

1 **The impact of ethylene glycol and hydrogen sulfide on the performance of cellulose**
2 **triacetate membranes in natural gas sweetening**

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8 **Abstract**

9 In natural gas sweetening, gas dehydration with glycols is typically carried out upstream of
10 membrane separation of carbon dioxide. This means that when process upsets occur, these
11 glycols can reach the membrane unit. In this work, we study the impact of two common
12 glycols (monoethylene glycol and triethylene glycol) on the gas transport performance of
13 CTA. We find that the glycol absorbed into the membrane initially obstructs the permeation
14 of CH₄ and CO₂, due to pore filling or antiplasticisation effects, but the permeability then
15 increases again, indicative of polymer relaxation and a loss of crystallinity in the polymer.
16 The smaller helium molecule is significantly less affected by the presence of the glycols,
17 possibly because its lower solubility within glycol limits its movement through the swollen
18 structure. However, after removing the glycols with a methanol wash, the membrane
19 performance recovers with only a slight residual plasticisation observed. In addition, the
20 permeation of H₂S, a common contaminant within natural gas streams, was studied across a
21 range of temperatures. At the partial pressures studied (up to 0.75 kPa), H₂S had very little
22 effect on the membrane performance even in long-term exposure for up to 300 days.

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25 Keywords: Cellulose triacetate; hydrogen sulphide; ethylene glycol; triethylene glycol;
26 plasticization.

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1. Introduction

Natural gas is a primary energy resource that will occupy over 25% of the global electricity market in the next decades, as well as acting as a transport fuel and direct heating resource [1]. The composition of raw natural gas varies widely but typically contains impurities such as nitrogen (N_2), carbon dioxide (CO_2), water (H_2O) and hydrogen sulphide (H_2S) that require removal to meet pipeline specifications. Membrane separation has been used for many decades for acid gas removal, known as natural gas sweetening, with advantages in energy efficiency, land footprint and a lack of chemical consumption [2]. Although many new membrane materials have been developed, cellulose triacetate (CTA) membranes still retain the bulk of this separation market because of their high CO_2 – methane (CH_4) selectivity, commercial readiness and acceptance as a low risk option by the industry [3, 4].

Raw natural gas is usually saturated with water which is generally removed upstream of the membrane unit to avoid pipeline corrosion and hydrate formation [5-7]. Glycols such as monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) are the most common solvents utilised for this purpose [8, 9]. Due to the extremely low vapour pressure of glycols (28Pa for monoethylene glycol [10] and <1Pa for triethylene glycol [11] at 35°C), carryover of these solvents in the vapor state is usually limited. However, carryover of entrained glycol droplets can occur [7]. This is a significant issue, because glycol is known to plasticise polymers [12], and the entrainment of the glycol solution into the membrane unit can thus alter the permselectivity of the membrane [13]. A study on the effect of MEG and TEG vapours on CO_2/CH_4 separation across a facilitated transport membrane has been reported [14]. However, to the best knowledge of the authors, there is no study on the effect of glycol solutions on the gas separation performance of CTA membranes.

Hydrogen sulfide is a common species in natural gas with concentration varying from 4 – 10000 ppm [15] that will enter the membrane unit with the natural gas. Many studies on CO_2 removal from natural gas by cellulose acetate membranes have observed the co-permeation of H_2S with CO_2 in the membrane unit [15-17]. Li et al (1987) reports the performance of cellulose acetate membranes in the presence of H_2S – H_2O mixtures [18]. However, the impact of temperature on H_2S permeation through the CTA membrane has not been well studied. Heilman et al. [19] reported the permeability and sorption of H_2S into several polymer films including a cellulose acetate film manufactured by Polaroid but the results presented were limited. Data on the long term effect of H_2S on CTA gas separation performance is also limited.

In this investigation, the effect of two standard glycols, MEG and TEG, on the gas separation of CTA membranes over a 2000 hour period is investigated. The permeation of H_2S through CTA membrane at different partial pressures (0.2 – 0.75 kPa) and temperatures (22 – 80°C) is also reported, as is the long term impact of H_2S on the membrane performance over a 7200 hour period.

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2. Experimental

2.1. Membrane fabrication

The polymer utilised in the investigation was a commercial cellulose triacetate powder supplied by Cellulose Company – Daicel Corporation, Japan. The degree of substitution of acetyl groups on the polymer is 2.85, corresponding to a degree of acetylation of 61.6%.

Dense CTA membranes were fabricated by a solvent casting method. The polymer powder was dried under vacuum at 100°C overnight prior to membrane fabrication. The dried powder was then dissolved in dichloromethane (ChemSupply, Australia) to form a 1 wt % solution. The solution was filtered to remove any impurities before casting into glass petri-dishes. The petri-dishes were kept covered for 24 hours for solvent evaporation. Afterward, the membranes were dried under vacuum at 35°C for 24 hours and 100°C for another 24 hours and the final membranes stored in a desiccator to prevent exposure to moisture. The membranes were stored for two weeks before utilisation in permeability measurements, to allow the initial rapid loss of permeability due to physical aging to occur. The thickness of each membrane was measured with a micrometer to be in the range of 65 to 75 µm. At least two membranes were tested for each experimental condition to confirm the reproducibility.

The membrane density (ρ) was determined by the buoyancy technique using a XS205 DualRange balance (Mettler Toledo, Australia) with maximum 0.06% error. The density was based on the difference in weight of membrane samples in air (m_{air}) and in n-hexane (m_{hexane}) at room condition ($22 \pm 1^\circ\text{C}$) (Equation 1). The density (ρ_{hexane}) of n-hexane (Chem-supply, Australia, 95%) was 0.655 g/ml as measured by a calibrated pycnometer.

$$\rho = \frac{m_{\text{air}}}{m_{\text{air}} - m_{\text{hexane}}} \rho_{\text{hexane}} \quad (1)$$

2.2. Gas permeation measurement

A variable volume constant pressure (VVCP) gas permeation apparatus was utilised to measure the permeability of gas mixtures through CTA membranes across the pressure range from 100 to 900 kPa gauge and temperature range from 22 to 80°C. The gas permeation set-up has been reported in previous studies [6, 20, 21]. The H₂S mixed gas (1000ppm H₂S in balance N₂, Coregas Australia) was fed into the feed side of the permeation cell with stage cut less than 0.2%. A sweep gas of absolute helium (99.99% purity, Coregas Australia) at 1 atm absolute pressure flowed across the permeate side of the membrane cell at 35 ml/min and was directed to a gas chromatograph (490 micro GC, Agilent technologies Australia) for concentration analysis. The GC was calibrated against pure N₂ and a mixture of 1000 ppm H₂S in N₂ to generate the calibration curve.

For measuring the permeability of individual gases (He (99.99% purity, Coregas Australia), CH₄ (99.9% purity, Coregas Australia) and CO₂ (99.5% purity, BOC Australia), a constant volume - variable pressure (CVVP) gas permeation apparatus was used. The gas permeation rig was operated at 35°C and the setup was also as reported in previous studies [21, 22]. The membrane with an effective area of 10.75 cm² was installed into the permeation cell and placed under a vacuum overnight prior to the gas permeation measurement. The gas permeation coefficient, P (Barrer or 10⁻¹⁰ cm³(STP).cm/cm².s.cmHg), was determined from the slope of the pressure versus time curve, under steady state conditions.

1 2.3. Static long-term aging of CTA in glycol solutions and H₂S

2 The long term impact of ethylene glycol (MEG, 99.8% purity - anhydrous, Sigma Aldrich
3 Inc., America) and triethylene glycol (TEG, 99% purity – 0.1% water, Chemsupply,
4 Australia) on the CTA membranes was determined by immersing the membranes into pure
5 glycol solutions, separately at ambient conditions (22 ± 2°C) for up to 2000 h (80 days). The
6 solutions were stored in glass containers and kept inside a desiccator to prevent exposure to
7 moisture. The water content of the glycol solutions was regularly determined by a volumetric
8 Karl Fischer titrator (915 KF Ti-Touch, Metrohm AG Switzerland) to ensure the glycol
9 concentration remained above 99.0%, which is similar to the concentration of lean glycol in
10 industrial dehydrators [7]. Membrane samples were removed regularly to test the sorption
11 uptake and the pure gas permeability in a “wet” state.

12 To determine the sorption uptake, the membrane was removed from the solution and excess
13 liquid droplets on the membrane surfaces removed by wiping with a tissue. The membranes
14 were then weighed to record the mass uptake (m_t). The total glycol uptake was calculated via
15 Equation 2 where m_o is the original mass of the membrane and m_∞ the value at equilibrium
16 sorption.

$$17 \quad \text{Glycol uptake (\%)} = \frac{m_\infty - m_o}{m_o} \times 100 \quad (2)$$

18 Some “wet” membrane samples were also immersed in methanol (MeOH, 99.8% purity –
19 0.1% water, Chemsupply Australia) for 168 hours (1 week) to extract the glycol from the
20 membrane structure. The washed membranes were removed from the MeOH solution and
21 dried by vacuum overnight before testing the gas permeation in this “dry” state. To confirm
22 the extraction efficiency of MeOH, thermogravimetric analysis was conducted (TGA 209 F1
23 Libra®, Netzsch Australia).

24 Fresh CTA membranes were also aged in pure methanol at ambient conditions for up to 550
25 hours. The wet membranes were removed from the solution and dried in vacuum overnight to
26 evaporate all methanol before testing.

27 Similarly, the long-term impact of H₂S on the performance of CTA membranes was
28 conducted by placing dense membranes in a sealed chamber at room temperature (22 ± 2°C).
29 The chamber was evacuated and then filled with the experimental gases (1000ppm H₂S in
30 balance N₂ or pure N₂) to 750 kPa absolute pressure. After a specified aging period of up to
31 7200 hours (300 days), the membranes were removed and the permeability recorded. The
32 chamber was evacuated for around 5 minutes to remove the toxic gases before opening and
33 removing the membranes.

34 Differential scanning calorimetry (DSC) was used to determine the glass transition
35 temperature (T_g) of original and “wet” state CTA using a differential scanning calorimeter
36 DSC 8500 with a DSC high pressure cell addendum (Perkin Elmer, Australia). The heating
37 rate was 20°C/min, from 22°C to 250°C, under 1600 kPa nitrogen pressure to prevent glycol
38 evaporation. The T_g was determined by the centre point of the endothermic transition. The
39 result for MEG was compared to the Fox equation for ideal mixtures (Equation 3) [23, 24].

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (3)$$

where w_1 , T_{g1} , w_2 , T_{g2} are the weight fraction and glass transition temperature in Kelvin of CTA and glycol, respectively. The Tg of pure CTA was taken as $190 \pm 5^\circ\text{C}$ [25] while that of MEG was -118°C [26]. It was not possible to find the glass transition temperature for pure TEG.

Wide angle X-ray diffraction (WAXD) analysis was conducted to study the impact of glycols on the crystallinity of the CTA polymer. A D8 Advance Diffractometer (Bruker, Germany) was used to analyse the membranes over a 2θ range from 5° to 35° at a rate of 0.02° every 5 seconds with a Ni-filtered CuK_α radiation source, 30mA and 40kV. Bragg's equation was applied to calculate the mean distance, d -spacing, between polymer chains (Equation 4),

$$\lambda = 2d \sin \theta \quad (4)$$

Where λ is the radiation wavelength (1.54 \AA) and θ is the incident angle.

3. Results and discussion

3.1. Sorption Uptake of glycol liquids in Cellulose Triacetate

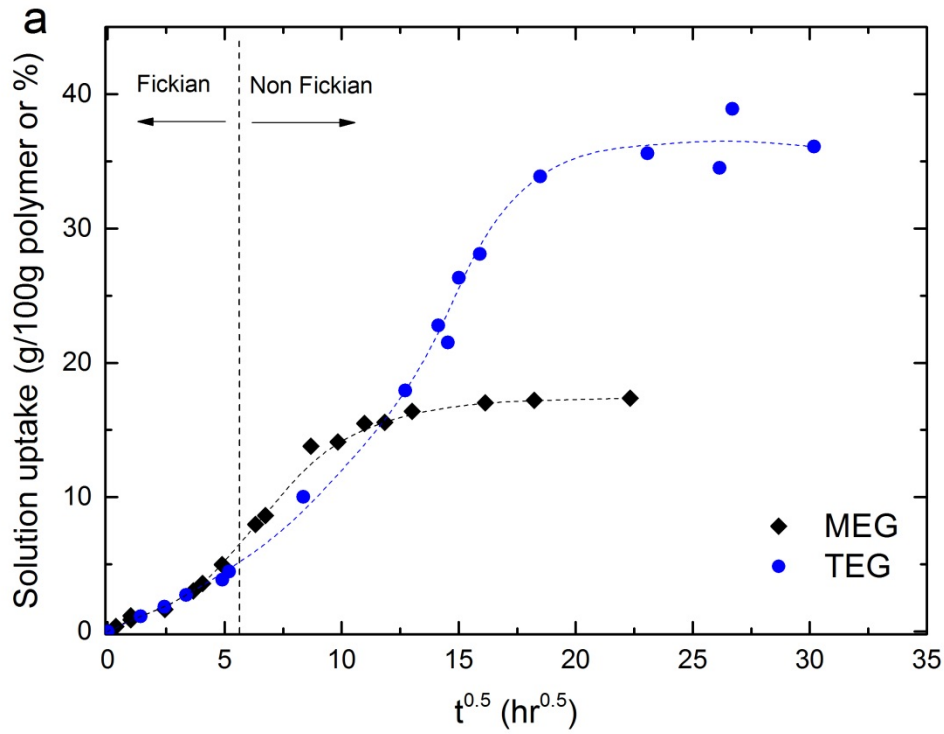
The sorption uptake of both MEG and TEG (**Figure 1**) shows a sigmoidal shape which indicates that while the glycols initially swell the CTA membrane by Fickian diffusion, polymer relaxation or plasticisation occurs as the solute concentration increases [27-30]. The transition from Fickian diffusion to non-Fickian polymer relaxation occurs at roughly 30 hours of exposure of these $70\mu\text{m}$ membranes to the solution. It should be noted that the transition time would be of the order of seconds for commercial membranes where the active layer is of the order of a hundred nanometers in thickness.

The equilibrium solubilities of the two penetrants are summarised in **Table 1**. The solubility of the glycols is greater for TEG than MEG by mass (**Figure 1**). However, comparison on a molar basis indicates that the CTA membrane accommodates similar amounts of both glycols.

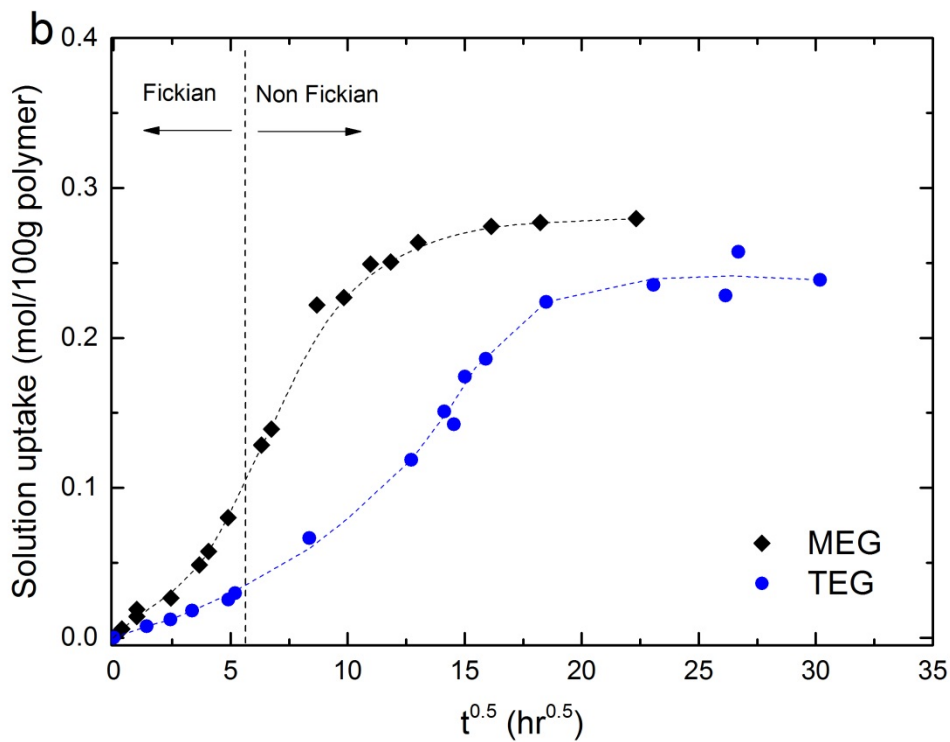
Table 1 Solubility of glycols in the CTA membrane

Liquids	MEG	TEG
Molecular Weight (g/mol)	62.1	150.2
Solubility	wt %	18.8 ± 0.4
	mol/100g polymer	0.30 ± 0.006
		37.7 ± 0.7
		0.25 ± 0.005

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4 **Figure 1** The sorption kinetics of ethylene glycol (MEG) and triethylene glycol (TEG)
 5 solutions in a CTA membrane (70 μ m thickness) at 22°C: (a) mass basis and (b) molar basis.
 6 The dashed lines are added to guide the eye.

