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Upper bound of polymeric membranes for mixed-gas CO_2/CH_4 separations

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ABSTRACT

Membrane polymers with high permeability and high selectivity are preferred for gas separations. However, there exists a trade-off or upper bound, i.e., polymers with higher permeability often exhibit lower selectivity, and vice versa. The upper bound for separation of various gas pairs has been empirically drawn and theoretically rationalized using pure-gas data. However, for CO_2/CH_4 separation, the high pressure CO_2 and non-methane hydrocarbons can plasticize polymers, increasing mixed-gas CO_2 permeability and decreasing mixed-gas CO_2/CH_4 selectivity. This study aims to apply a modified free volume theory to interpret CO_2/CH_4 separation performance in polymeric membranes. The model satisfactorily describes the pure-gas upper bounds for various gas pairs including CO_2/CH_4, the effect of high pressure CO_2 on mixed-gas CO_2/CH_4 separation properties, and the practical mixed-gas upper bound for CO_2/CH_4 separations. The CO_2 is found to have an estimated glass transition temperature of 108 K. The assumptions of this model are discussed, and future work to improve this model is proposed.

1. Introduction

The removal of CO_2 from natural gas is one of the most important industrial gas separations [1]. 20% of natural gas contains CO_2 higher than the pipeline specifications (2%) [2,3]. The CO_2 reduces the Btu value of natural gas, increases transport cost and can be corrosive in the presence of water vapor. Therefore, the CO_2 must be removed, which is achieved mainly by amine absorption, a cumbersome and energy-intensive process. Polymeric membranes for CO_2/CH_4 separations have been extensively explored, due to its simplicity in operation, compactness and light-weight, modularity for scale-up, and potentially high energy-efficiency [2,4,5]. As an example, Fig. 1a illustrates the intensive search of novel high performance polymers for membrane CO_2/CH_4 separations at about 25 °C. This type of plot was popularized by Robeson [6–9]. Each point represents the pure-gas separation property for one particular polymer in the form of thick films. The upper bound line in the figure gives a rough estimate of the highest selectivity possible for a given permeability in membrane polymers [8].

The pure-gas upper bound has been observed for many gas pairs using polymeric membranes, and it has been empirically described as [6,7]

$$\alpha_{A/B} = \beta_{A/B}/P_A^{\lambda_{A/B}} \tag{1}$$

where $\alpha_{A/B}$ is selectivity of gas A over B, P_A is permeability coefficient of gas A, and $\beta_{A/B}$ and $\lambda_{A/B}$ are constants. Freeman proposed a theory based on activation energy providing a fundamental rationale to the existence of the upper bound for membrane polymers. The constants of $\beta_{A/B}$ and $\lambda_{A/B}$ are satisfactorily correlated with physical properties of gas components and polymers [8,10]:

$$\lambda_{A/B} = (d_B/d_A)^2 - 1 \tag{2}$$

and

$$\beta_{A/B} = \frac{S_A}{S_B} S_A^{\lambda_{A/B}} \exp\left\{-\lambda_{A/B}\left[b - f\left(\frac{1-a}{RT}\right)\right]\right\} \tag{3}$$

where d is the kinetic diameter of gas molecules (Å), S is gas solubility in polymers (cm^3(STP)/cm^3 polymer cmHg), R is the gas constant, and T is absolute temperature. The constants a and b are independent of gas type, and have values of 0.64 and 11.54 for glassy polymers, respectively [8]. The parameter f is a measure of polymer chain rigidity, the only adjustable parameter used to model the empirical upper bounds. The value of f is found to be 12,600 cal/mol [8] and 14,154 cal/mol [14] in summarized upper bounds in 1991 and 2008, respectively.

The Freeman theory has been extended to predict the pure-gas upper bound for the separation of hydrocarbon pairs such as

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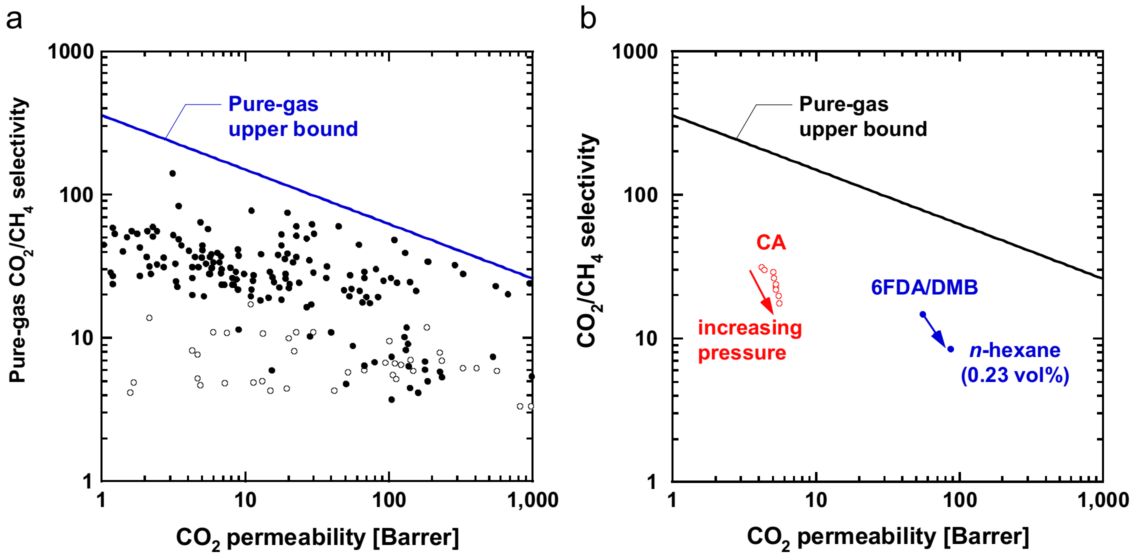

