 ± 0.6	14.1 ± 0.2	
	mol/100g polymer ¹	0.207 ± 0.006	0.133 ± 0.002	
	(cm ³ (STP)/cm ³ polymer.bar) ²	620	663	0.39 5.3

3 ¹ Solubility of liquid toluene and xylene (1.0 vapor activity) at 35°C

4 ² Solubility of gases recorded at 35°C and 5.4 kPa for toluene, 1.6 kPa for xylene (0.8
5 vapor activity), at 6.75 Bar for methane and 0.75 Bar for carbon dioxide.

6

7 *3.2. Gas and vapour sorption isotherm in CTA membranes*

8 The gas sorption isotherms of CO₂ and CH₄ in CTA are plotted in Figure 2, and correspond
9 well with the data of Puleo, Paul and Kelley[43]. The nonlinear concave shapes of the isotherms
10 are described well by the dual-mode sorption model (Equation 3) [43-47] where k_D is the
11 Henry's law constant, p is the gas pressure, C'_H is the maximum adsorption capacity in the
12 Langmuir region and b is the Langmuir affinity constant.

$$13 \quad C = k_D p + \frac{C'_H b p}{1 + b p} \quad (3)$$

14 The parameters fitted to Equation 3 are summarised in Table 2. The deviations in these
15 parameters for methane compared with previous work [43] are due to inaccuracies in the data
16 fitting approach at these low concentrations.

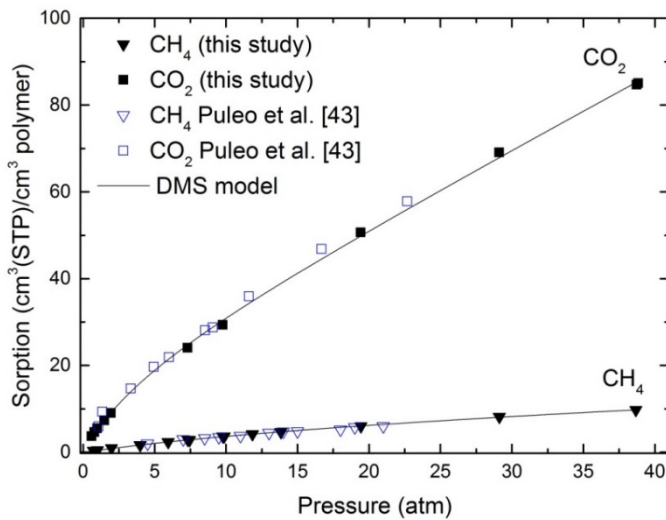
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1 **Table 2**

2 The dual-mode sorption parameters for CH₄ and CO₂ in CTA membranes at 35°C

Penetrant	k_D (cm ³ (STP)/cm ³ .atm)	C'_H (cm ³ (STP)/cm ³)	b (atm ⁻¹)	Reference
CO ₂	1.75 ± 0.06	20 ± 3	0.21 ± 0.05	This study
CH ₄	0.12 ± 0.02	8 ± 2	0.042 ± 0.008	
CO ₂	1.647	19.63	0.291	[43]
CH ₄	0.184*	3.15	0.134	

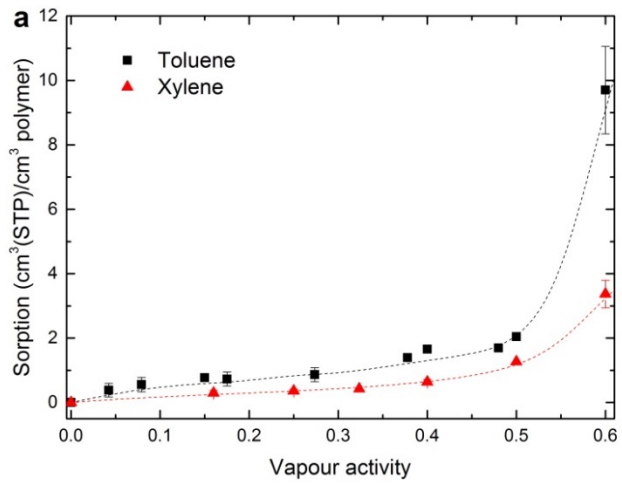
* The study of Puleo, Paul and Kelley quoted a k_D value of 1.84 [43] but the authors believe this to be a typographical error, as the data calculated from this value do not match with results presented in the paper.