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1 3.2. Impact of glycol liquids on CTA membrane performance

2 3.2.1. The impact of methanol on CTA membrane in glycol extraction step

3 The impact of these glycols on CTA membrane performance was determined by testing the
 4 permeation of pure He and CH₄ through the original fresh membranes, the “wet” membranes
 5 (after absorbing glycols for a specified time) and the “dry” membranes (after removal of the
 6 glycols). As the saturation partial pressures of the glycols are relatively low (11 Pa for MEG
 7 and <1 Pa for TEG at 20°C [7, 14]), the removal of the glycols from “wet” CTA membranes
 8 was not possible by simple drying, but was instead conducted by solvent exchange with
 9 methanol prior to drying. Thermogravimetric analysis for the “dry” CTA confirmed that both
 10 glycols and methanol were removed totally by this solvent exchange.

11 The selection of methanol as a glycol solvent was based on Hildebrand and Hansen solubility
 12 theory, which suggests that effective solubilisation is favoured between components having
 13 least heat of sorption per unit volume [31-33]. The approach defines three solubility
 14 parameters, a hydrogen bonding component (δ_h), a polar interaction component (δ_p) and a
 15 nonpolar interaction component (δ_d). The Hansen solubility parameter is the square root of
 16 the sum of squares of these components [31, 33] with similar values indicating good mutual
 17 solubility. Specifically, the mutual solubility of components is strongest when the radius of
 18 interaction between the Hansen solubility parameters is smallest [31] (**Table 2**). As a result,
 19 the solubility of methanol – glycol mixtures system is more favoured than methanol – CTA
 20 or glycol – CTA mixtures. A solubility envelope for CTA polymer was constructed by Klein
 21 et al. (1975) based on Hansen’s approach [34] and the liquids utilised in this study are outside
 22 the boundary. This further indicates that there will be no dissolution of the CTA polymer into
 23 the solutions during the sorption and aging experiments.

24 **Table 2** Hildebrand and Hansen solubility parameters of different liquids and CTA [31, 33]

Components	MEG	MeOH	TEG	CTA
Hydrogen bonding components (δ_h), MPa ^{0.5}	26.0	22.3	18.6	11.0
Polar interaction components (δ_p), MPa ^{0.5}	11.0	12.3	12.5	12.7
Nonpolar interaction components (δ_d), MPa ^{0.5}	17.0	15.1	16.0	18.6
Hansen solubility parameter* (δ), MPa ^{0.5}	33.7	29.6	27.5	25.1
Radius of interaction** between components and CTA ($R_{component - CTA}$), MPa ^{0.5}	15.4	13.3	9.2	0
Radius of interaction** between components and methanol ($R_{component - methanol}$), MPa ^{0.5}	5.5	0	4.1	13.3

* Hansen solubility parameter $\delta = \sqrt{\delta_h^2 + \delta_p^2 + \delta_d^2}$, MPa^{0.5}

** Radius of interaction: $R_{ij} = \sqrt{(\delta_h^i - \delta_h^j)^2 + (\delta_p^i - \delta_p^j)^2 + 4(\delta_d^i - \delta_d^j)^2}$, MPa^{0.5}

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1 3.2.2. *The impact of glycols on CTA membrane performance*

2 The impact of contact with MEG on the permeability of He and CH₄ through the CTA
3 membrane is shown in **Figure 2**. Over the first 30 hours, the “wet” membranes showed a
4 significant decline in both helium and methane permeability (**Figure 2a**). This decline is too
5 great to be caused by physical aging alone (see Section 3.4). Rather, it suggests that the
6 absorbed MEG reduces either the diffusivity and solubility of penetrants through the
7 membrane matrix [35]. As helium is not strongly adsorbed to any polymer, it is unlikely that
8 the decline in He permeability results from competitive sorption. This suggests that the
9 decline in this permeability occurs through a ‘pore blocking’ mechanism [35, 36], where
10 MEG molecules occupy the free volume and block pathways through the polymer structure,
11 causing a loss of diffusivity. This phenomenon is often referred to as “anti-plasticisation” [37,
12 38]. Conversely, the loss in CH₄ permeability could occur through either competitive
13 sorption or pore blocking, or a combination of both.

14 A dramatic increase in CH₄ permeation occurs at the 30 hour mark, which is a time roughly
15 comparable to that observed earlier for the onset of polymer relaxation (**Figure 1**). However,
16 no comparable impact is observed in He permeability. Polymer relaxation will impact the
17 larger molecule (CH₄) significantly more than He, as larger free volume elements are created
18 [39, 40]. It is also likely that CH₄ can more readily penetrate the glycol-rich regions that form
19 in the membrane, as it has significantly greater solubility in MEG than Helium (see **Table 3**).
20 Therefore, the MEG continues to obstruct the diffusion of He in the “wet” membrane,
21 resulting in a continuous decline of He permeability (**Figure 2a**). Consequently, the He/CH₄
22 gas selectivity also drops significantly once polymer relaxation commences (**Figure 2c**).

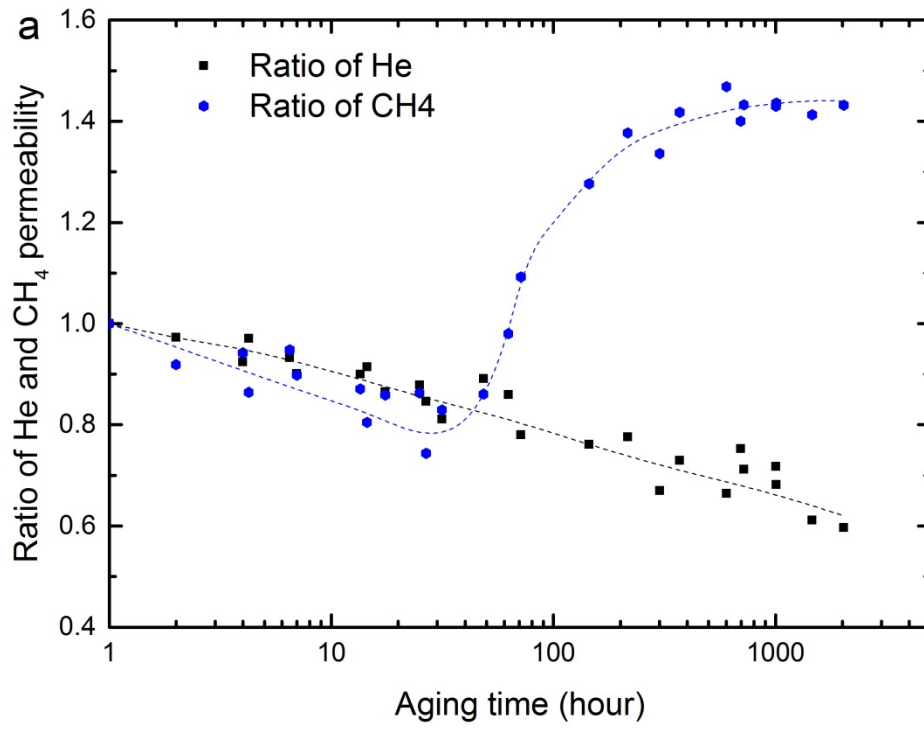
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24 **Table 3** Henry’s Law coefficient (MPa) for gases in glycols at 298K

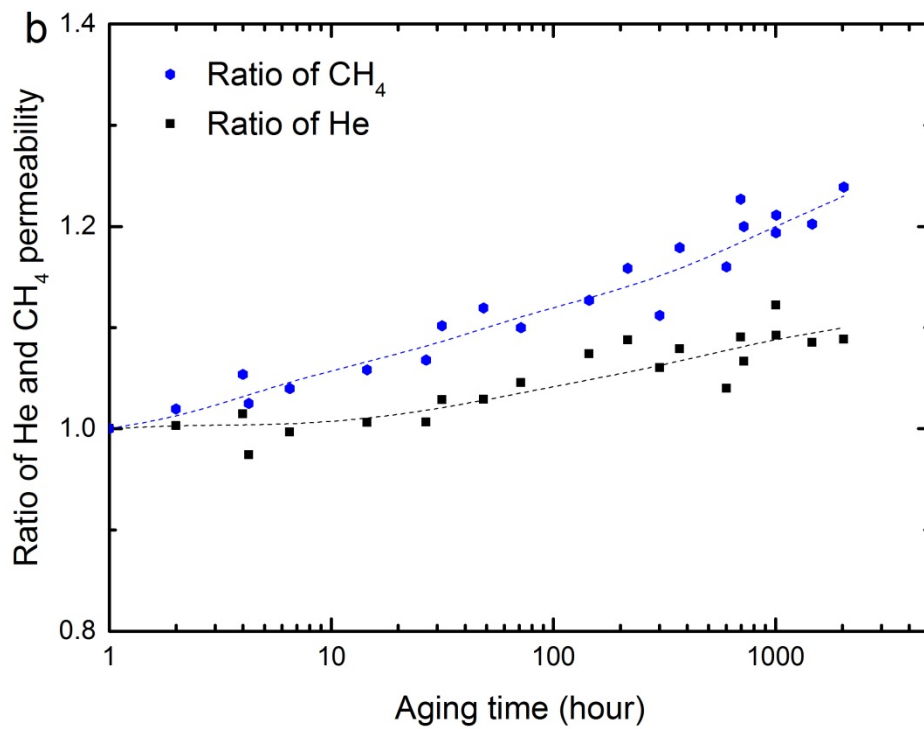
	CO ₂	CH ₄	He
MEG	78.5 ^a [62]	968.6 ^a [62] 656.3[63, 64]	6775[63]
TEG	11.95[65] 10.5 ^b	179.2[65] 177 ^b	1410 ^b

25 ^aData is at 303K

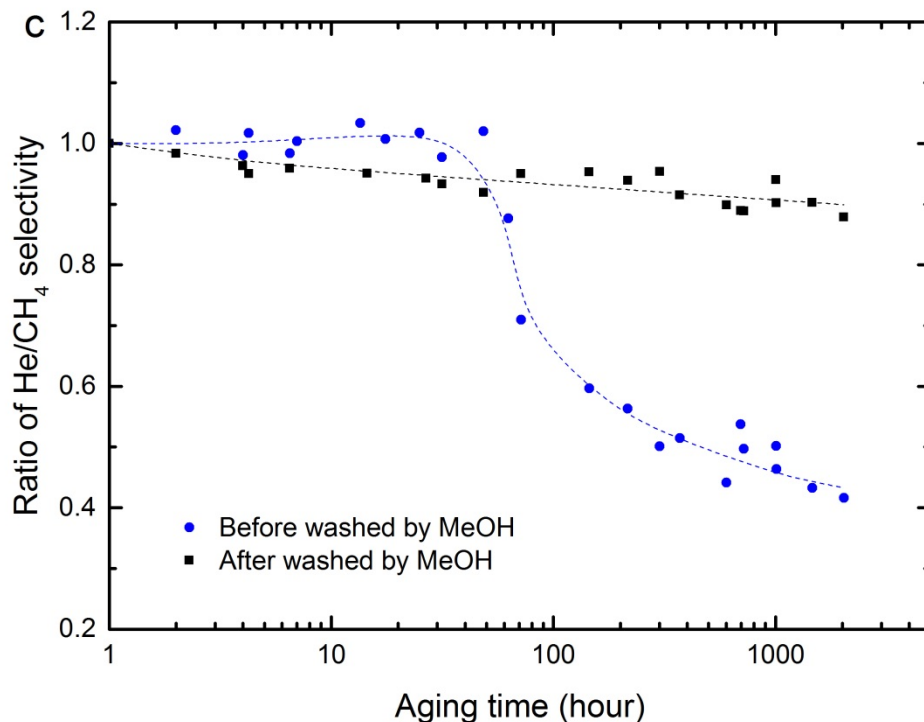
26 ^bCalculated using the Glycol package within Aspen HYSYS V8.6 at 1 Bar total pressure.



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2 **Figure 2** Change in permeability of He and CH₄ as time progresses at 35°C and 750 kPa feed
 3 pressure for CTA membranes: (a) aged in ethylene glycol (MEG) solution at 22°C; (b) aged
 4 in MEG and washed by methanol for 168 hours at 22°C; and (c) He/CH₄ selectivity. The
 5 dashed lines are added to guide the eye.

6

7 After extracting MEG from the CTA membrane with methanol, both He and CH₄ show a
 8 small, but significant increase in permeability with time (**Figure 2b**). The increase is greater
 9 for the larger CH₄ than for He, again suggesting that it is caused by a net increase in free
 10 volume. This implies that even after the complete removal of the glycol, the polymer
 11 structure is not fully recovered from the effects of polymer relaxation. This result is also
 12 supported by a decrease in the density of the “dry” membranes after aging in glycols in
 13 comparison with fresh CTA (**Table 4**).

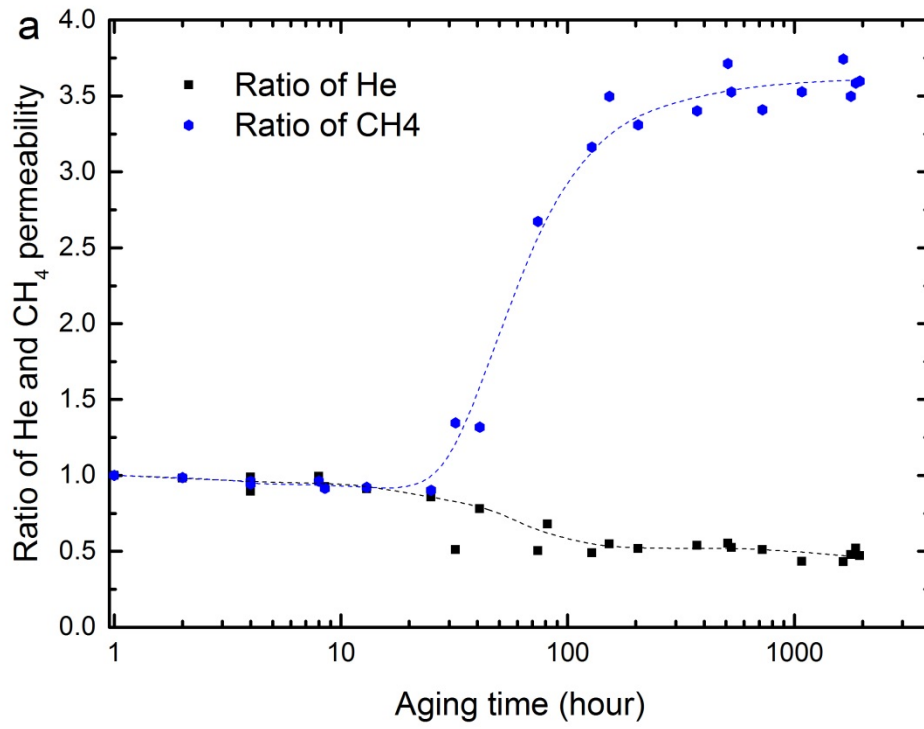
14 **Table 4** Density of CTA membranes before and after aging in glycol and methanol.

Glycols	Density (g/ml)		
	“Dry” CTA membranes after aging in glycols for 2000 hours	“Dry” CTA membranes after aging in methanol for 550 hours	Original CTA membranes
MEG	1.277 ± 0.008	1.297 ± 0.003	1.299 ± 0.001
TEG	1.270 ± 0.010		

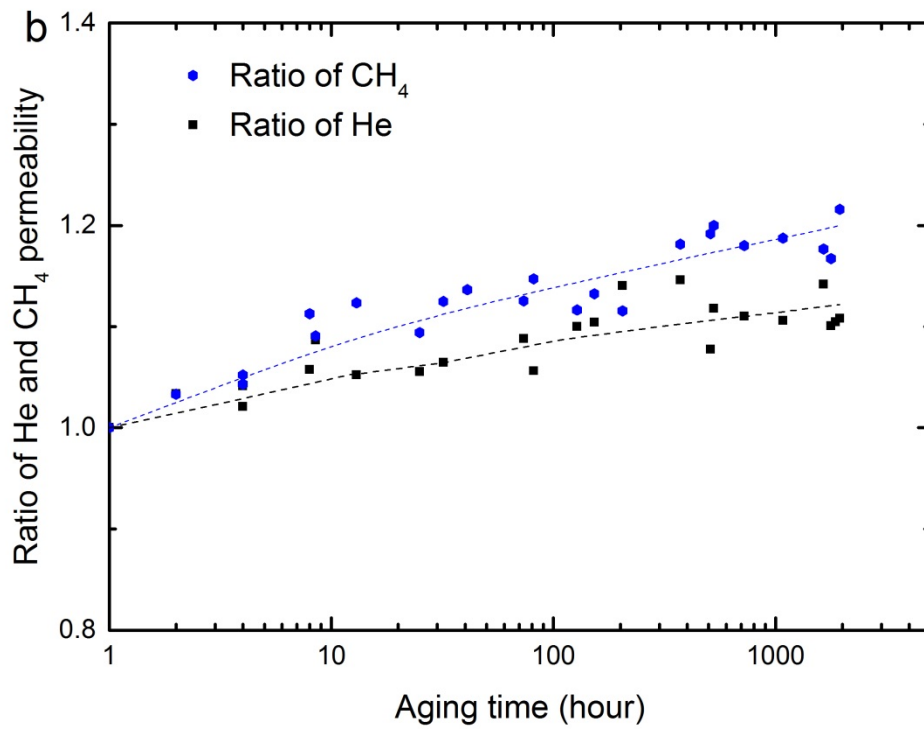
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1 Control membranes aged in methanol alone did not show the same increase in permeability
2 with time (**Supporting information, Fig. S1**). Methanol has been reported to plasticise CTA
3 in a pervaporation study [41], but the effect is minimal here, relative to the greater impact of
4 the glycol exposure.

