

The ‘ideal selectivity’ vs ‘true selectivity’ for permeation of gas mixture in nanoporous membranes

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Abstract. In this study, we proposed and validated a novel and non-destructive experimental technology for measuring the permeation of binary gas mixture in nanoporous membranes. The traditional time lag rig was modified to examine the permeation characteristics of each gas component as well as that of the binary gas mixtures. The difference in boiling points of each species were explored. Binary gas mixtures of CO₂/He were permeated through the nanoporous carbon molecular sieve membrane (CMSM). The results showed that, due to the strong interaction among different molecules and with the porous network of the membrane, the measured perm-selectivity or ‘true selectivity’ of a binary mixture can significantly deviate from the ‘ideal selectivity’ calculated from the permeation flux of each pure species, and this deviation is a complicated function of the molecular properties and operation conditions.

1. Introduction

Membrane technology is developing quickly to overtake traditional cryogenic distillation in separation processes, due to its such advantages as: low capital/operation costs, efficiency, easy to scale up and friendly to environment, etc. [1]. Its rapid progress demands new technologies of membrane characterization and evaluation for gas separation applications. Currently, many research publications evaluated the separation performance of a membrane according to the ‘ideal selectivity’ of a gas pair, which is calculated as the ratio of permeabilities of each pure component measured at similar conditions [2]. Such practice has been found to be inaccurate in many studies, because it represents an oversimplified picture for the complicated diffusion process of gas mixtures in porous media [3]. The traditional time lag [4] technology is popularly used in literature to measure the permeation of pure gas [5]. The diffusion cell technology [6] is capable of measuring the permeation of binary or multicomponent gas mixture, whereas an inert gas is used as the ‘sweeping gas’ at the permeate side of membrane to carry the permeants to such analytical instruments as gas chromatography (GC) [7], or mass spectrometry (MS) [8]. In addition to the high cost nature of the diffusion cell technology, the presence of the sweeping gas, normally helium, can disturb the system by causing back-diffusion across the membrane. Therefore, it is difficult to measure the ‘true’ permeation behaviours of each component in membrane separation processes.

To overcome the defects of the existing experimental technologies, this study proposed an improved technology for measuring the ‘true’ permeation properties of each species in a binary gas mixture. The technique explores the difference in the condensability between two components and is simple in structure, versatile, non-destructive and easy to operate. To validate the feasibility of this



technology, inorganic carbon molecular sieve membrane (CMSM) [9] was used as the permeation media while the binary gas mixtures of CO₂/He were prepared at different compositions.

2. Experimental

Figure 1 shows the schematic diagram of the proposed technology, of which traditional time lag rig was modified by adding a cold trap at the U-shape stainless steel tube (1/4 inch in diameter) before the downstream vessel. Liquid N₂ (T = 77K) in the cold trap can condense the heavy component into solid/liquid phase (with constant or negligible vapor pressure) but allows for the light component to reach the downstream vessel for pressure readings. It is seen in table 1 that CO₂ can be easily condensed into solid phase while other gases remained in gas phase. The vapor pressure of solid CO₂ was found to be $\sim 1.2 \times 10^{-6}$ Pa [9] at 77K, which is negligible at the experimental conditions. This means that, by condensing the permeate CO₂ into solid phase, the ‘true’ permeation behaviour of the other component is revealed. What is more, by adding/removing the cold trap at different time intervals, the ‘true’ permeation behaviour of the other component as well as the binary mixture can be derived.