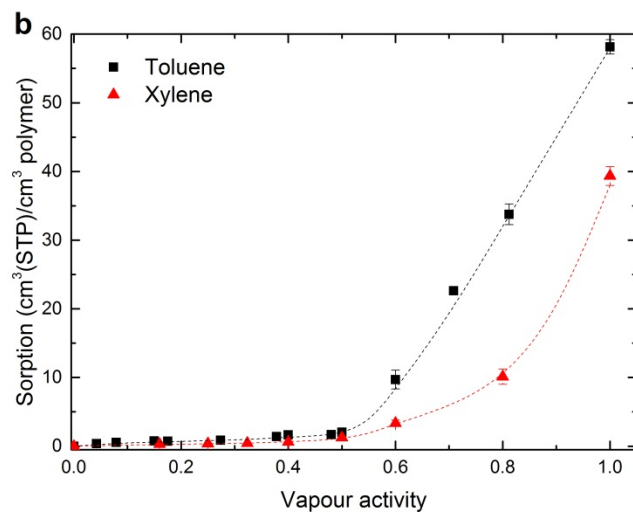
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4 **Figure 2 The sorption isotherms of CO₂ and CH₄ in cellulose triacetate at 35°C**

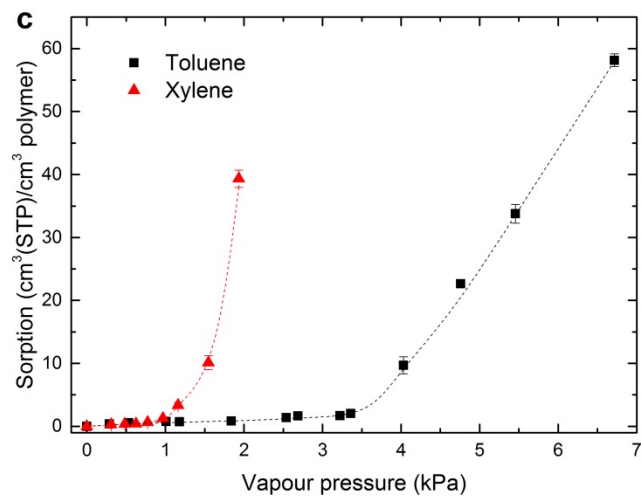
5 The vapour sorption isotherms of toluene and xylene in CTA membranes are provided in Figure
6 3. The isotherms are S-shaped [48-50], which has also been observed for the sorption of
7 methanol, acetone, dimethyl carbonate and methyl acetate into CTA [50]. Specifically, dual
8 mode sorption is observed at low vapour activity (Figure 3a), which reflects the sorption of
9 hydrocarbons into the macrovoids of the polymer matrix [13]. At vapour activity greater than
10 0.5, there is a rapid increase in sorption (Figure 3b) which is associated with swelling and
11 plasticisation of the polymer [50, 51]. The sorption of toluene is stronger than xylene at the
12 same vapour activity due to the difference in partial pressure of toluene in comparison with
13 xylene at the specified activity. However, when plotted as a function of the vapour pressure,
14 the sorption of xylene and toluene is identical for a vapour pressure up to 0.65 kPa (Figure 3c).
15 The polymer is plasticised by xylene at this vapour pressure while toluene plasticised the
16 membranes at 3.4 kPa.