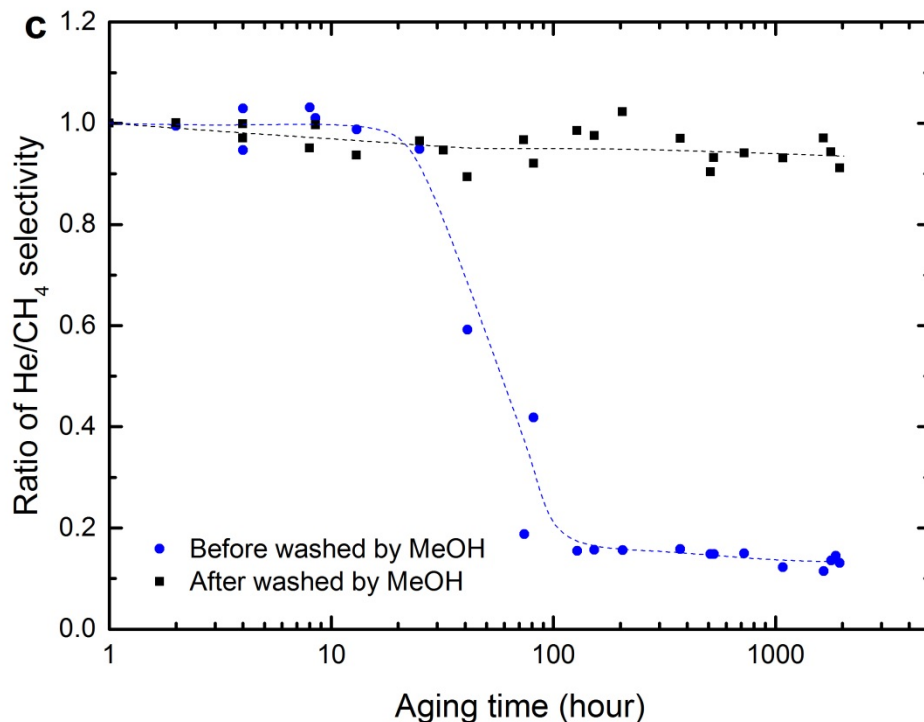
5 The impact of TEG on the CTA membrane was also studied as shown in **Figure 3**. The trends
6 in performance are identical, with the magnitude significantly greater. This reflects the higher
7 solubility of TEG in CTA (**Table 1**) and in turn, the higher solubility of CH₄ in TEG (**Table**
8 **3**).



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2 **Figure 3** Change in permeability of He and CH₄ as time progresses at 35°C and 750 kPa feed
 3 pressure for CTA membranes: (a) aged in triethylene glycol (TEG) solution at 22°C; (b) aged
 4 in TEG and washed by methanol for 168 hours at 22°C; and (c) He/CH₄ selectivity. The
 5 dashed lines are added to guide the eye.

6 It is notable that the permeability enhancement after removal of the glycols with methanol is
 7 quite similar, at around 10% over the aging period. The plasticising effect of TEG on the
 8 CTA membrane is likely stronger than MEG given the lower Hansen radius of interaction for
 9 the TEG – CTA pair (Table 2). However, there are fewer moles of TEG absorbed per unit of
 10 CTA membrane and the solution uptake is slower (**Figure 1b**), meaning that the effective
 11 plasticising molar concentration is lower at any given time during the aging process. All these
 12 aspects result in the similar plasticisation effect of TEG and MEG on the CTA membrane.

13

14 3.2.3. The impact of glycols on CO₂ permeation through CTA membrane

15 The impacts of MEG and TEG on the permeation of CO₂ were also studied by testing the
 16 permeability of CO₂ with 200 kPa feed pressure (**Table 5**). The feed pressure was selected to
 17 prevent CO₂ – induced plasticisation which can occur between 500 – 1200 kPa CO₂ pressure
 18 depending upon the degree of acetylation, membrane thickness and testing temperature [39,
 19 42, 43]. In general, the impact of glycols on CO₂ permeation is similar to the impact on CH₄.
 20 The absorption of glycols into membranes enhanced the permeability of CO₂ and the impact
 21 was more significant in membranes aged in TEG. In addition, the CO₂ permeability through
 22 the “dry” membranes was also enhanced due to the residual plasticisation arising from the
 23 glycol absorption.

1 The permeability ratio for CO₂ in both the “wet” and “dry” membranes was lower than that of
 2 CH₄. This reflects the smaller kinetic diameter of CO₂ [40], which means that its diffusivity is
 3 less affected by polymer relaxation. Further, while CO₂ has a stronger affinity for glycol than
 4 CH₄ (see Table 3), the ratio of the Henry’s Law coefficients suggests a solubility selectivity
 5 for CO₂/CH₄ in pure glycol of around 12. This selectivity ratio is lower than that observed for
 6 pure CTA (28 ± 1), suggesting that movement through glycol rich regions of the membrane is
 7 less CO₂ selective than in the dry polymer. Consequently, the selectivity of CO₂/CH₄ declines
 8 slightly in the ‘wet’ polymer.

9

10 **Table 5** The impact of glycols on the change of permeabilities (*P*) of CH₄ and CO₂ and
 11 CO₂/CH₄ gas selectivity ($\alpha_{\text{CO}_2/\text{CH}_4}$) of CTA membrane at 35°C

		Ratio of P(CO ₂)*	Ratio of P(CH ₄)*	Ratio of $\alpha_{\text{CO}_2/\text{CH}_4}$
“Wet” CTA**	Aged in MEG	1.34 ± 0.04	1.44 ± 0.02	0.93 ± 0.03
	Aged in TEG	2.88 ± 0.1	3.61 ± 0.04	0.80 ± 0.03
“Dry” CTA	Aged in MEG	1.19 ± 0.01	1.21 ± 0.04	0.98 ± 0.04
	Aged in TEG	1.18 ± 0.04	1.20 ± 0.02	0.99 ± 0.04

* Permeability relative to the fresh CTA membrane i.e. P(CO₂) = 7.20 ± 0.2 barrer, P(CH₄) = 0.254 ± 0.007 barrer and $\alpha_{\text{CO}_2/\text{CH}_4}$ = 28 ± 1. The permeation pressures were 200 kPa absolute for pure CO₂ and 750 kPa absolute for pure CH₄.

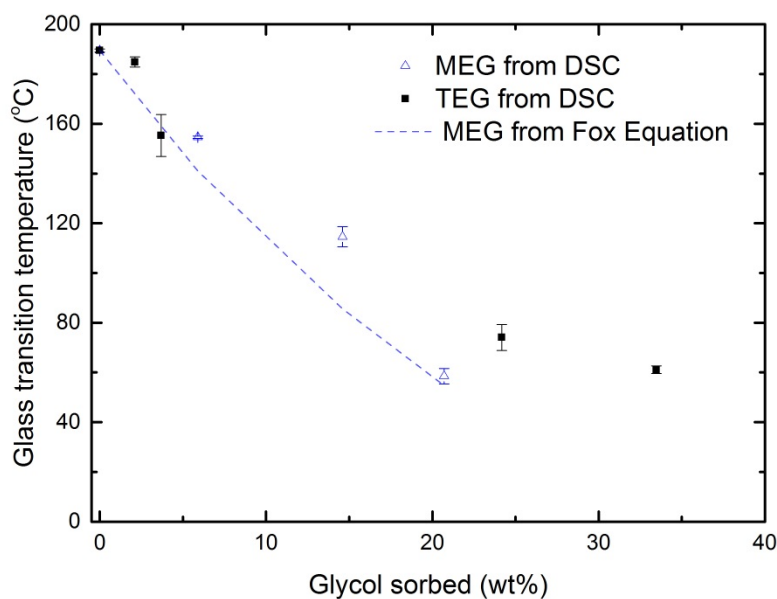
** The aging times for CTA membranes in MEG was 1440 hours in comparison with 2000 hours in case of TEG

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14 3.2.4. The impact of glycols on the glass transition temperature and crystallinity

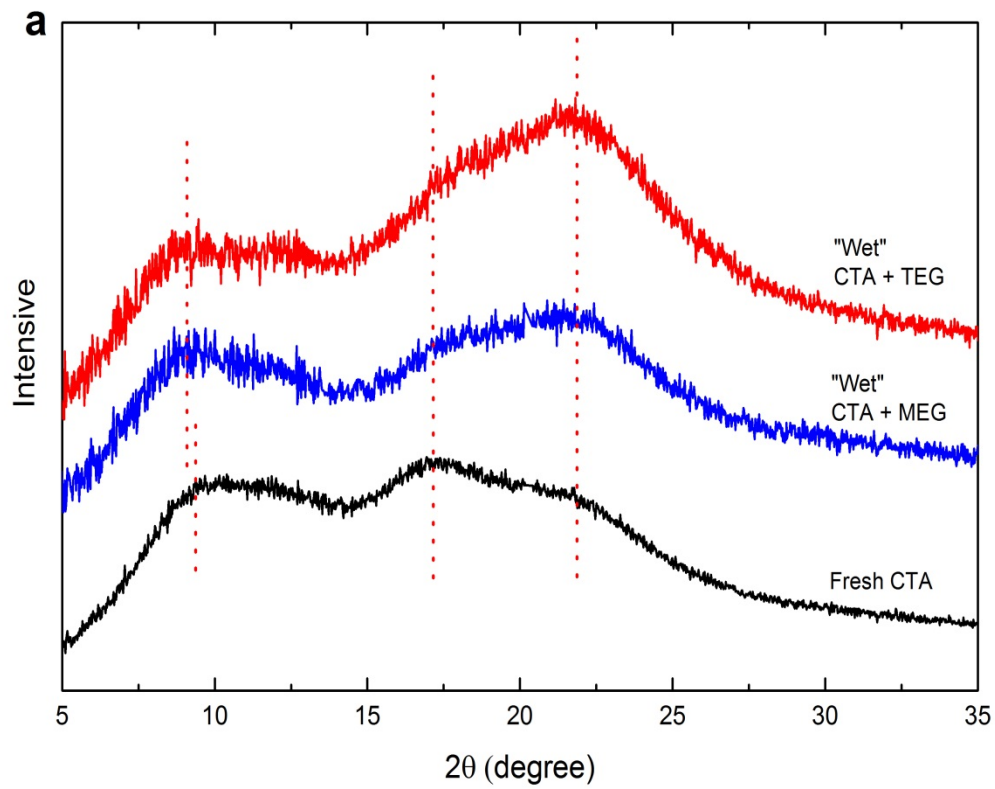
15 The dramatic changes in solubility and permeability that occur after 30 hours of immersion of
 16 the membranes in glycol are clearly caused by polymer relaxation of some type. Such
 17 changes are also often related to a fall in the glass transition temperature as the composition
 18 of the membrane material changes, so that this dramatic shift also correlates to a transition
 19 from a glassy to a rubbery state. However, DSC measurements of the glycol-swollen
 20 membranes suggest that the transition to a rubbery state does not occur under the conditions
 21 shown here, as this temperature does not fall to the experimental temperature (22 - 35°C)
 22 (Figure 4).



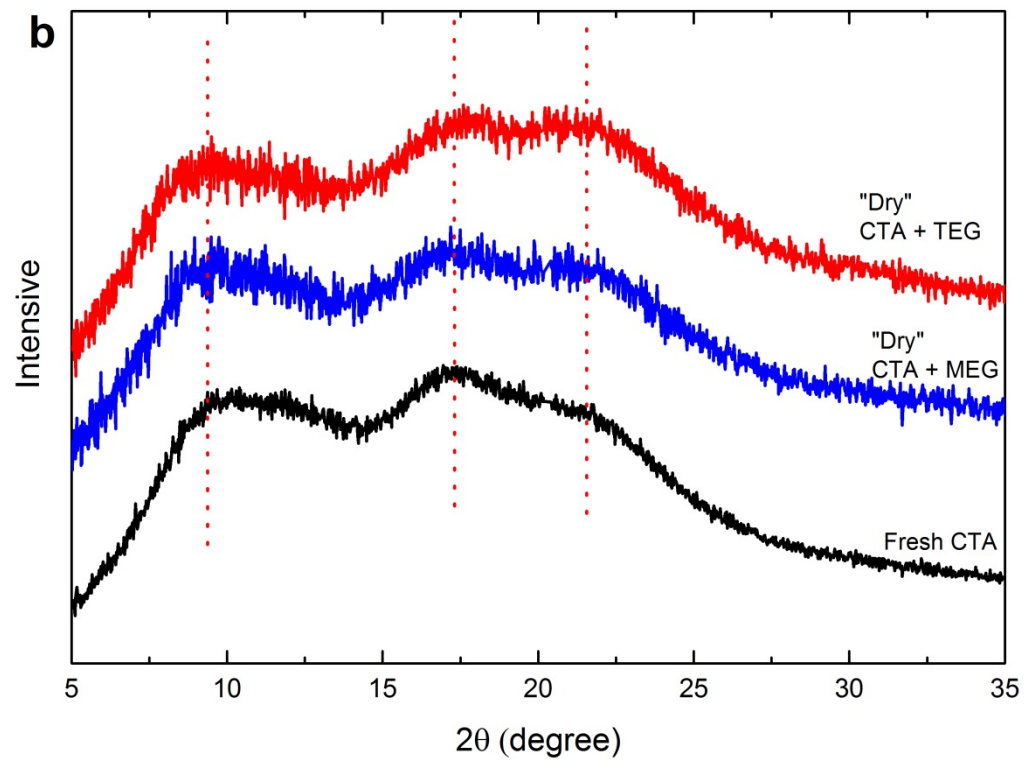
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2 **Figure 4** The change in glass transition temperature as glycol is sorbed into CTA, measured
 3 by dynamic scanning calorimetry (DSC) and calculated from the Fox Equation (T_g of MEG is
 4 -118°C [26]).

5 It is well known that the CTA polymer can contain areas of crystallinity. WAXD analysis
 6 was consistent with these reports with two typical semi-crystalline peaks observed at $2\theta \sim 10^\circ$
 7 [35, 44, 45] and 17° [46, 47], and a van der waals amorphous halo at $20 - 21^\circ$ [45, 46, 48, 49]
 8 in the fresh CTA membrane (Figure 5). By using an X-ray diffraction deconvolution method
 9 [50], the crystallinity index of this membrane was calculated to be $56 \pm 5\%$ which is
 10 compatible with the literature [51]. However, exposure of this membrane to liquid MEG and
 11 TEG resulted in an increase in the relative intensity of the amorphous peak in comparison
 12 with the crystalline peaks of the WAXD scan. The crystallinity index dropped to $47 \pm 3\%$
 13 when aged in MEG and $32 \pm 6\%$ when aged in TEG. This increase in the amorphous nature
 14 of the “wet” membrane arises from the polymer relaxation described above. The greater
 15 decrease in crystallinity caused by TEG is also consistent with the stronger affinity of TEG to
 16 CTA than MEG (**Table 2**).



1



2

3 **Figure 5** Wide angle X-Ray Diffraction (WAXD) results for CTA membranes when (a)
 4 saturated with glycols; and (b) after washing with methanol; in comparison with a fresh CTA
 5 membrane.

6

7

1 After removal of the glycols by methanol, the relative intensity of the amorphous peak
 2 reduced again and the crystallinity index recovered to $53 \pm 1\%$ and $50 \pm 3\%$ for membranes
 3 aged in MEG and TEG, respectively. Again, the lower crystallinity of “dry” membranes in
 4 comparison with fresh CTA confirmed the partial recovery of the polymer as concluded in
 5 section 3.2.2.