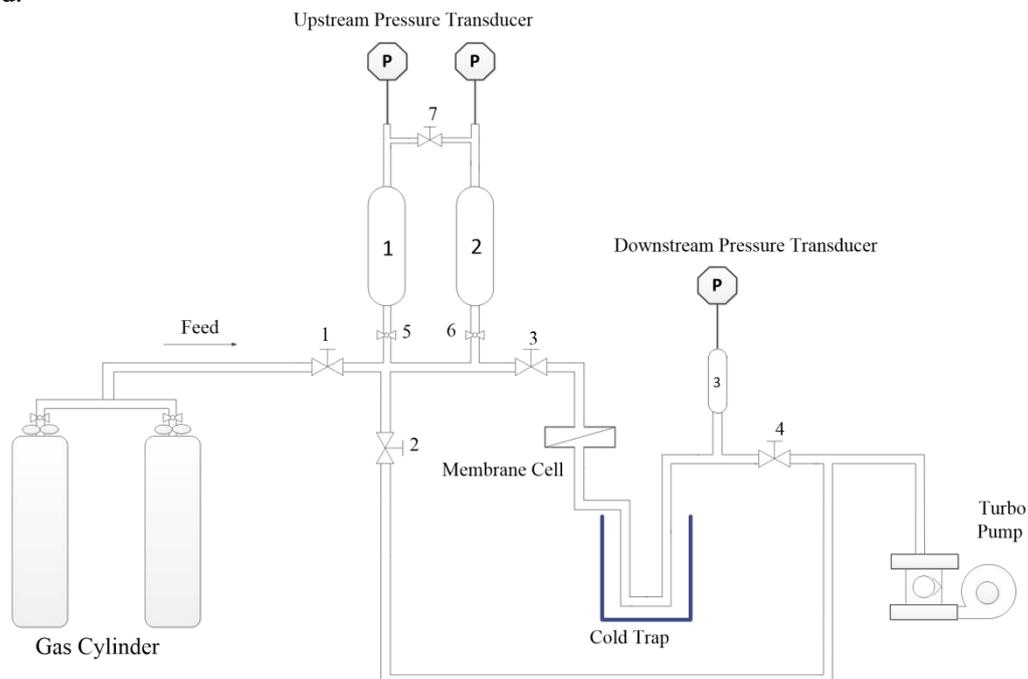


Figure 1. Diagram of improved time lag rig.

Table 1. Properties of CO₂ and He.

Gases	Boiling point (K)	Vapor pressure at 77K	LJ diameters (Å)
He	4.2	----	2.60
CO ₂	194.5 [†]	1.2×10^{-6} Pa	3.30

[†]-CO₂ sublimation point

The permeation experiments were conducted at room temperature on a CMSM derived from Kapton polyimide [10]. To make the gas mixture of required composition (e.g., CO₂:He = 1:1), one specie (He) was firstly charged into vessel 1 (V ~ 500 ml) in figure 1 to designated pressure (e.g., 1bar) and then isolated. The rest of the system was evacuated by vacuuming before the other gas (e.g., CO₂)

was filled into the vessel 2 to the designated pressure (e.g. 1 bar) and isolated as well. After cleaning the pipeline with vacuum, valve 5, 6 and 7 were opened (while other valves are closed) to mix the two gases in an open loop. A hot air gun was used to slightly heat up one cylinder (up to $\sim 50^\circ\text{C}$) to generate forced convection in the open loop to assist the mixing. After two hours of mixing, the system was allowed to cool down to room temperature.

The steady state permeation flux is calculated from the gradient of pressure-time response (dP/dt) of the downstream vessel, as shown in equation (1) while the permeability is calculated in equation (2):

$$J = \frac{V}{SRT} \cdot \frac{dP}{dt} \quad (1)$$

$$Pe = \frac{J}{\Delta P} l \quad (2)$$

where J is the flux ($\text{mol}/\text{m}^2 \cdot \text{s}$), V is the volume of downstream vessel, and S is the cross sectional area of membrane. P_e is the permeability (barrer), ΔP is the pressure difference from upstream to downstream pressure, and l is the thickness of the membrane, respectively.

3. Results and discussions

Figure 2 shows the permeation result of a binary mixture of CO_2 -He. The solid line represents the pressure response of downstream vessel under the cold trap while the dotted line shows the response without the cold trap, respectively. We see that the two curved overlap with each other when cold trap was not applied, supporting the reliability of the data.

The detailed procedures are described as follows: At $t=0$, the cold trap was applied, so that the penetrated CO_2 was condensed into solid phase, while He reached the downstream vessel and gave the pressure response. After reaching the steady state, the 'true' flux of He can be obtained from the gradient of the solid line. Next, at $t=3000\text{s}$, the cold trap was removed and the solid CO_2 would evaporate to gas phase quickly. We see that the dotted line became overlapped with the solid line after the cold trap was removed. The pressure response at this stage would directly correspond to the 'true' permeation of the binary mixture. The steady state CO_2 flux in this binary permeation can be calculated by subtracting the pre-obtained He flux from the total flux. The same process was repeated twice afterwards (by applying and then removing the cold trap), to double check the results and the steady state assumption.