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4 **Figure 3 The solubility of toluene and xylene in cellulose triacetate at 35°C: (a) at 0.0 –**
 5 **0.6 vapour activity; (b) across the full range of vapour activities; and (c) as a function**
 6 **of vapour pressure rather than activity.**

1 We attempted to model these sorption isotherms using advanced dual mode sorption models
2 [13, 52, 53], the Flory – Huggins model [3, 54-56] and Guggenheim – Anderson – Boer
3 (GAB) model [50, 57] but none provided a good fit. This suggests that a more advanced, multi-
4 parameter model is required to simulate this type of behaviour.

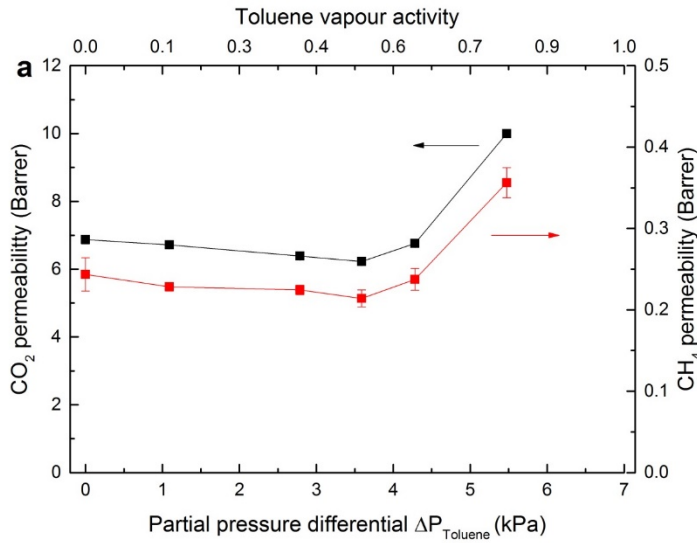
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6 *3.3. The impact of toluene and xylene on CO₂/CH₄ separation at low CO₂ Pressure*

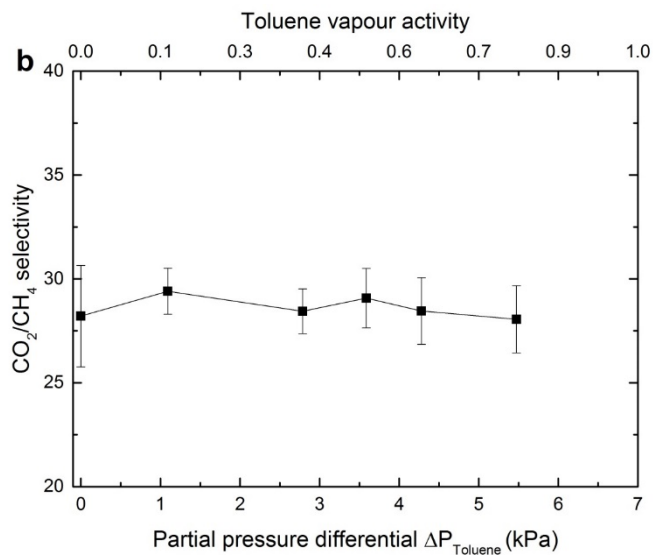
7 The impact of toluene vapour on the permeability of CTA in a mixture of 10% CO₂ in methane
8 is shown in Figure 4. The permeability of CO₂ and CH₄ fell by 10% and 12%, respectively, as
9 toluene partial pressure increased to 3.5 kPa (0.5 vapour activity). This is consistent with the
10 literature where a decline in CO₂ permeability of 10% was also observed when the toluene
11 vapour pressure was varied in the range of 0.3 – 2.5 kPa [6, 15]. The decline in gas permeability
12 may be partly attributed to “pore blocking” [58, 59], also known as “anti-plasticisation” [8, 60,
13 61]. This is where hydrocarbons molecules fill the free volume and block the penetrant
14 transport pathways in the polymer. The fall in permeability may also relate to the competitive
15 sorption of toluene, displacing CO₂ and CH₄ from sorption sites. Conversely, once the vapour
16 pressure exceeds 3.5 kPa, there is a rapid increase in permeability. This corresponds to toluene-
17 induced plasticisation, consistent with the sorption isotherm (Figure 3b). Interestingly, the
18 presence of toluene vapour has no effect on the selectivity of CO₂/CH₄ in the membrane, which
19 is consistent with previous literature reports [6].