Fig. 1. (a) Pure-gas upper bound of polymeric membranes for CO_2/CH_4 separations at 25–35 °C [6,7]. (b) Effect of plasticization on mixed-gas separation property. For cellulose acetate (CA, ○), increasing feed pressure from 3.5 atm to 26 atm increases CO_2 permeability (assuming a film thickness of 1 μm) and decreases CO_2/CH_4 selectivity at 24 °C [11,12]. For the polyimide (6FDA/DMB, ●), addition of 0.23% *n*-hexane in the CO_2/CH_4 mixture (10/90) at 1000 psig and 48 °C increases CO_2 permeability and decreases CO_2/CH_4 selectivity [13].

propylene/propane [15] and ethylene/ethane [16], and to predict the effect of temperature on the upper bound [17,18]. Other theories have also been applied to interpret the pure-gas upper bounds, such as Meares's use of cohesion energy density to interpret diffusivity upper bound [19], Sanchez–Lacombe's lattice fluid theory to interpret solubility upper bound [20], and free volume theory to interpret permeability upper bound [21].

These theories provide satisfactory results in describing the upper bound behavior for pure-gas separation and presumably, mixed-gas separation for light gas pairs. However, in a highly plasticizing environment, such as CO_2 removal from natural gas, high pressure CO_2 and non-methane hydrocarbons can be significantly sorbed in the polymer, swell the polymer matrix and increase polymer inter-chain spacing and chain mobility (i.e., plasticization), leading to weaker size-sieving ability and thus reduced gas selectivity [22–24]. As shown in Fig. 1b, when tested with a CO_2/CH_4 (70.6/39.4) mixture at 24 °C, cellulose acetate (CA) showed increased CO_2 permeability and decreased CO_2/CH_4 selectivity with increasing feed pressure [11]; a polyimide (6FDA/DMB) exhibited increased CO_2 permeability and decreased CO_2/CH_4 selectivity when *n*-hexane vapor was introduced to the CO_2/CH_4 (10/90) mixture at 1000 psig and 48 °C [13]. The mixed gas CO_2/CH_4 separation properties significantly deviate from their pure gas properties and therefore, the upper bound for pure-gas CO_2/CH_4 separations will not be applicable to practical CO_2/CH_4 separations, where natural gas streams are contaminated with CO_2 and non-methane hydrocarbons.

This paper intends to provide a theoretical framework based on the free volume theory to quantitatively describe the upper bounds for the pure-gas and mixed-gas CO_2/CH_4 separations using polymeric membranes. Firstly, a free volume theory is developed to correlate the pure-gas upper bounds for various gas pairs in polymeric membranes. Secondly, the theory is extended to model the effect of CO_2 pressure on mixed-gas CO_2/CH_4 separation properties due to plasticization. Thirdly, the theory is applied to predict the upper bound for mixed-gas CO_2/CH_4 separations in the presence of CO_2 and non-methane hydrocarbons. Finally, the assumptions of the model and the need for future development are discussed.

2. Theory

2.1. Background

The steady state permeability of a polymer to gas A, P_A, is defined as [25–27]

$$P_A=\frac{N_A l}{A_m(f_{2A}-f_{1A})} \tag{4}$$

where N_A is the steady state flux of gas through the film, l is the film thickness, A_m is the film surface area, and f_{2A} and f_{1A} are the upstream (i.e., high) and downstream (i.e., low) fugacity of gas A, respectively. Permeability coefficients are commonly expressed in units of Barrers, where 1 Barrer$=10^{-10}$ cm^3(STP) cm/(cm^2 s cmHg). For asymmetric membranes with unknown film thickness, permeance (P_A/l) is often used to characterize the flux with units of gas permeation unit (gpu), where 1 gpu$=10^{-6}$ cm^3(STP)/(cm^2 s cmHg).

The use of fugacity is necessary to understand the transport properties in the polymeric membrane when the feed gas is non-ideal. For example, with a feed gas containing 80% CO_2 and 20% CH_4 at 68 atm, the fugacity coefficient for CO_2 and CH_4 is 0.681 and 1.01, respectively [26], which is calculated using the Soave–Redlich–Kwong (SRK) Equation of State. This indicates that the fugacity based permeability (intrinsic property of the polymer) is 147% of the pressure based permeability for CO_2 and 99% for CH_4. In addition, the mixed-gas CO_2/CH_4 selectivity would be underestimated by 32%, if the pressure-based permeability is used.

The transport of gas molecules through polymeric membranes usually follows the solution-diffusion mechanism, and the permeability, P_A, is often given by [25]

$$P_A=S_A\times D_A \tag{5}$$

where D_A is the average effective diffusivity (cm^2/s).

The selectivity of a membrane for gas A over gas B is the ratio of their pure-gas or mixed-gas permeabilities:

$$\alpha_{A/B}=\frac{P_A}{P_B}=\left(\frac{S_A}{S_B}\right)\left(\frac{D_A}{D_B}\right) \tag{6}$$