6

7 3.3. Permeation of hydrogen sulphide on CTA membrane

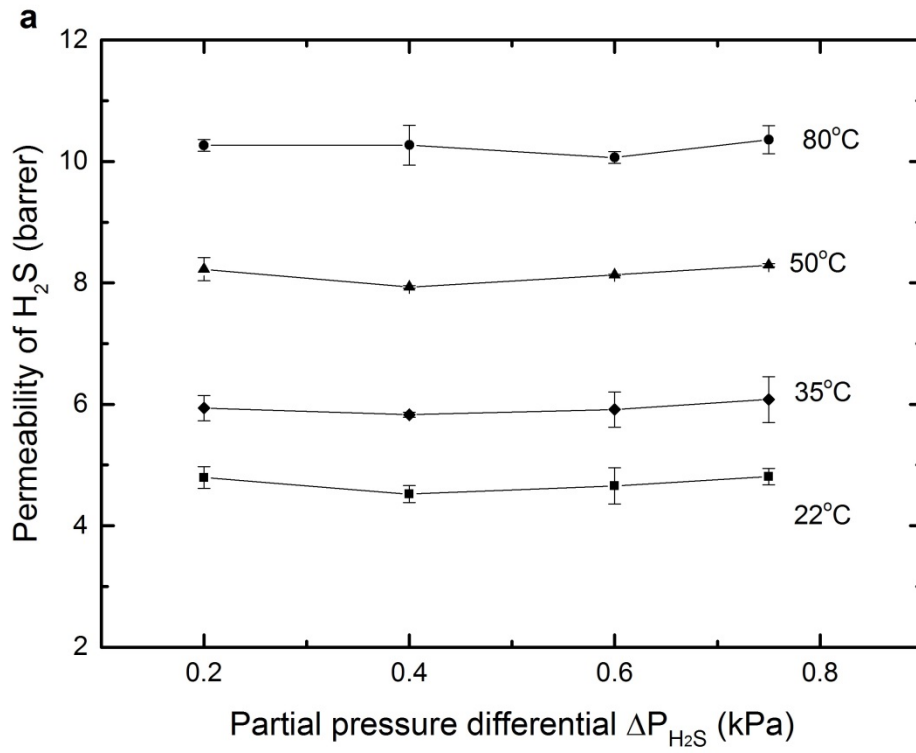
8 The permeability of H₂S and N₂ through the CTA membranes was studied at different feed
 9 pressures (**Figure 6**). For the temperature range 22 – 80°C, the permeability of H₂S was
 10 independent of the feed gas pressure within the error margins, and was between 4.7 and 10.2
 11 Barrer, rising with temperature. The H₂S permeability coefficient measured in this
 12 investigation is higher than reported in the literature (summarised in **Table 6**). The deviation
 13 may due to the difference in degree of acetyl substitution (DS). A lower degree of acetyl
 14 substitution results in less free volume within the membrane matrix and thus a lower
 15 diffusivity [51]. However, it also probably reflects the lower H₂S partial pressures applied in
 16 this study. At these lower partial pressures the Langmuir component of the sorption isotherm
 17 is more dominant, resulting in higher solubility [36, 52]. There was no evidence of H₂S
 18 plasticization of the CTA membrane, as indicated in **Figure 6a**. To the best knowledge of the
 19 authors, only one study has observed plasticisation of CTA by H₂S, and this was at a much
 20 higher partial pressure of 69 kPa [18, 53, 54].

21

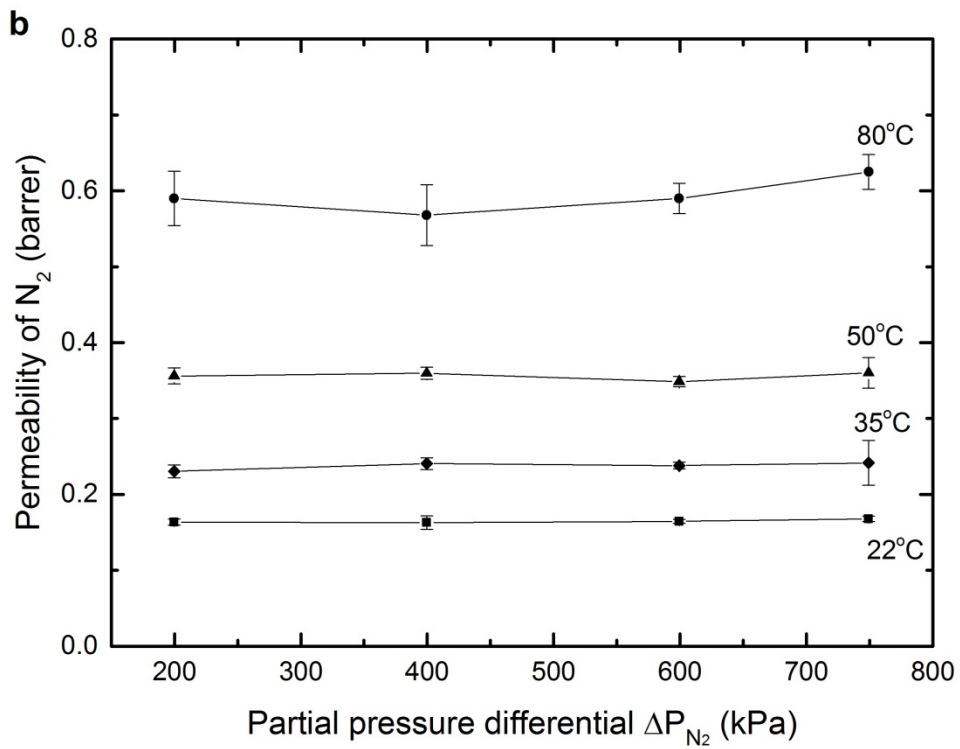
22 **Table 6** The permeability of hydrogen sulphide in cellulose acetate membranes

Polymer	Feed gas conditions	Partial pressure (kPa)	Temperature (°C)	P _{H₂S} (Barrer)	Reference
CTA (DS 2.9)	1000 ppm H ₂ S in balance N ₂	0.1 – 0.8	22	4.7 ± 0.2	This study
			35	5.9 ± 0.1	
			50	8.1 ± 0.1	
			80	10.2 ± 0.1	
CA film (DS not stated)	H ₂ S 99.9% purity	23 – 94	94	1.3	[19]
			94	2.0	
			30	3.3 ± 0.2	
			98	4.5	
			93	6.1	
Cellulose diacetate (DS 2.45)	H ₂ S/CO ₂ /CH ₄ (6/29/65)	60	35	2.1	[66]
Asymmetric CA (DS not stated)	H ₂ S/CO ₂ /CH ₄	68.9	25	4.17	[16]

23



1



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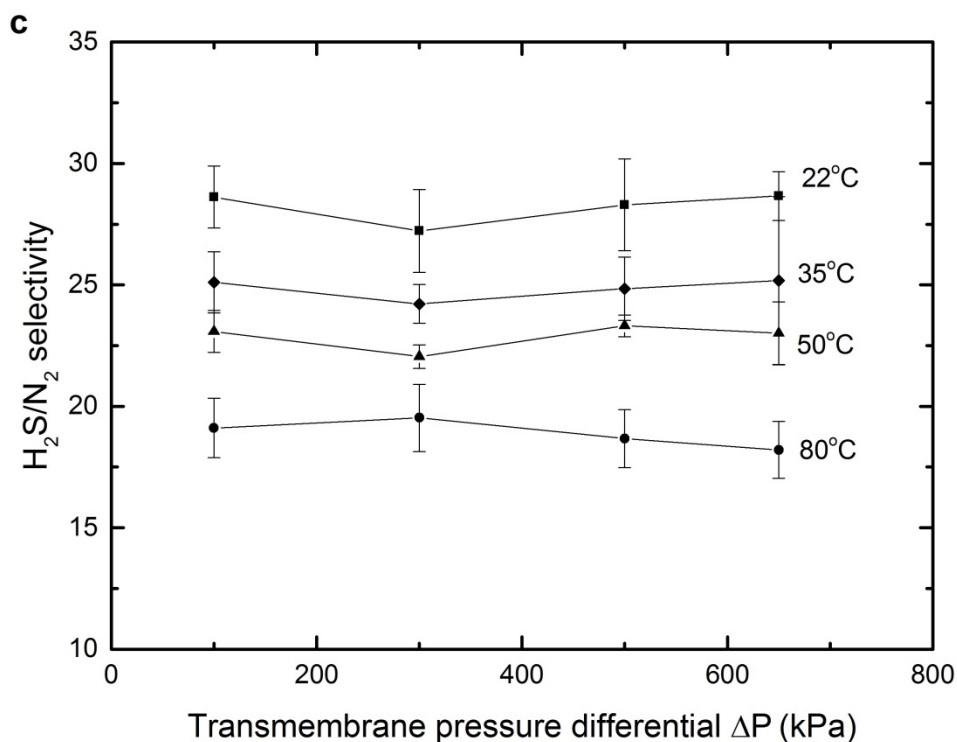


Figure 6 Gas permeability in CTA membranes with a feed gas of 1000ppm H₂S in balance N₂ (a) permeability of H₂S; (b) permeability of N₂; (c) H₂S/N₂ gas selectivity.

The permeability of nitrogen was also independent of feed pressure, indicative of standard behaviour for this inert gas (**Figure 6b**). The H₂S/N₂ gas selectivity (**Figure 6c**) showed the favourable permeation of H₂S in the membrane over N₂. Similar phenomena has been observed when introducing H₂S – N₂ gases through other glassy polymers, such as polysulfone and cyclic perfluoroether [55]. This is due to the higher critical temperature of H₂S which results in greater solubility.

The permeability coefficients of H₂S and N₂ at a zero partial pressure differential ($\Delta p_i \rightarrow 0$ kPa) were extrapolated from the data presented in **Figure 6**. This enables the activation energy for permeation (E_p) to be determined (**Table 7**). The positive values of E_p for all gas species in this investigation suggest that diffusivity is dominant over solubility [56]. Furthermore, the activation energy is higher for the gas species with lower critical temperature (lower gas sorption), again reflecting a lower heat of sorption [57, 58].

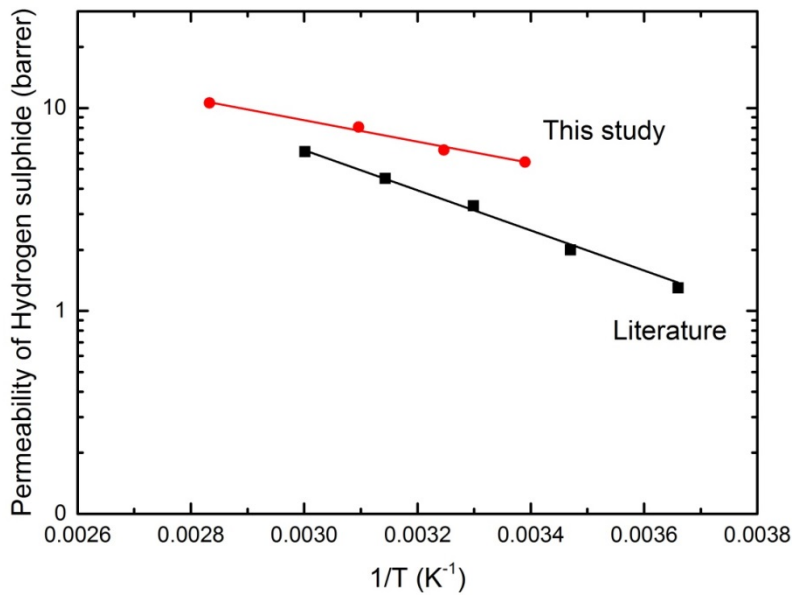
Table 7 Activation energy for permeation in CTA membrane at zero pressure

	CH ₄ *	N ₂	CO ₂ *	H ₂ S	SO ₂ *
Kinetic diameter (Å) [67]	3.80	3.64	3.30**	3.60	3.60
Critical temperature (K) [68]	190.6	126.2	304.2	373.2	430.8
Activation energy for permeation, E_p (kJ/mol)	18.6 ± 0.2	18.7 ± 2	8.5 ± 0.7	10.1 ± 0.7	7.3 ± 0.7

* The permeability of methane and carbon dioxide were reported in a previous study [21]

** Some recent studies argue that the kinetic diameter of CO₂ relevant to diffusion could be larger at 3.43 – 3.63 Å [40, 69, 70]

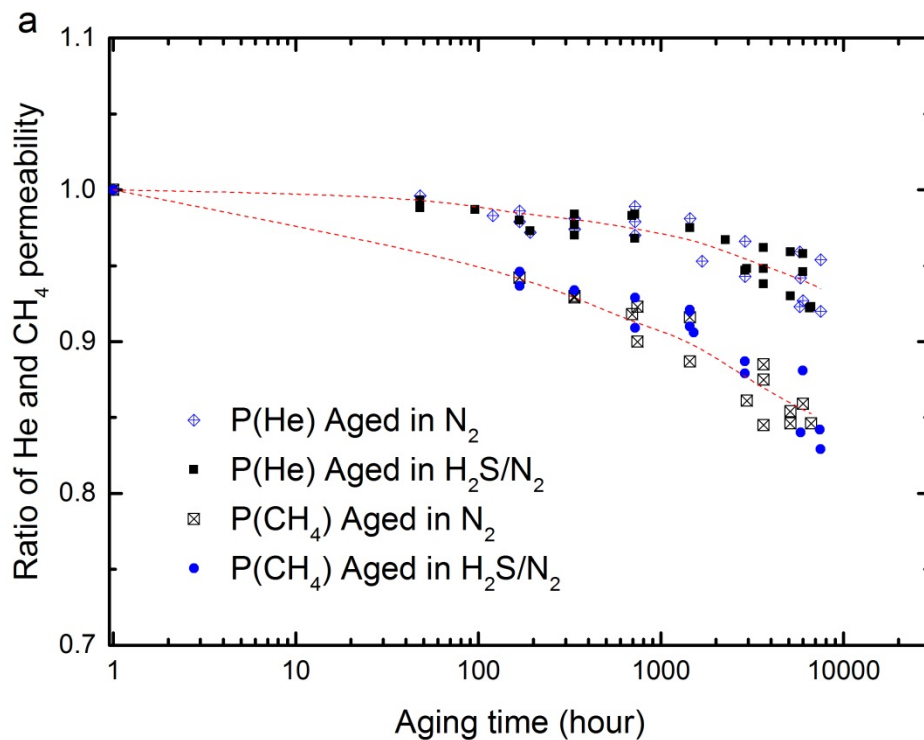
1 Heilman et al. reported an activation energy for H₂S permeation of 19 kJ/mol [19] when
2 operating with a feed pressure of 94 kPa in comparison with 10.1 kJ/mol calculated in this
3 study (**Figure 7**). Again, the deviation may be due to differences in both degree of acetylation
4 and operating pressures.



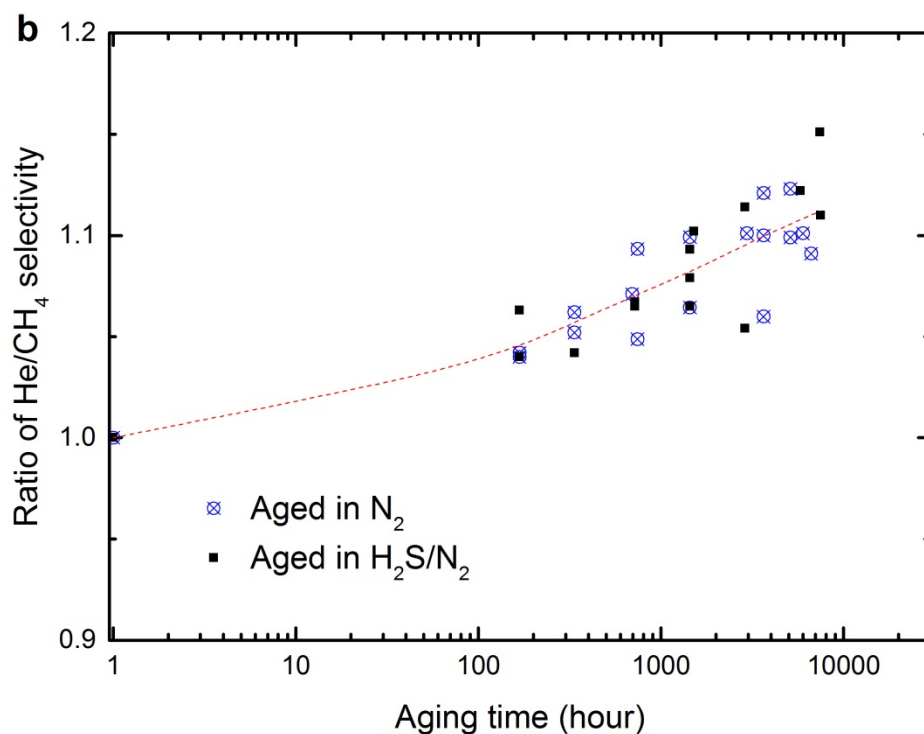
5
6 **Figure 7** The permeability coefficients of H₂S as a function of temperature at zero partial
7 pressure differential (this study) and 94 kPa (Heilman et al.[19])

8
9 *3.4. Long-term aging of CTA membrane in H₂S*

10 The long-term impact of H₂S on CTA membranes was studied by aging the membranes
11 separately in 1000 ppm H₂S in balance N₂ and in pure N₂. After a specified aging period up
12 to 7200 hours, the membranes were tested for the permeation of pure He and CH₄ at 35°C and
13 750 kPa absolute feed pressure. To reduce the variability between membrane samples, the
14 change of permeability and selectivity of the aged membranes as time progresses is expressed
15 as the ratio of permeability and He/CH₄ selectivity of the aged membranes to the original
16 fresh membrane (**Figure 8**).



1



2

3 **Figure 8** Change in (a) permeability of He and CH₄ and (b) He/CH₄ selectivity as time
 4 progresses for CTA membranes at 35°C, 750 kPa after aging separately in 1000 ppm H₂S in
 5 balance N₂ and pure N₂ at 750 kPa and 22 ± 2°C. The permeability of He and CH₄ in a fresh
 6 CTA membrane was 21.6 ± 0.2 barrer and 0.265 ± 0.009 barrer, respectively, giving an
 7 He/CH₄ gas selectivity at 81 ± 3. The dashed lines are added to guide the eye.

1 Gas permeability generally falls with time due to the densification of membrane matrix as
2 observed in **Figure 8a** and in other studies [21, 56, 59, 60]. As observed in section 3.2.2, the
3 changes in free volume impact most the penetrant of larger kinetic diameter (CH₄) [21, 56,
4 59]. Consequently, the He/CH₄ selectivity is enhanced during aging as indicated in **Figure**
5 **8b**.