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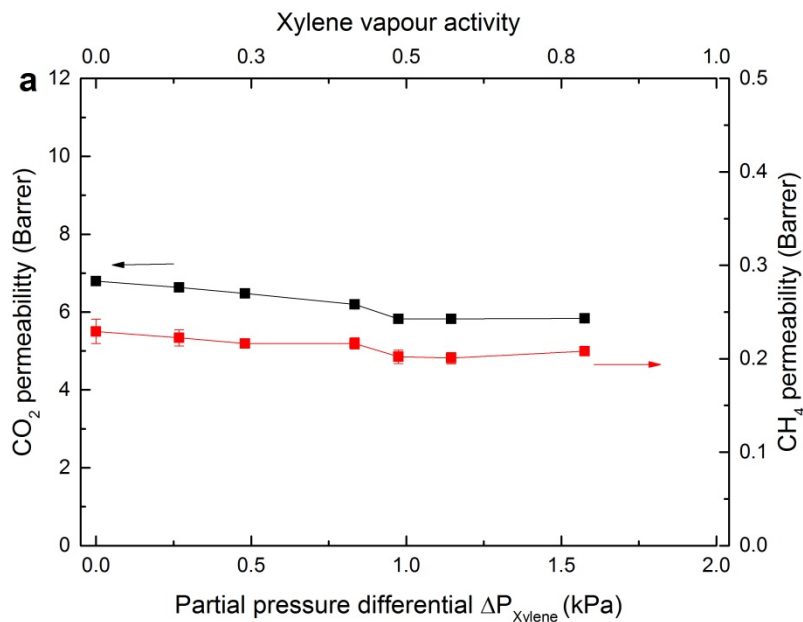


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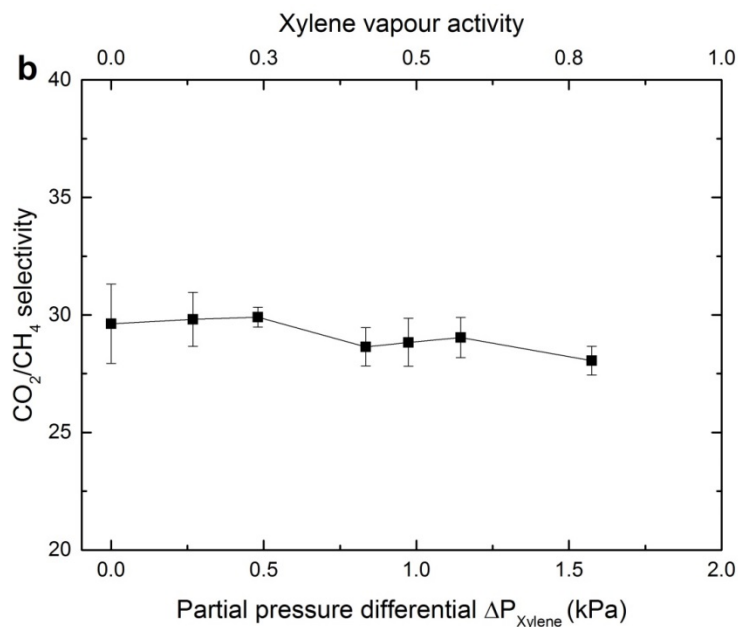
4 **Figure 4 The permeability of CO₂ and CH₄ (a) and CO₂/CH₄ selectivity (b) through**
5 **CTA membranes exposed to toluene at various vapour pressures, for 10% CO₂/CH₄**
6 **mixed gas feed at 7.5 bar and 35°C**

7

8 The impact of xylene on CO₂/CH₄ separation in CTA membrane is provided in Figure 5.
9 Similar to toluene, the presence of xylene in the feed gas reduced the permeability of CO₂ and
10 CH₄ slightly, with a decrease of 12 to 14% in gas permeability at 1.0 kPa xylene partial pressure
11 (0.5 vapour activity). However, at higher xylene vapour pressures, up to 1.6 kPa (0.8 activity),
12 the CO₂ and CH₄ permeabilities remain unchanged with plasticisation not clearly evident. This
13 probably reflects the much smaller increase in solubility for the xylene penetrant at 0.8 activity
14 relative to toluene (see Figure 3a).



