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Water vapor permeation through cellulose acetate membranes and its impact upon membrane separation performance for natural gas purification

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ABSTRACT

Cellulose acetate is the predominant material used in membrane separation of acid gases from natural gas and biogas. However, the sensitivity of these membranes to water vapor is not well understood. In this work, flat-sheet membranes of two different degrees of acetylation, were exposed to both dry and humidified CH_4 and CO_2/CH_4 mixtures. Positron Annihilation Lifetime Spectroscopy experiments showed that the number of free volume elements decreased as water concentration increased, indicating pore filling effects. The size of the free volume elements declined initially, followed by an increasing trend at vapor partial pressures greater than 2.5 kPa, indicating polymer swelling. Gas permeabilities of CH_4 and CO_2 followed a similar trend, with an initial decline due to hindered diffusion and competitive sorption, followed by an increase as the humidity exceeded 2.5 kPa. Water vapor permeabilities increased from 11,000 to 27,000 Barrer as the water activity increased but a change in the rate of increase was also noted at 2.5 kPa. At humidities in excess of 0.8, the extent of membrane swelling was such that equilibrium was not established even after 8 h of operation. Importantly, plasticization had significantly less impact on the polymer with a higher degree of acetylation.

1. Introduction

Natural gas production is estimated to be over 3300 billion cubic meters per year worldwide [1] and the removal of acid gases from the raw gas is the largest industrial market for membrane gas separation. While the composition of raw natural gas is different from reservoir to reservoir, it primarily consists of methane (70–90%), with small amounts of C_1–C_4 hydrocarbons such as ethane, propane, butane, along with higher molecular weight fractions. Water vapor, carbon dioxide, acidic gases, mercury, hydrogen sulfide, helium and nitrogen are also present in raw natural gas as impurities. A glycol dehydration unit is typically used for removing water from the natural gas feed streams prior to membrane processing [2]. However, some water vapor may still reach the membrane if the glycol unit is not working effectively. Further, glycol units are not always used in smaller installations such as biogas processing.

Cellulose acetate was the original membrane material used for CO_2 separation from natural gas, building on the experience gained using this material for the desalination of saline water. Cynara® (part of Cameron) and UOP Separex® (part of Honeywell) are the two major membrane manufacturers currently supplying cellulose acetate based modules. Depending on the degree of acetylation, which corresponds to the extent of substitution of the hydroxyl groups in the glucoside repeating unit with acetyl groups (Fig. 1), the polymer is named as cellulose acetate, cellulose diacetate or cellulose triacetate.

Dehydration units (mostly diethylene or triethylene glycol dehydrators) are widely used upstream of the membrane unit to prevent hydrate formation [3], typically reducing the water content to ~100 ppm at around 70 bar, 60 °C [2]. It has previously been reported that the presence of water and some hydrocarbon derivatives (e.g. acetone) can damage and dissolve the membrane [4], but the sensitivity of the separation performance of cellulose acetate membranes to water vapor is not well understood. Almost all studies on the effects of water vapor on cellulose acetate membranes were conducted in the 1980 s [4–8]. The permeation measurements in this period often assumed ideal mixing of water vapor and gas and neglected the impact of concentration polarization upon the permeation properties.

Due to its small size and high hydrogen bonding affinity [9–11], water vapor can have a very significant effect upon membrane

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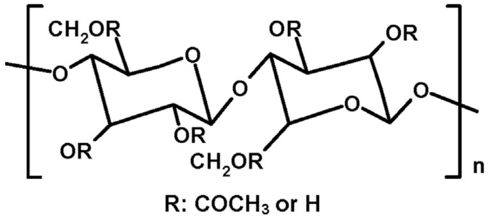

Fig. 1. Chemical structure of cellulose acetate.

performance [6,12–14]. It is argued that the clustering of water into multimolecular groups can act to 'fill' the free volume within the polymer structure, resulting in a loss of fractional free volume [15,16]. It has been reported that these water clusters result in a decrease in the penetrant diffusivity as water vapor activity increases in a phenomenon referred to as 'antiplasticization' [17–23]. Conversely, water molecules can plasticize or swell the membrane structure, causing an increase in free volume and a corresponding increase in diffusivity with increasing vapor concentration [24–27]. Depending on the hydrophobicity of the membrane and the activity of water vapor, these phenomena may coexist in a multi-component separation system, in both cases causing a loss of selectivity.

In this work., the mixed vapor/gas permeation system developed within our group to eliminate concentration polarization effects [14] combined with Positron Annihilation Lifetime Spectroscopy (PALS) [28] is applied to quantify the permeation of water/CO_2 mixtures through cellulose acetate membranes more accurately, allowing for a better understanding of the behavior of water vapor in a simulated natural gas sweetening environment. Two types of cellulose acetate with different degree of acetylation are investigated during exposure to humidified methane and wetted carbon dioxide and methane mixtures.