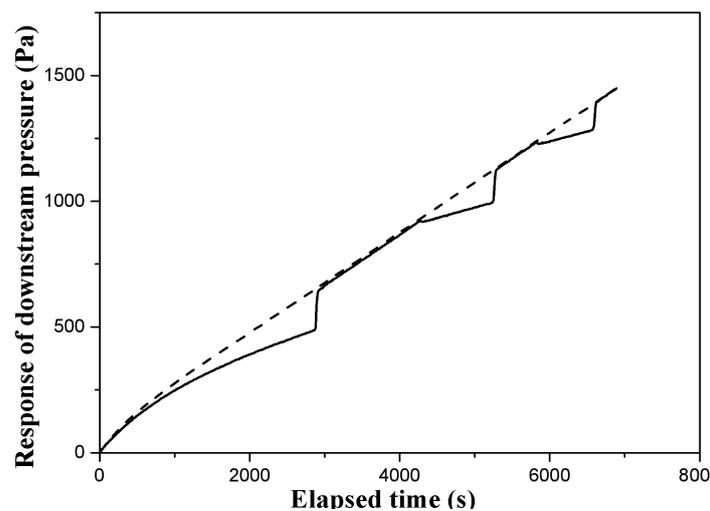


Figure 2. Permeation of gas mixture of CO_2 (1bar) – He (1bar), dash line – without cold trap, solid line – with cold trap.

The permeabilities of He & CO₂ were computed from the experimental results and listed in table 2. The ‘ideal’ selectivity is defined as the ratio of the permeability of pure species as shown in equation (3):

$$\alpha_{ij} = \frac{Pe(i)}{Pe(j)} \quad (3)$$

The relative permeability of a specie, P_r , is defined as the ratio of its permeability in binary permeation to its permeability in unary permeation [11] at the same partial pressure, as shown in equation (4):

$$P_r = \frac{Pe}{Pe^*} \quad (4)$$

Permeation of pure CO₂ and He were also measured on the rig at similar conditions, respectively, and from which the ‘ideal’ perm-selectivity was calculated and compared in table 2 with the ‘true’ selectivity measured with the improved time lag technology.

Table 2. Comparison of the ‘True’ and ‘Ideal’ permeation selectivities of CO₂/He.

P_{total} (CO ₂ : He)	Binary permeation		Unary permeation		$\alpha_{\text{He}/\text{CO}_2}^{\text{True}}$	$\alpha_{\text{He}/\text{CO}_2}^{\text{Ideal}}$	P_r (CO ₂)	P_r (He)
	Pe (CO ₂) (barrer)	Pe (He) (barrer)	Pe* (CO ₂) (barrer)	Pe* (He) (barrer)				
2bar (1:1)	31.00	50.70	45.80	144.00	1.64	3.14	0.677	0.352
3bar (2:1)	32.00	30.00	43.00	144.00	0.94	3.35	0.744	0.208
4bar (3:1)	36.00	17.50	40.20	144.00	0.49	3.58	0.896	0.122

It is seen in table 2 that the ‘True’ selectivity of He/CO₂ can be very different from the ‘Ideal’ selectivity (up to a factor of 4, as the feed pressure changes) due to the interaction or competitive adsorption-diffusion between two species. This is in agreement with our expectation, as the heavy/slowly diffusing CO₂ molecules [10] can dramatically affect the diffusion flux of weakly adsorbed/light molecules of He. What is more, CO₂ is moderately adsorbed on carbon while He is largely non-adsorbing, which results in a strong surface flux as its concentration increases. This explains our observation that, when the partial pressure of CO₂ increases from 1 bar to 3 bar in the feed, the ‘True’ perm-selectivity ($\alpha_{\text{He}/\text{CO}_2}^{\text{true}}$), decreased from ~1.6 to ~0.5, while the ‘Ideal’ selectivity, ($\alpha_{\text{He}/\text{CO}_2}^{\text{ideal}}$), remained largely unchanged at ~3.