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Figure 5 The permeability of CO₂ and CH₄ (a) and CO₂/CH₄ selectivity (b) through cellulose triacetate membranes exposed to xylene at various vapour pressures, for 10% CO₂/CH₄ mixed gas feed at 7.5 bar and 35°C

8 As a comparison, the negative impacts of aromatic hydrocarbons on polyimide membranes are
 9 much more significant, with a decline of 90% in gas permeabilities reported in the literature
 10 [8] and a 30 – 50% drop in CO₂/CH₄ selectivity [5, 14]. The resistance of cellulose triacetate
 11 membranes to these hydrocarbon contaminants, relative to other polymeric membranes, is
 12 attributed to the much greater solubility of CO₂ within the CTA polymer. As is evident from
 13 Table 3, the separation of CO₂ and CH₄ in CTA is based on high solubility selectivity, with
 14 relatively limited diffusivity selectivity, reflecting relatively large free volume elements.
 15 Conversely, polyimides separate CO₂ from CH₄ more on the basis of diffusivity selectivity.

1 The major impact of plasticisation, such as observed here when xylene and toluene is added, is
 2 to increase free volume and thus to reduce diffusivity selectivity. This clearly has a greater
 3 influence on polyimides than on CTA.

4

5 **Table 3**

6 **Selectivity ratios of permeability, solubility and diffusivity for pure CO₂ and CH₄ for**
 7 **some dense films at 7.5 bar and 35°C**

Polymer	P(CO ₂)/P(CH ₄)	S(CO ₂)/S(CH ₄)	D= P/S D(CO ₂)/D(CH ₄)	Reference
CTA	30	13.6	2.2	This study
Matrimid® 5218	42	2.8	15	[62]
6FDA – IDPA	49	3.5	14	[14]

8

9 *3.4. The impact of toluene and xylene on CTA membranes at higher CO₂ pressure*

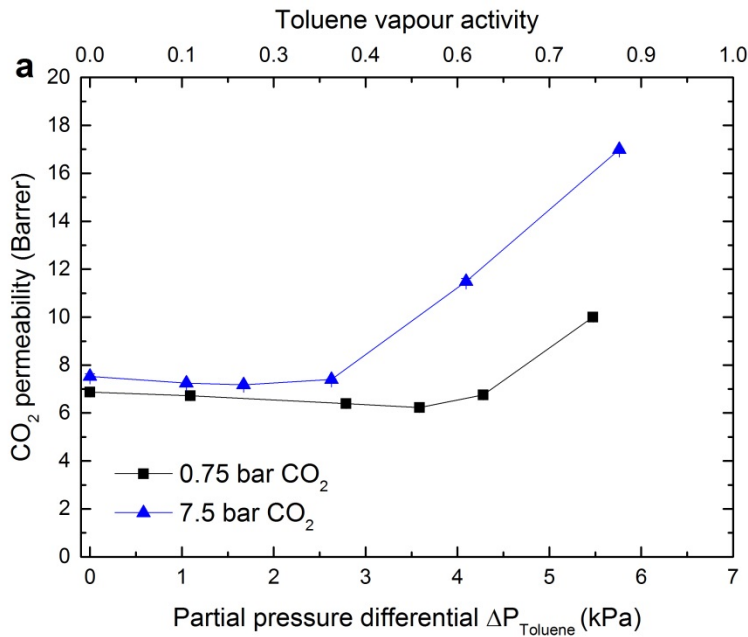
10 The partial pressure of CO₂ in the raw natural gas can be over 7 bar depending on the source
 11 [5], so the impact of toluene and xylene on CTA membranes at 7.5 bar pure CO₂ pure was also
 12 studied. As shown in Figure 6, the higher CO₂ pressure results in a slightly higher permeability
 13 in the absence of any aromatic hydrocarbon. This permeability was maintained for up to 18
 14 days of exposure to the pure CO₂ at 7.5 Bar feed pressure. This increase in permeability may
 15 reflect both plasticisation by CO₂ and the absence of CH₄ as a competitor for sorption sites.