6 **Figure 8** showed that the aging process of CTA membranes was not affected by the presence
7 of 0.75 kPa partial pressure of H₂S. This is consistent with the H₂S permeability result in
8 **Figure 6**, where no plasticisation is observed for these partial pressures of H₂S on the CTA
9 membranes at the same pressure and temperature. The partial pressure of H₂S in a natural gas
10 sweetening process is typically 0.02 – 3 kPa (assuming 30 bar operating pressure) [15], which
11 is much lower than the plasticisation pressure for H₂S, observed to be up to 69 kPa in the
12 presence of CO₂ [18, 54]. This result is confirmed by the present work.

14 **4. Conclusions**

15 The impact of glycols on dense CTA membranes has been studied for up to 2000 hours. The
16 absorption of ethylene glycol and triethylene glycol into the CTA membrane enhanced the
17 permeation of CH₄ and CO₂ through the wet membranes but resulted in a gradual decline in
18 the permeation of He. This reflected relaxation of the polymer structure. In particular,
19 WAXD analysis confirmed that a significant loss of crystallinity occurred during exposure to
20 these glycols, providing more accessible free volume in the structure. Methane and CO₂ were
21 able to move through the glycol-rich regions within the swollen membrane, whereas these
22 regions blocked the movement of He. It should be noted that the changes in free volume
23 observed here, while similar in magnitude, are expected to occur much faster in the thinner
24 active layers (<1 micron) used in industrial membrane systems [59, 61].

25 Importantly, the use of a methanol wash was able to reverse these effects, with only small
26 residual swelling observed after removal of the glycol. The use of such a methanol wash may
27 be an important mitigation strategy when glycol overflow into the membrane unit occurs in
28 industrial practice. However, it would require careful application to prevent a collapse of the
29 structure of the porous support layer of the membrane during methanol removal due to
30 surface tension effects.

31 This study has also shown that cellulose triacetate membranes are stable upon exposure to
32 0.75 kPa H₂S for up to 7200 hours. No plasticisation was observed after aging the membranes
33 at 0.75 kPa H₂S and 22°C for 7200 hours. However, it should be noted that in many
34 applications of CTA in natural gas sweetening, the H₂S partial pressures are considerably
35 higher than studied here and the onset of plasticisation cannot be discounted in such
36 scenarios.

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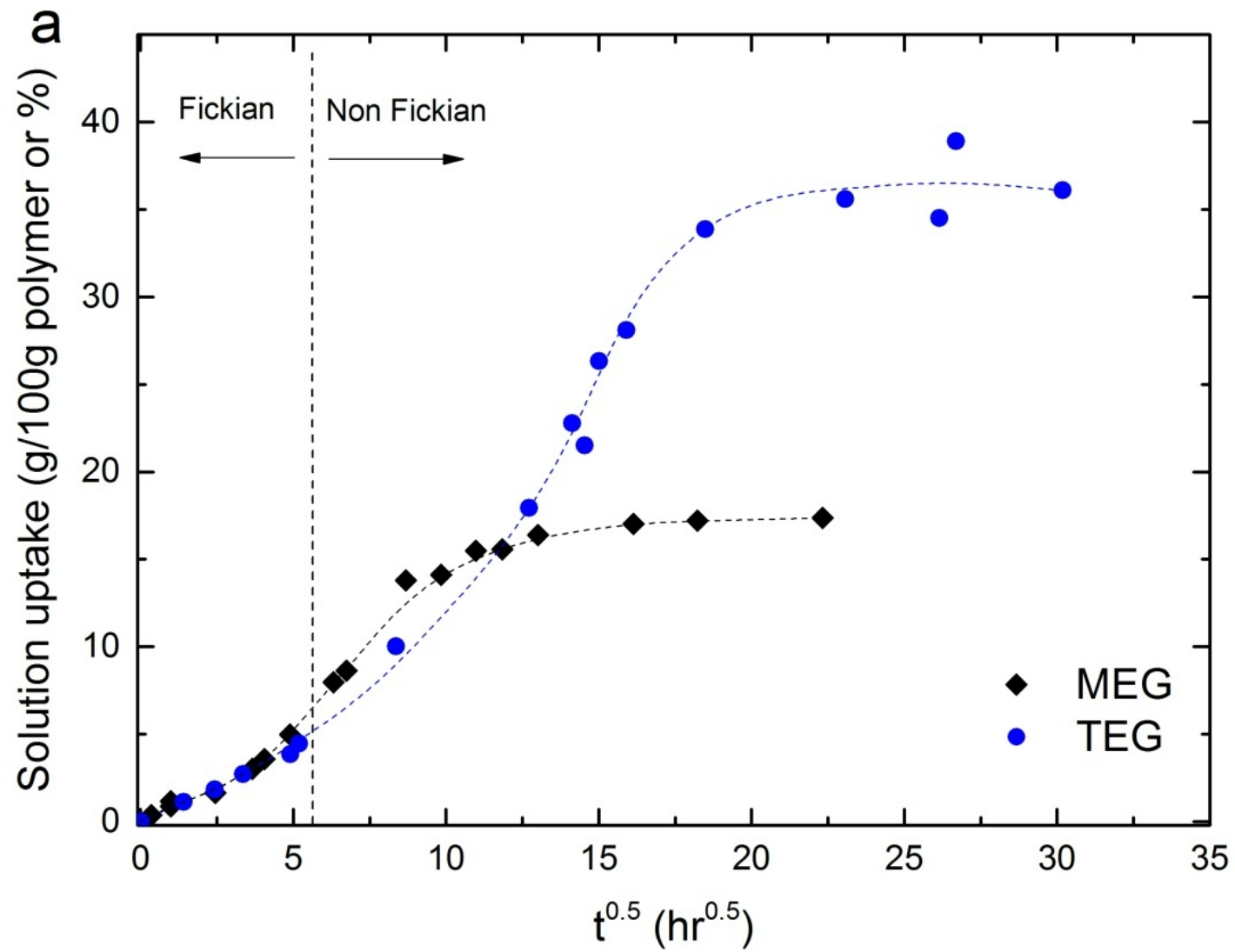
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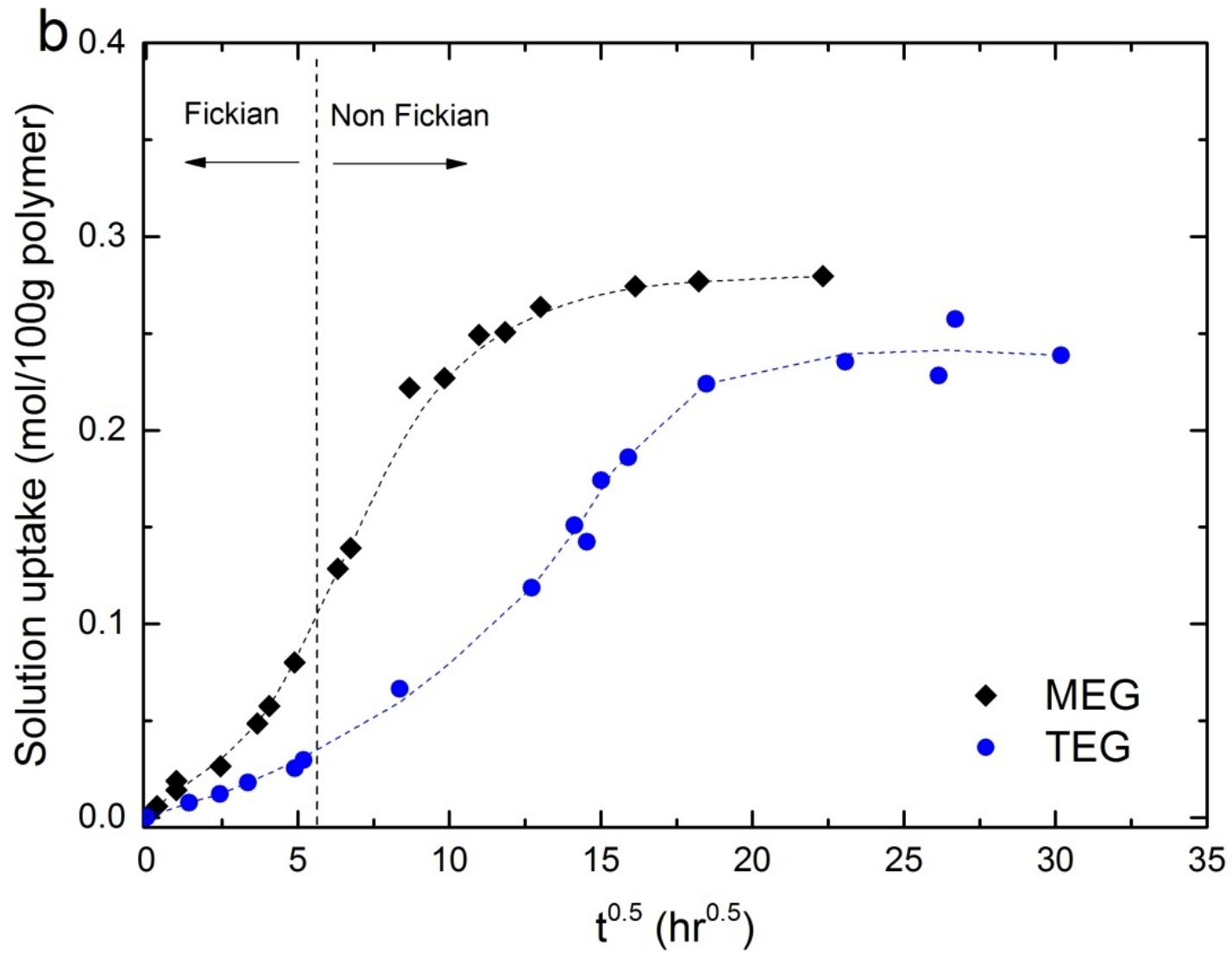
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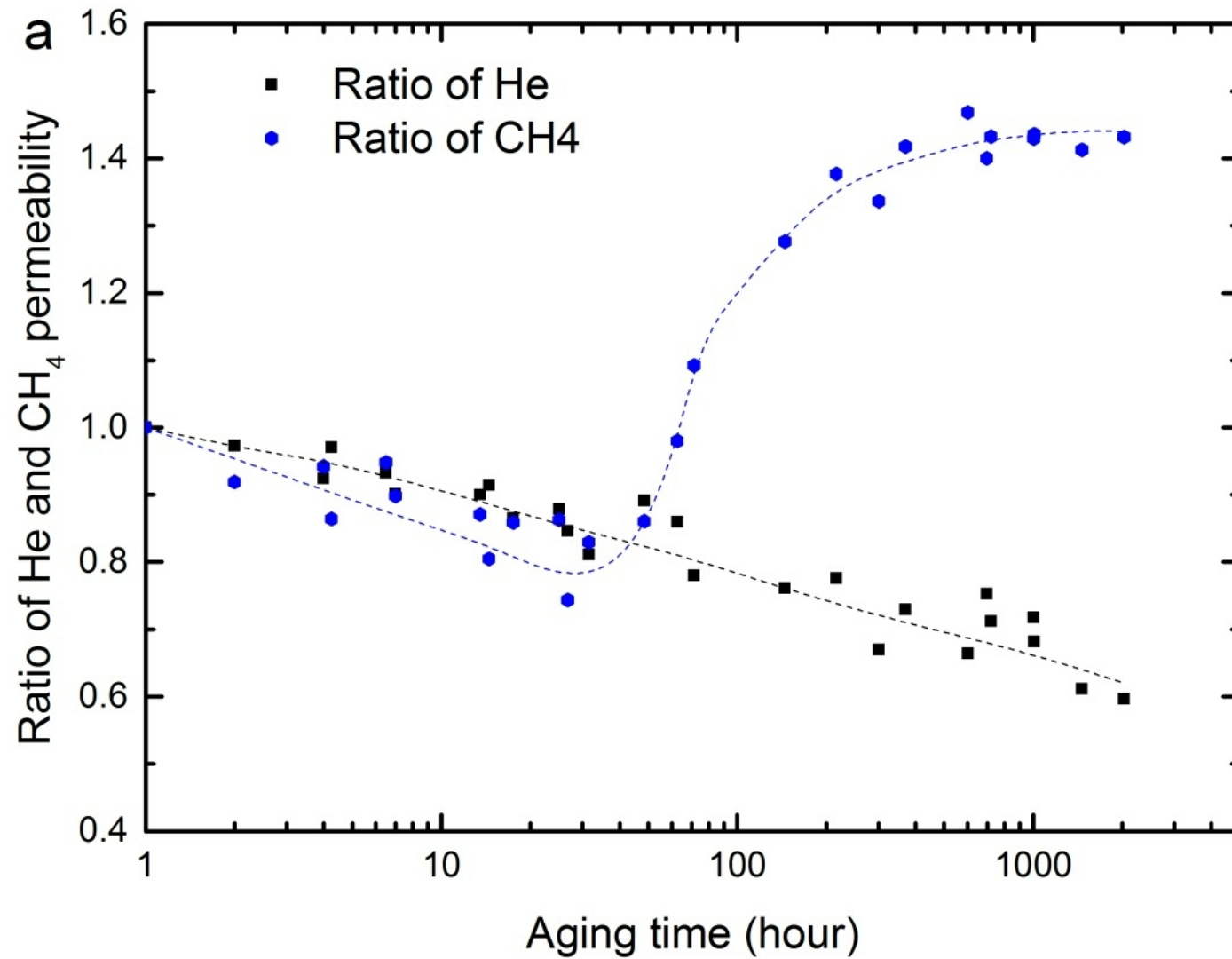
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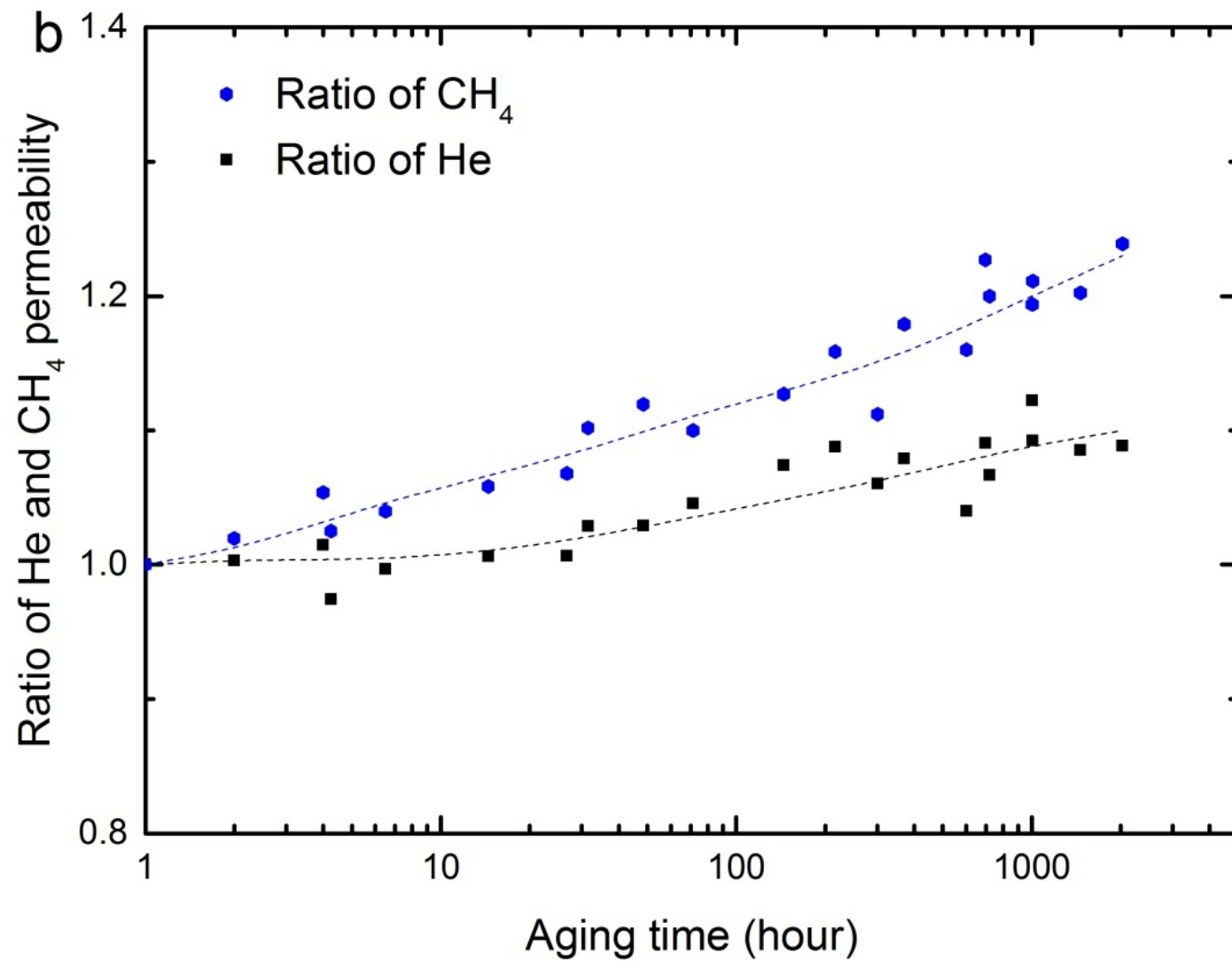
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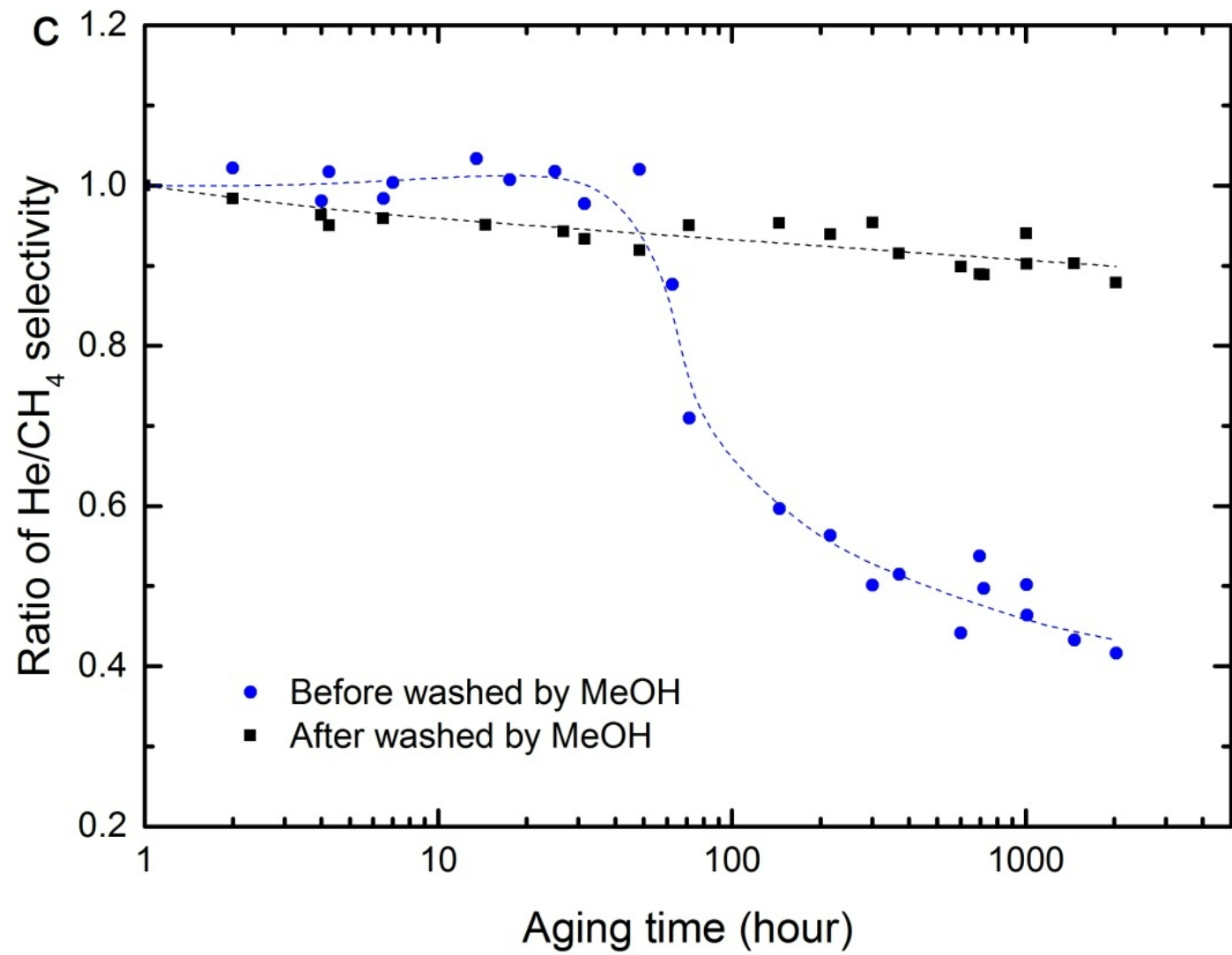
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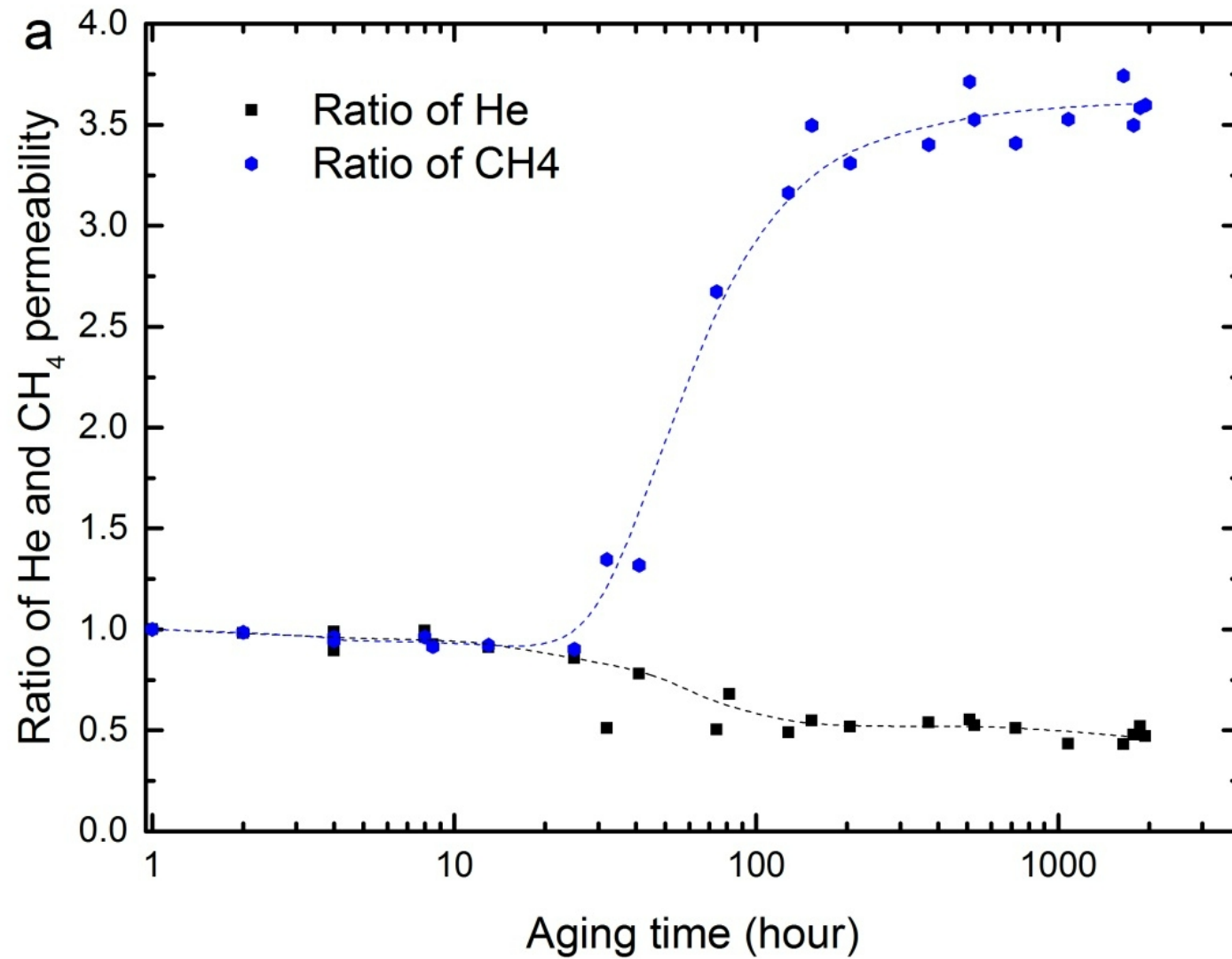