2. Experimental

2.1. Materials

Cellulose acetate with acetylation degrees of 51.6% (CDA) and 61.6% (CTA) (equivalent to degrees of substitution of 2.2 and 2.85, respectively) were kindly supplied by Daicel Corporation, Japan, in a powder state. The chemical structure of a typical cellulose acetate is presented in Fig. 1. Prior to membrane fabrication, the polymers were dried at 100 °C under vacuum overnight to ensure the complete removal of moisture.

2.2. Membrane preparation

Dense cellulose acetate membranes were prepared by a casting method using dichloromethane (DCM, Analytical reagent, Chem-Supply, Australia) for CTA and tetrahydrofuran (THF, Analytical reagent, Chem-Supply, Australia) for CDA. The casting solution (1 wt%) was filtered into glass petri dishes. The petri dishes were covered and left to dry at room temperature for 24 h. The homogeneous membranes were then removed from the petri dishes using a small amount of distilled water and dried under vacuum at 35 °C for 24 h, followed by 100 °C for 24 h to remove the residual solvent. The dried membranes were kept in a desiccator to prevent any subsequent absorption of atmospheric moisture. Membrane thicknesses for the dense flat sheet films were determined from the mean value of at least 40 locations across the film using a micrometer (Mitutoyo, Japan) and varied from 50 to 60 μm. Typically the thickness variation within a sample was less than 8 μm.

2.3. Characterization

The buoyancy technique is a standard displacement technique for measuring membrane densities and is adopted widely in the literature [29–31]. A well-dried membrane was weighed in air (w_{air}), then in hexane (AR, Chem-Supply, Australia) (w_{Hexane}) using an analytical balance (Mettler Toledo AB204-5). The density of the polymer membrane ($\rho_{polymer}$) was calculated using the hexane density (ρ_{Hexane}) via the following equation:

$$\rho_{polymer} = \left(\frac{w_{air}}{w_{air} - w_{Hexane}}\right)\rho_{Hexane} \tag{1}$$

The mass uptake of water was determined by immersing the membrane sample in pure water at 35 °C for at least 3 days, to ensure that water sorption equilibrium was attained. The water uptake was calculated from

$$\text{Water uptake} = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100 \tag{2}$$

where w_{wet} and w_{dry} are the weights of a water-swollen membrane at equilibrium state and dry state, respectively.

The dry and wetted membranes, prepared in the same way as for the water uptake experiment, were measured using Wide-angle X-ray diffraction (WAXD). The measurements were performed on a D8 Advance X-ray diffractometer (Bruker, Germany) at 5 s per step of 0.02°, using a Ni-filtered CuKα radiation source at 40 kV and 30 mA. The samples were analyzed over a range from 3° to 30°. The mean d-spacing, which represents the mean distance between polymer chains, was calculated by using Bragg's equation

$$\lambda = 2d \sin \theta \tag{3}$$

where λ is the wavelength of the radiation, 1.54 Å, and 2θ is the maximum intensity in a halo peak. The degree of crystallinity was determined based on the percentage of the crystalline area in the XRD profile using the deconvolution method [32].

The free volume distribution of the membrane samples over a range of vapor activities was determined using positron annihilation lifetime spectroscopy (PALS) at ambient temperature. Positrons are emitted from a radioactive isotope source (^{22}NaCl) and enter into the surrounding sample. The positrons are thermalised via inelastic collisions within the samples and are either annihilated as free positrons in the bulk of the membrane or became trapped in micro-pores or regions of lower than average electron density. A positron forming a bound state with an electron of opposite spin (para-positronium) has the shortest lifetime (τ_1, ~125 ps), whereas localization of the positrons in the bulk of the material (areas abundant in electrons) results in annihilation at around τ_2 ~300–500 ps. The third component (τ_3), ortho-positronium (positron and electron in a bound state of the same spin) will sit in electron deficient regions, such as pores or voids and will lead to more protracted lifetimes ($<$142 ns). This component can provide information on the size of the free volume cavities or micropores within the sample. The intensity of the ortho-positronium (oPs), I3, is related to the relative concentration of free volume sites. The size of the pores can be calculated using a semi-empirical equation using the quantum mechanical model of Tao and Eldrup [33] based on the mean lifetime for ortho-positronium, where R is the diameter of the cavity and ΔR was determined to be 1.656 Å.

$$\tau_3 = 0.5 \times \left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \tag{4}$$

As described in a previous publication [34], PALS experiments were performed using an EG&G Ortec fast–fast coincidence system