16 The CO₂ permeability is otherwise similar at low partial pressures of either xylene or toluene.
 17 However, plasticisation clearly occurs at a lower partial pressure of xylene or toluene, when
 18 the CO₂ partial pressure is higher. At the higher CO₂ pressure, plasticisation first occurred at a
 19 vapour activity of 0.3 (partial pressure of 0.58 kPa for xylene and 2.0 kPa for toluene), versus
 20 0.5 with low CO₂ partial pressure. In this case, the CO₂ and the aromatic hydrocarbon act
 21 cooperatively to lower the glass transition temperature, so that a transition to a swollen rubbery
 22 state now occurs at a lower temperature for a given vapour pressure.

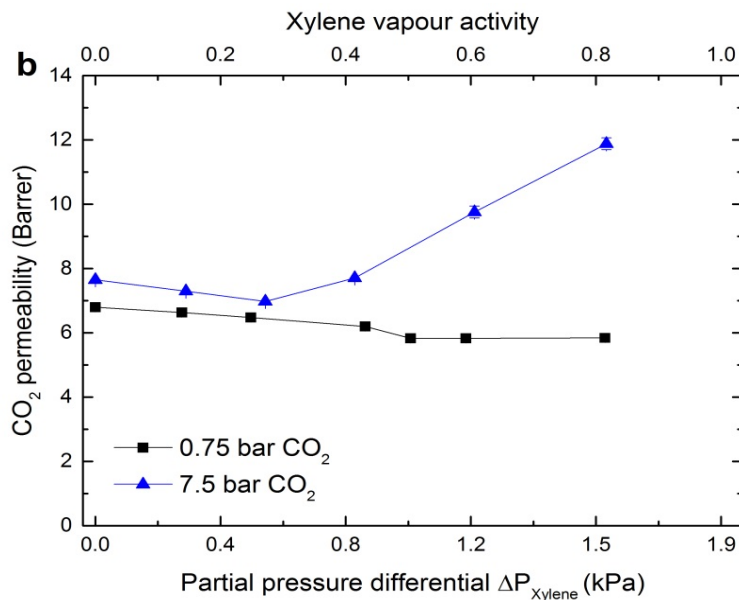
23 Such changes in the glass transition temperature are often described by the Fox Equation
 24 (Equation 4)[63]:

25
$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4)$$

26 Where T_g is the glass transition temperature in Kelvin and w the mass fraction of each
 27 component in a mixture of species 1 and 2. However, in the present case, this simple model
 28 (extended to three species) is unable to predict successfully the experimental data. Assuming
 29 glass transition temperatures of 190°C for CTA [64], -156 °C for toluene [65] and -78 °C for
 30 CO₂ [66], would suggest that a glass transition temperature of 178°C for the polymer at 0.75
 31 Bar CO₂ and 0.5 toluene activity, falling to 160°C for 7.5 Bar CO₂ and 0.3 toluene activity.
 32 These temperatures are clearly well above that of the experimental temperature of 35 °C.