Next, we look at the relative permeability, P_r , of each component to have an insight into the effect of the interaction between the two species. It is seen in table 2 that: 1) the interaction affect the permeation of both species (as both $P_r < 1$); 2) As the partial pressure of CO₂ in feed increased from 1 bar to 3 bar, P_r of CO₂ was increased by ~30% while that of He was decreased by ~60%. This suggests that this interaction or competitive adsorption-diffusion is a function of chemical potential, molecular mass, and diffusivity, etc. and is more significant for the light species.

All the above discussions suggest that the ‘ideal’ selectivity [12] can be very misleading when used to evaluate the separation performance of a membrane.

4. Conclusions

The proposed technology is an effective tool for measuring the ‘true’ permeation properties of binary gas mixtures. The ‘ideal’ selectivity based on the permeation of pure gas species can significantly deviate from the true values. This deviation is a function of molecular properties (mass, size, diffusivity) and operation conditions (temperature, pressure, concentration, etc.). This research laid solid fundamental for future research in membrane gas separation.

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References

- [1] A. S. Wiryoatmojo, H. Mukhtar, and Z. Man, "Development of polysulfone-carbon molecular sieves mixed matrix membranes for CO₂ removal from natural gas," in 2009 *International Conference on Chemical, Biological and Environmental Engineering - CBEE 2009*, 9-11 Oct. 2009, Singapore, Singapore, 2009, pp. 249-53.
- [2] N. Jusoh, Y. F. Yeong, T. L. Chew, K. K. Lau, and A. M. Shariff, "Current Development and Challenges of Mixed Matrix Membranes for CO₂/CH₄ Separation," *Separation and Purification Reviews*, vol. **45**, pp. 321-44, 2016.
- [3] S. Li, J. L. Falconer, R. D. Noble, and R. Krishna, "Modeling Permeation of CO₂/CH₄, CO₂/N₂, and N₂/CH₄ Mixtures Across SAPO-34 Membrane with the Maxwell–Stefan Equations," *Industrial & Engineering Chemistry Research*, vol. **46**, pp. 3904-11, 2007/06/01 2007.
- [4] K. Wang, "Diffusion anomaly and blind pore character in carbon molecular sieve membrane," *Chemical Engineering Science*, vol. **62**, pp. 3654-59, Jul 2007.
- [5] H. L. Frisch, "The time lag in diffusion," *The Journal of Physical Chemistry*, vol. **61**, pp. 93-95, 1957.
- [6] D. M. Ruthven, Principles of adsorption and adsorption processes: *John Wiley & Sons*, 1984.
- [7] X. L. Ma, S. Williams, X. T. Wei, J. Kniep, and Y. S. Lin, "Propylene/Propane Mixture Separation Characteristics and Stability of Carbon Molecular Sieve Membranes," *Industrial & Engineering Chemistry Research*, vol. **54**, pp. 9824-31, Oct 2015.
- [8] L. J. P. Van Den Broeke and R. Krishna, "Experimental verification of the Maxwell-Stefan theory for micropore diffusion," *Chemical Engineering Science*, vol. **50**, pp. 2507-22, 1995/08/01 1995.
- [9] S. Lagorsse, F. D. Magalhães, and A. Mendes, "Carbon molecular sieve membranes: Sorption, kinetic and structural characterization," *Journal of Membrane Science*, vol. **241**, pp. 275-87, 10/1/ 2004.
- [10] H. Suda and K. Haraya, "Gas permeation through micropores of carbon molecular sieve membranes derived from Kapton polyimide," *Journal of Physical Chemistry B*, vol. **101**, pp. 3988-94, May 1997.
- [11] R. Ash, R. M. Barrer, and C. G. Pope, "Flow of Adsorbable Gases and Vapours in a Microporous Medium. II. Binary Mixtures," *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. **271**, p. 19, 1963.
- [12] L. M. Robeson, "The upper bound revisited," *Journal of Membrane Science*, vol. **320**, pp. 390-400, Jul 15 2008.