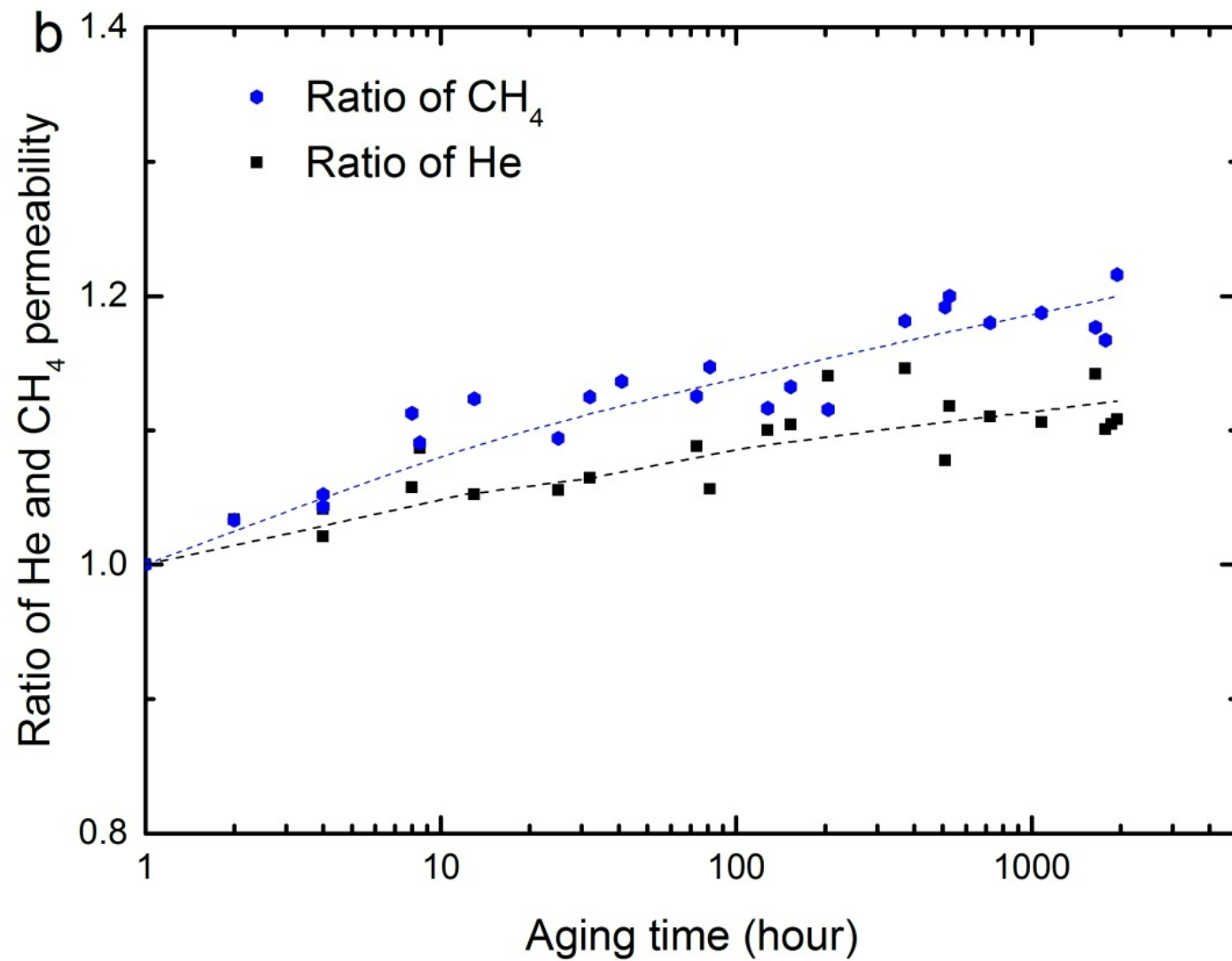


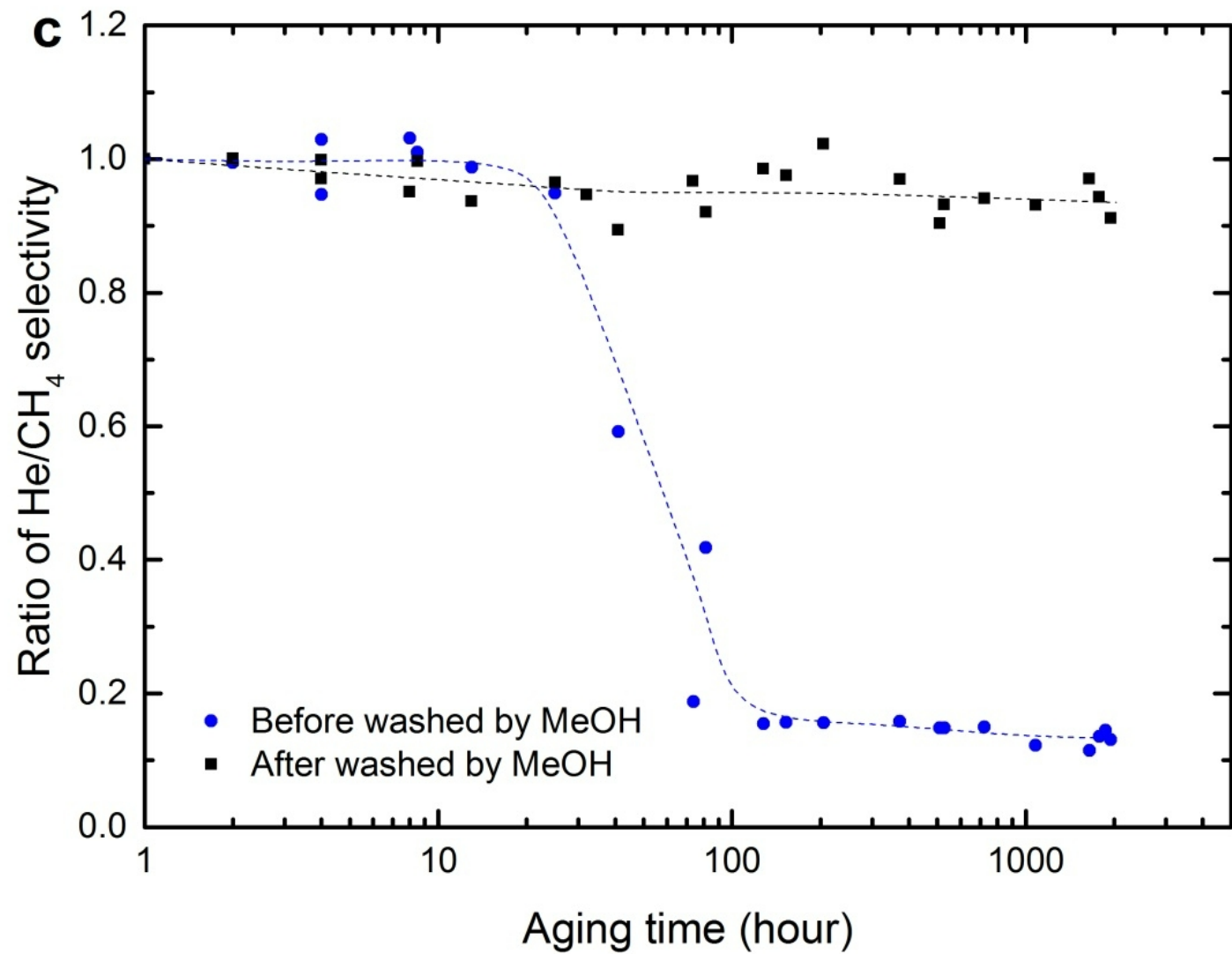


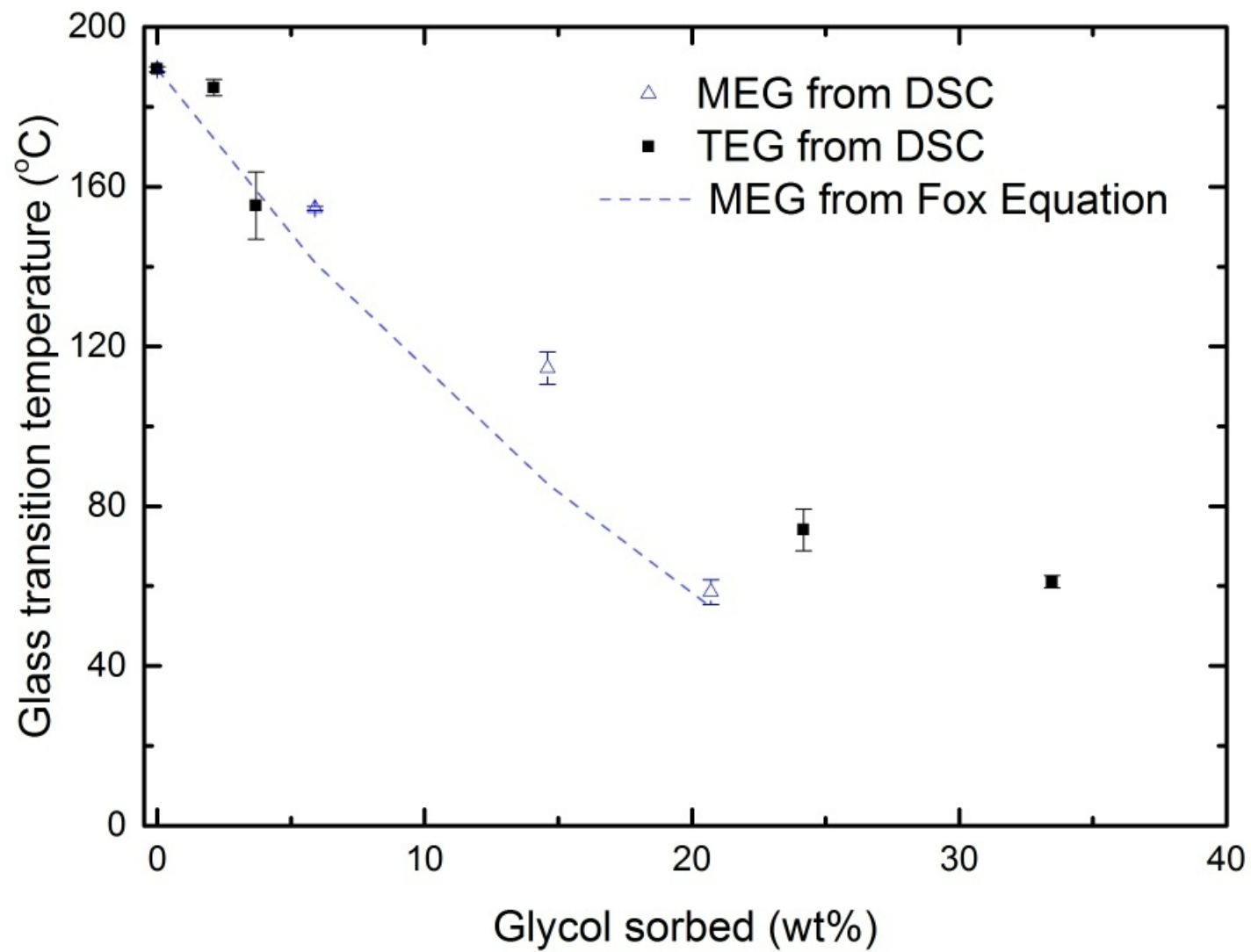


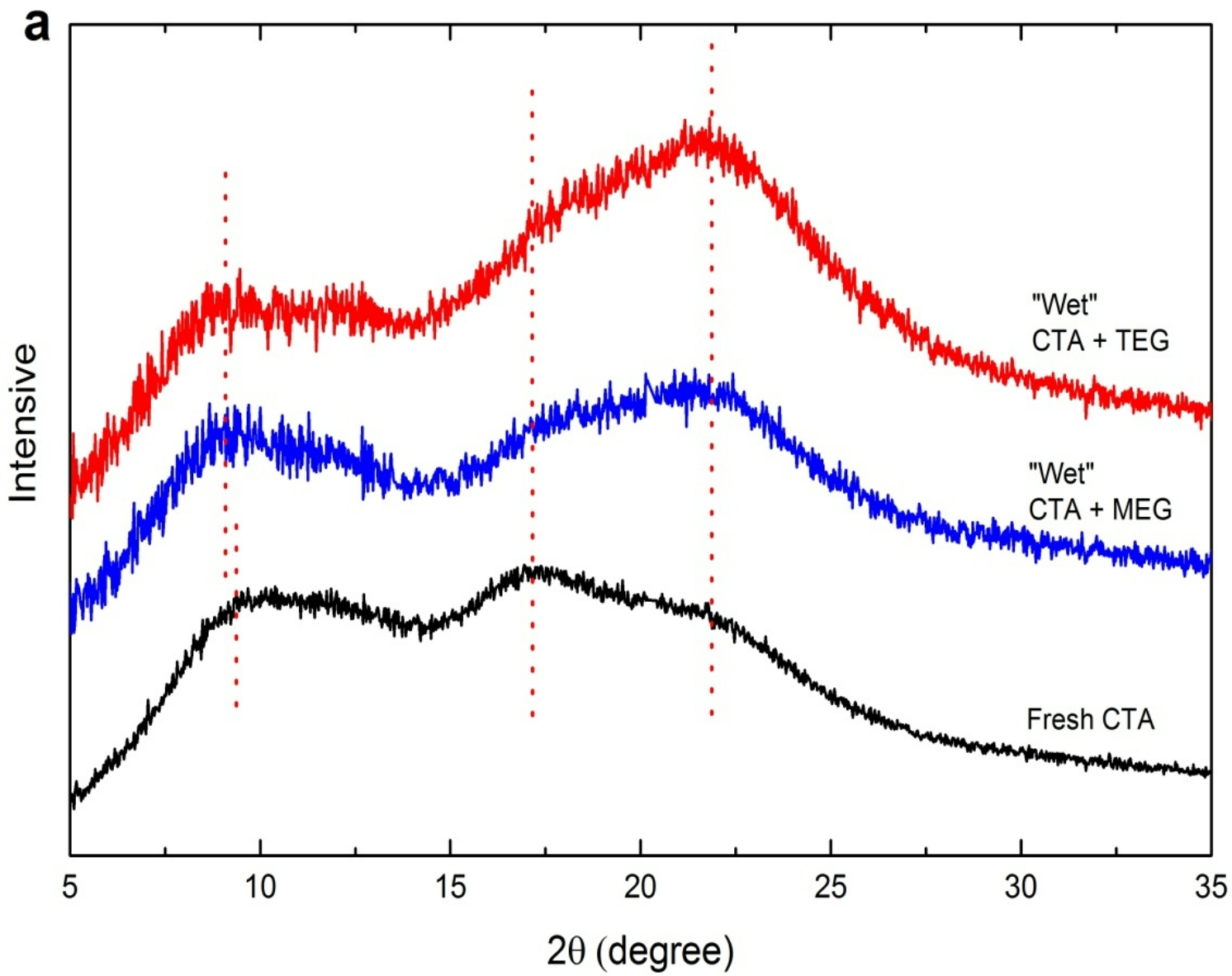


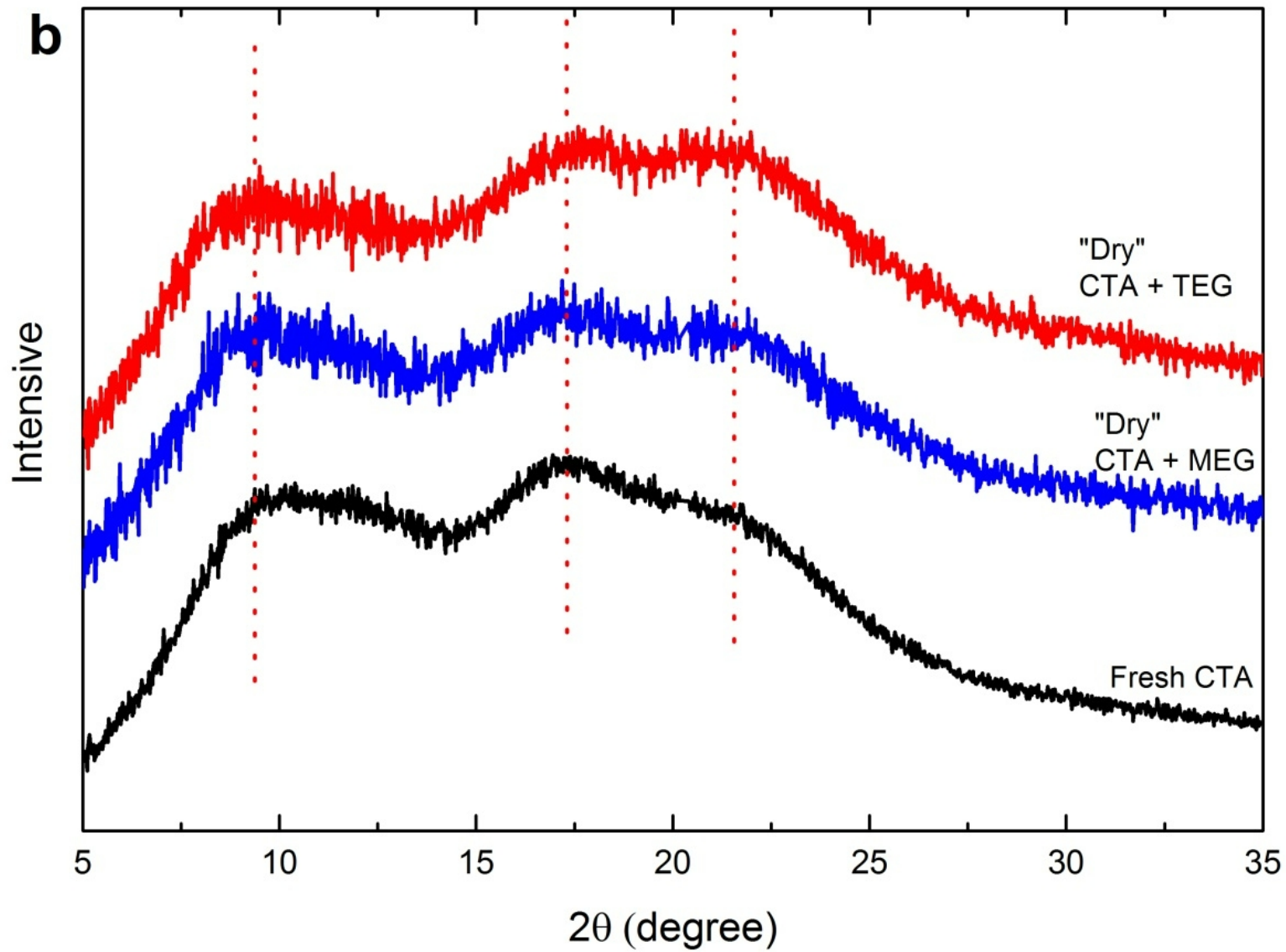


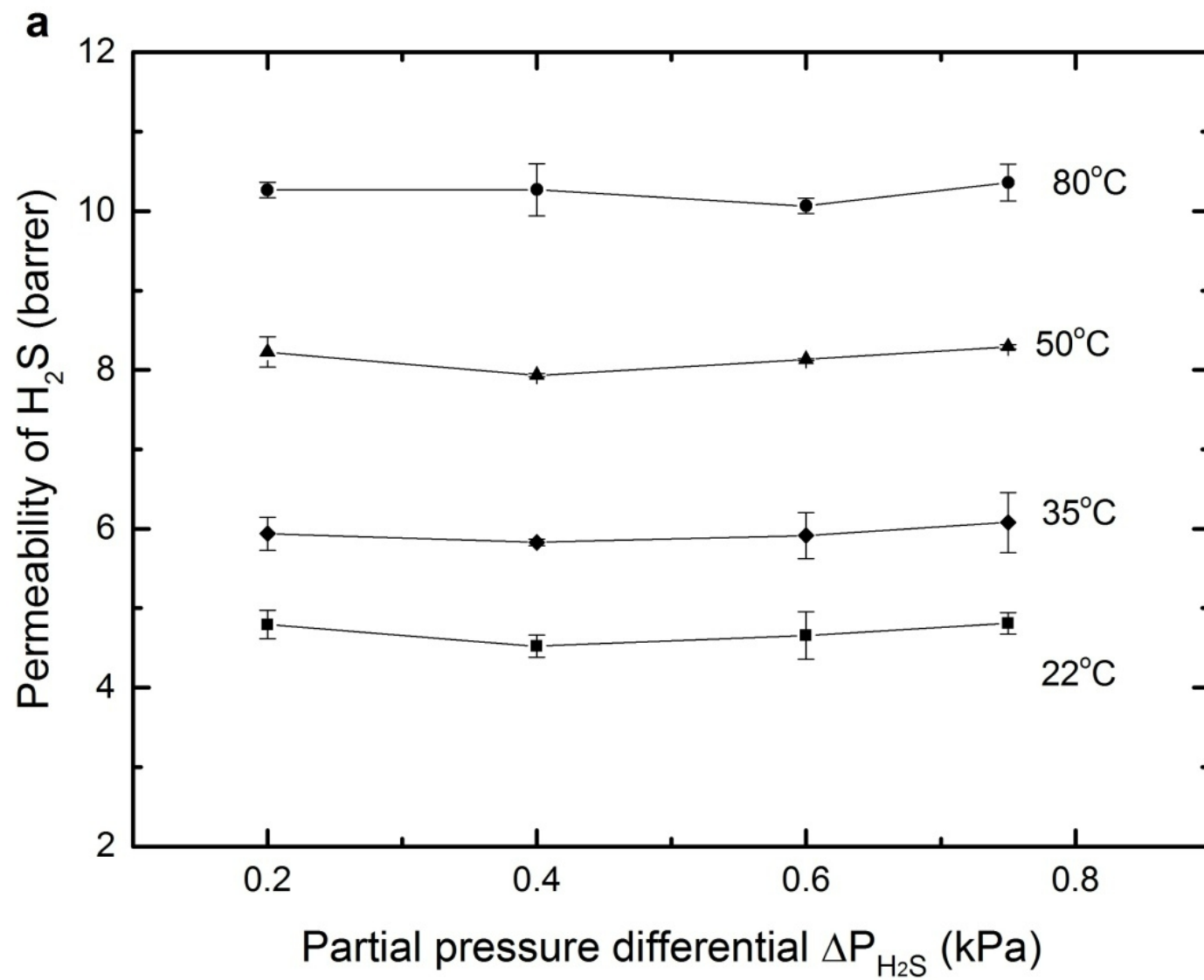


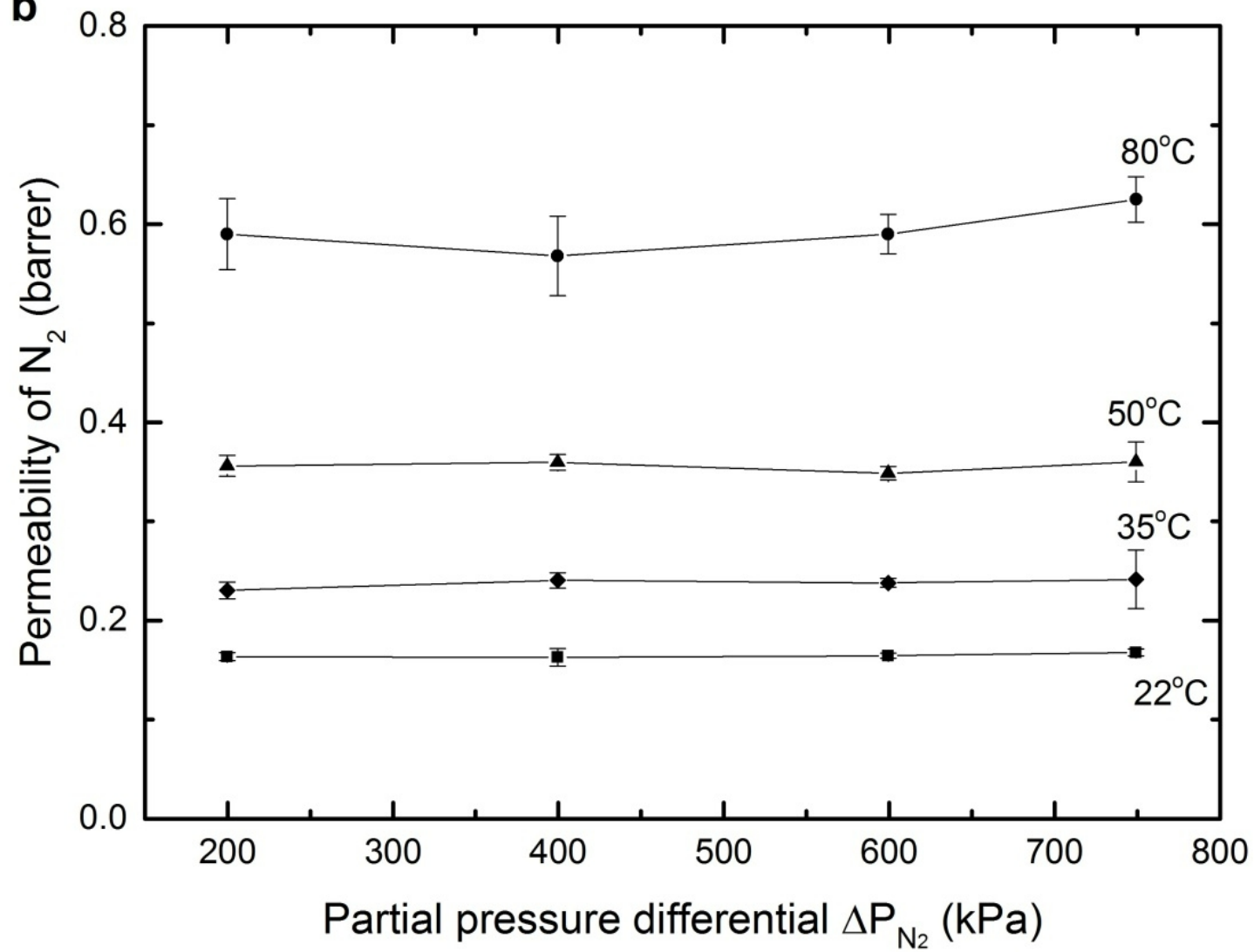