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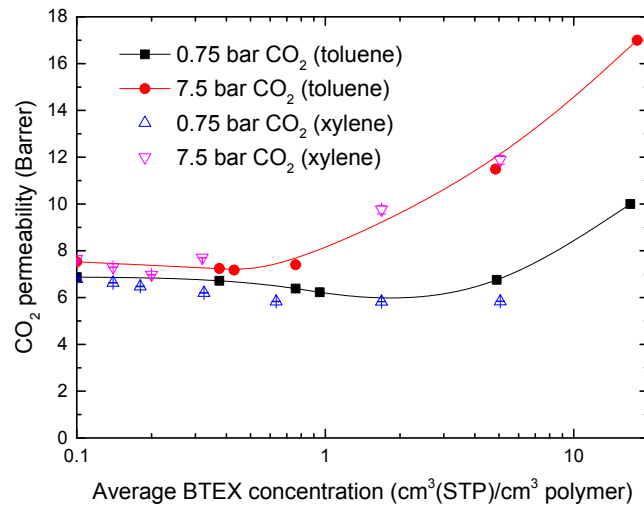
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3 **Figure 6 The permeability of CO₂ through a CTA membrane at 35°C exposed to (a)**
 4 **toluene and (b) xylene at various vapour pressures, for a 10% CO₂/CH₄ mixed gas (0.75**
 5 **Bar CO₂) and for pure CO₂ at 7.5 bar.**

6

7 It has also been suggested that plasticisation occurs at a specific penetrant concentration for all
 8 polymers within a particular family[67, 68]. To probe this hypothesis, the permeability data in
 9 Figures 4 to 6 was re-plotted against the average concentration of xylene or toluene within the
 10 membrane film. This average concentration was estimated by assuming a linear concentration
 11 profile across the film and a concentration on the permeate side of zero, so that the average
 12 concentration is exactly half that of the feed side (Figure 7). This Figure suggests that
 13 plasticisation occurs at around 0.8 cm³(STP)/cm³ polymer for both penetrants when there is
 14 significant concentrations of carbon dioxide also dissolved in the polymer, but at over 5
 15 cm³(STP)/cm³ polymer when CO₂ concentrations are low.

1 Finally, it is possible that the changes in behaviour observed here also relate to changes in
2 polymer crystallinity. As both the aromatic hydrocarbons and CO₂ absorb into the polymer,
3 they can reduce the proportion of crystalline regions. In turn, this will cause an increase in
4 accessible free volume and thus effects that appear similar to plasticisation.



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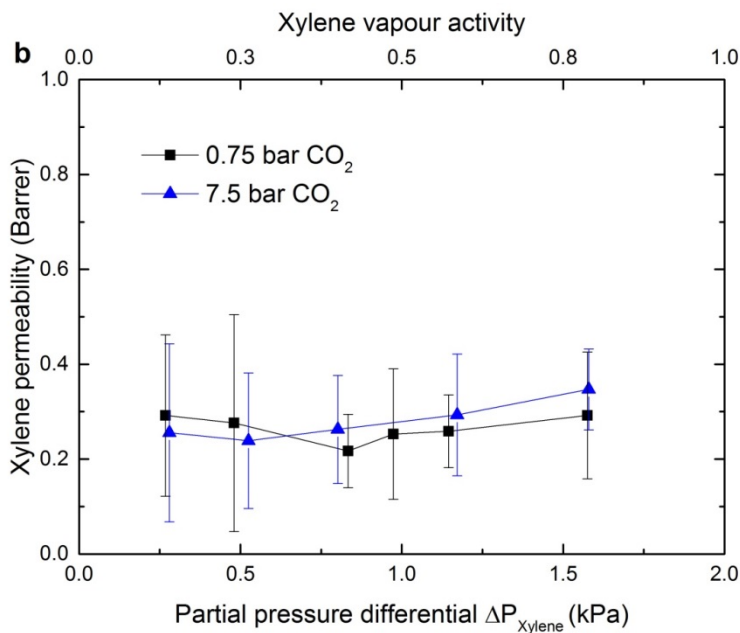
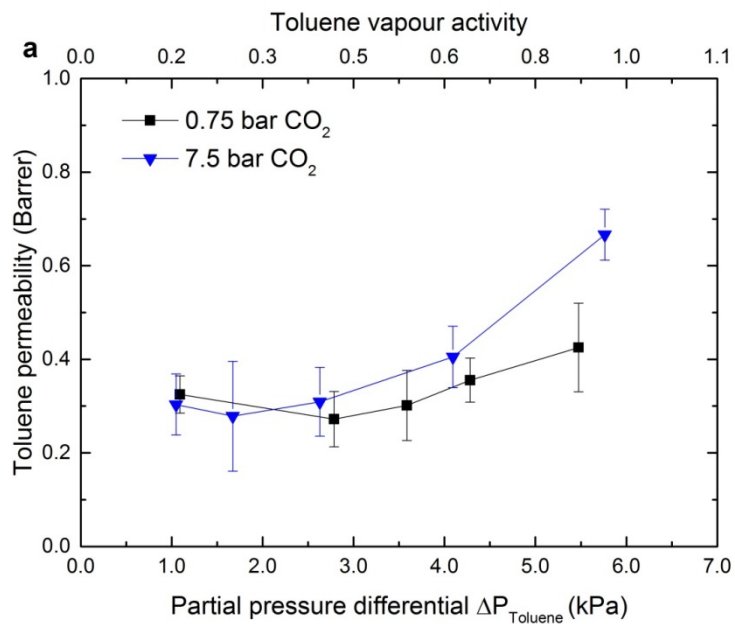
6 **Figure 7 - The permeability of CO₂ through cellulose triacetate membranes as a function**
7 **of the average xylene or toluene concentration within the membrane, for feed side CO₂**
8 **partial pressures of 0.75 and 7.5 bar and 35°C. The lines are drawn to guide the eye only.**

9

10 3.5. The permeabilities of toluene and xylene in CTA membranes

11 The permeabilities of toluene and xylene through the CTA membranes at two different CO₂
12 pressures are summarised in Figure 7. The changes in toluene permeability with vapour
13 pressure are similar to the trends for CO₂, where permeability declined with vapour pressure
14 initially and turned upward when the membranes were plasticised (Figure 6). In addition, at
15 high toluene vapour pressure, the higher CO₂ pressure also enhanced the permeation of toluene
16 through the plasticised membranes. These changes are less evident in the xylene data, where
17 the permeability is constant at all conditions within the error margins.

18 The permeability of toluene, xylene and methane at the same experiment conditions is in the
19 order P(Toluene) > P(xylene) ≈ P(CH₄) (refer to Figure 4a, Figure 5a and Figure 7). This can
20 be explained by the solution – diffusion mechanism of penetrant transport through the dense
21 membrane. The solubility of xylene and toluene are significantly greater than CH₄ due to the
22 higher critical temperatures of aromatic hydrocarbons (Table 3). However, the larger kinetic
23 diameters results in reduced diffusion of xylene and toluene through the membranes compared
24 with CH₄.



14 **Figure 8 The permeability of (a) toluene and (b) xylene at various vapour pressures and**
 15 **activities, for 10% CO_2/CH_4 mixed gas feed and pure CO_2 feed at 7.5 bar and 35°C**

1

2 **4. Conclusions**

3 The impact of toluene and xylene on dense CTA membranes was investigated. The sorption
4 kinetics of liquid toluene and xylene showed type II behaviour, indicative of significant
5 plasticisation of the structure. While these changes occurred over hours when measured with
6 thick films in the laboratory, the changes are expected to occur faster in industrial membrane
7 processes, where the active membrane layer is much thinner. The presence of toluene or xylene
8 at low vapour pressure reduced the permeation of CO₂ and CH₄ through the membrane. At
9 higher vapour pressures, plasticisation occurred, resulting in a dramatic increase in
10 permeability. For low CO₂ partial pressures (0.75 Bar), the plasticisation occurred at 0.5 vapor
11 activity, consistent with solubility measurements. However, in the presence of a higher CO₂
12 pressure (7.5 bar), plasticisation occurred at a low vapour activity of 0.3. This shift reflects a
13 lowering of the glass transition temperature in the presence of both penetrants and possibly a
14 reduction in the degree of crystallinity. The permeability of toluene and xylene itself through
15 the CTA membranes was also determined.

16

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Author/s:

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