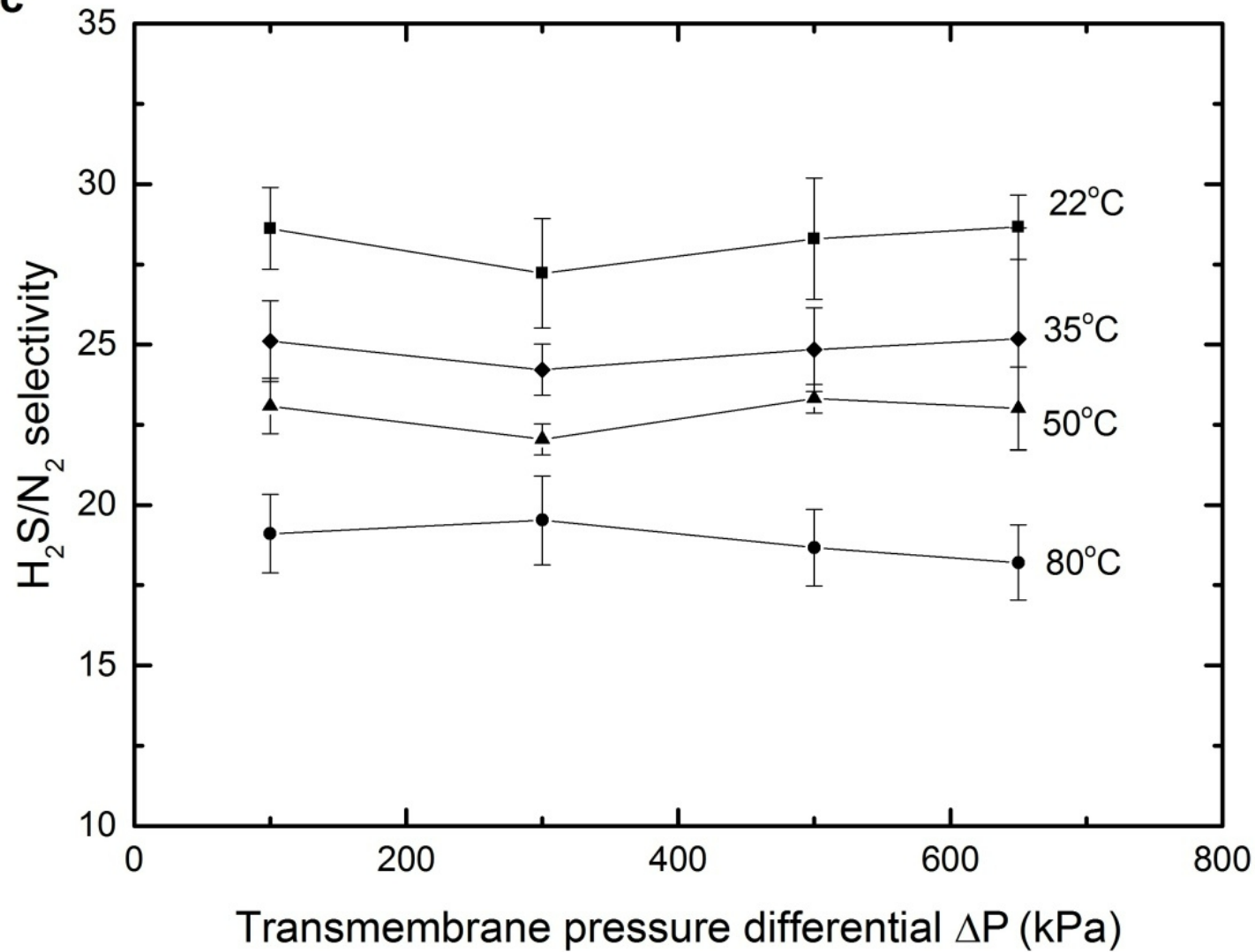


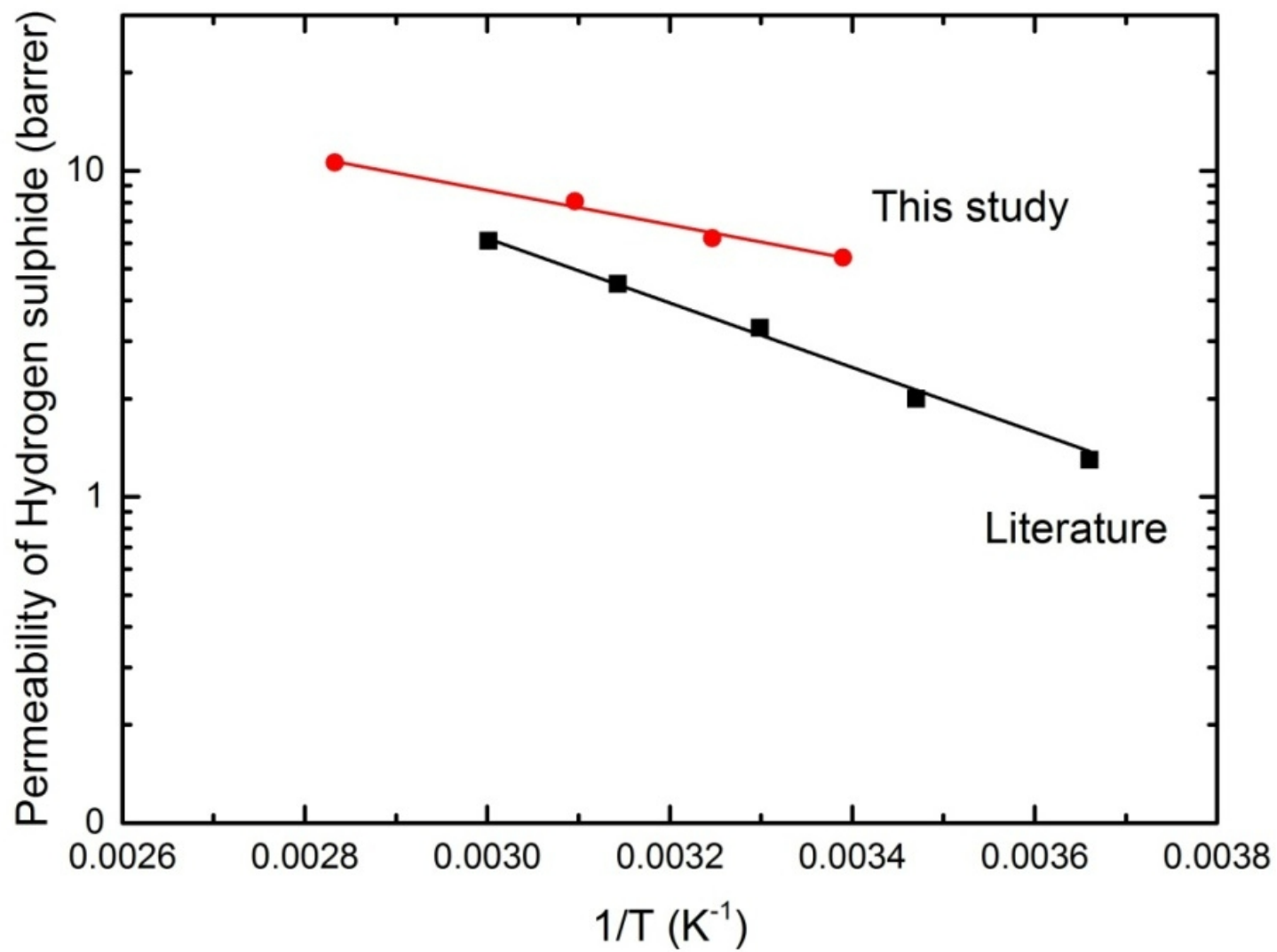


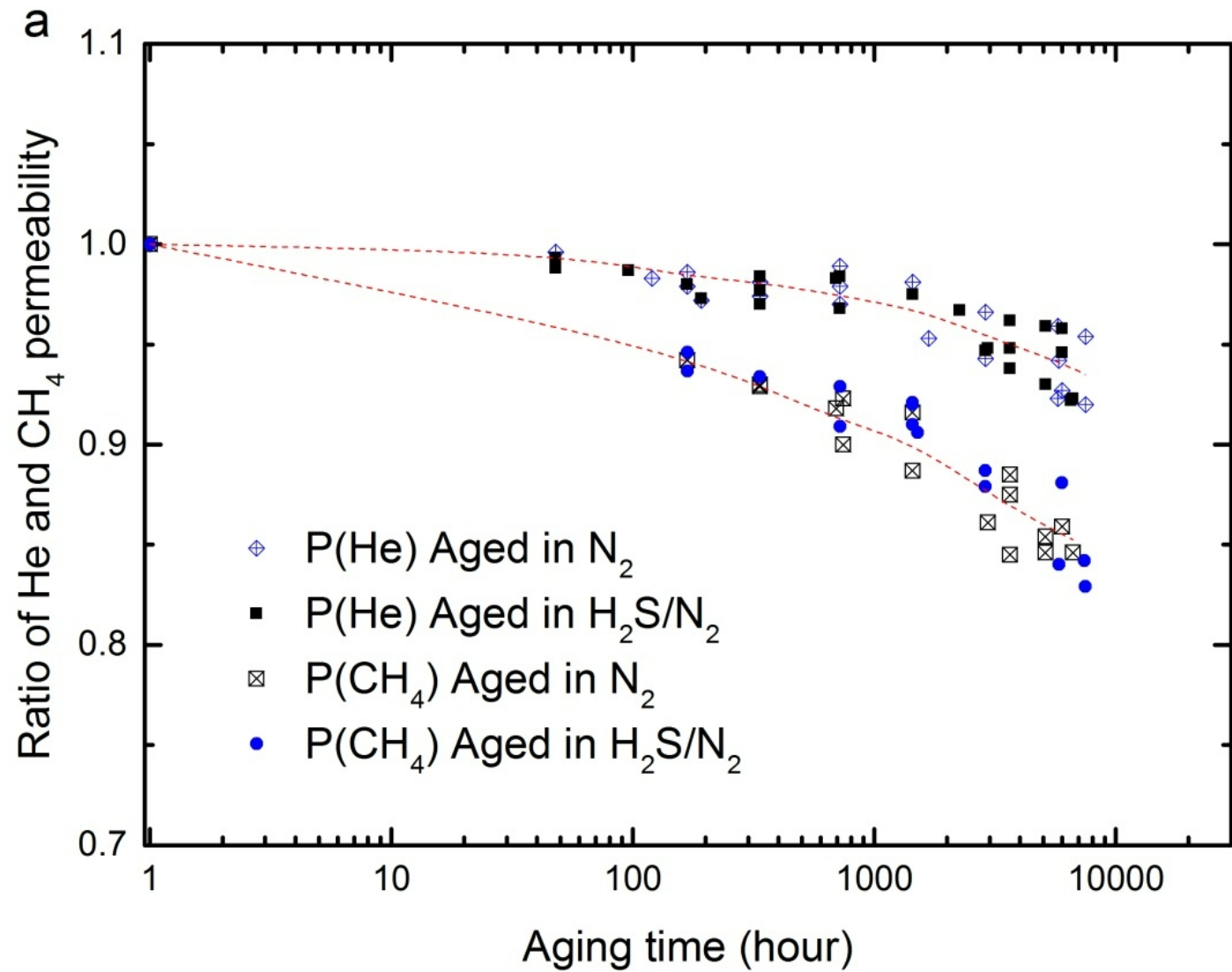


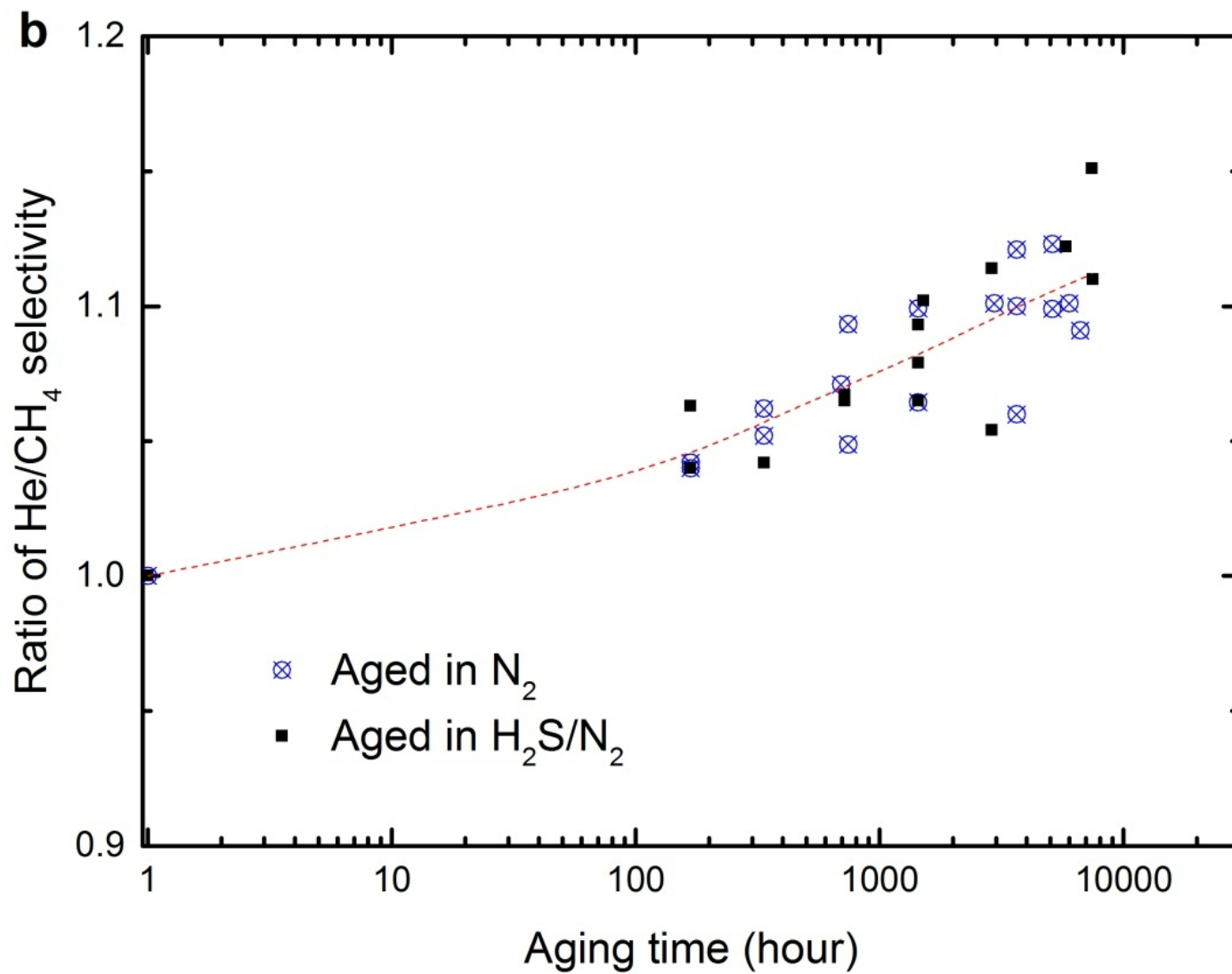
b

c









The impact of ethylene glycol and hydrogen sulfide on the performance of cellulose triacetate membranes in natural gas sweetening

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SUPPLEMENTARY INFORMATION

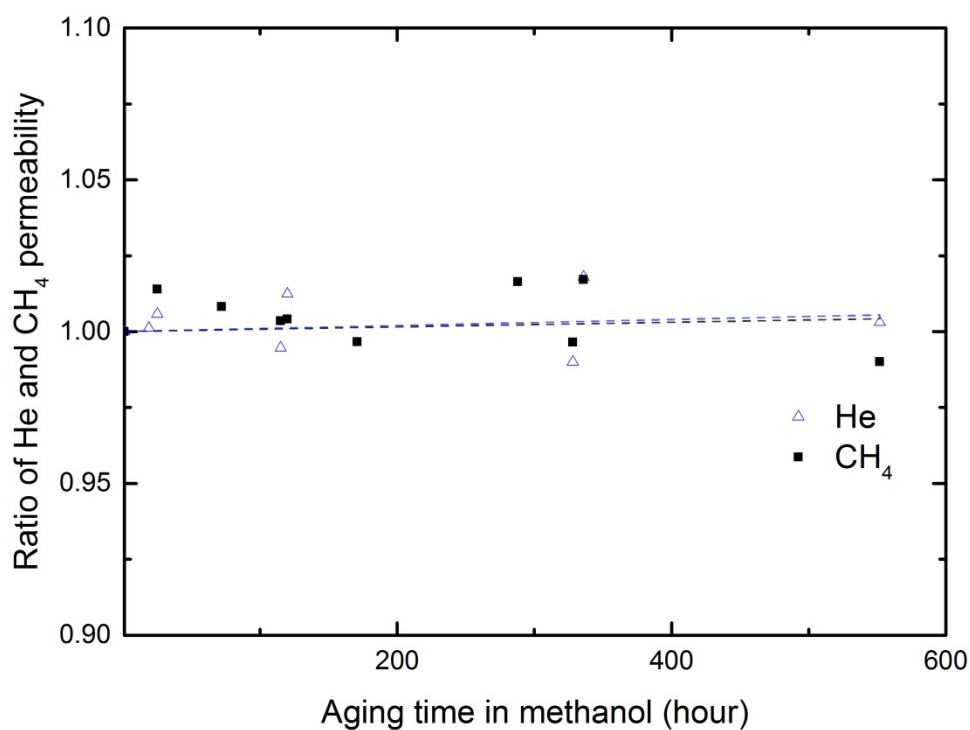


Figure S1

Change in permeability of He and CH₄ as time progresses for CTA membranes at 35°C, 750 kPa feeding pressure after aging in methanol solution

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