

흡착농도에 의존적인 Maxwell-Stefan 확산계수를 이용하여 silicalite-1 막을 통한 이산화탄소 또는 메탄의 투과 모델 연구

이상철*, J.L. Falconer¹
 군산대학교 신소재나노화학공학부
¹콜로라도대학교 화학 및 생물공학과
 (lee40f@kunsan.ac.kr*)

A study on permeation model of CO₂ or CH₄ through silicalite-1 membranes in single-component systems using occupancy-dependent Maxwell-Stefan diffusivities

Sang Cheol Lee*, J.L. Falconer¹
 School of Materials Science & Chemical Engineering, Kunsan National University,
¹Department of Chemical & Biological Engineering, University of Colorado, USA
 (lee40f@kunsan.ac.kr*)

서론

Zeolites are inorganic crystalline structures with uniform-sized pores of molecular dimensions. Different pore sizes and compositions of zeolites have been used to prepare membranes, and the zeolite membranes having various structures have been investigated to separate CO₂ from CH₄ [1,2]. Several researchers have experimentally and theoretically studied single and binary permeation of CO₂ and CH₄ through MFI membranes [2], but the permeation models considered have not well described occupancy-dependent diffusion in the single or the binary systems yet.

In this paper, we investigated how much the different M-S surface diffusivities affected permeation of CO₂ or CH₄ in MFI zeolite membrane systems. To analyze the permeation behavior, the M-S surface diffusivities were compared as a function of fractional surface occupancy of each species in single-component systems. Transient fluxes of CO₂ or CH₄ at three different feed pressures were compared using the three different M-S surface diffusivities.

이론

The permeation through thick zeolites and zeolite membrane at room temperature has been assumed to be limited by intracrystalline diffusion [1]. A generalized M-S theory qualitatively describes the intracrystalline diffusion for a single gas and a multicomponent gas mixture through zeolites. The theory is based on a balance between the driving force exerted on a particular species and the friction it experiences with the adsorbent surface and with all other species in the mixture [3].

For single-component diffusion, transport flux N can be expressed in terms of the chemical potential gradient $\nabla\mu$ [3]:

$$N = -\rho q^{sat} \mathcal{D} \frac{\theta}{RT} \nabla\mu = -\rho q^{sat} \mathcal{D} \Gamma \nabla\theta \quad (1)$$

where the chemical potential gradient is related to the fractional surface occupancy θ and the thermodynamic correction factor, $\Gamma = \left(\frac{\partial \ln p}{\partial \ln \theta} \right)$. ρ is the density of zeolite, q^{sat} is the saturation loading, and \mathcal{D} is the single-component M-S diffusivity. With single-component Langmuir isotherm applied, Γ is described by

$$\Gamma = \frac{1}{1-\theta} \quad (2)$$

The single-component flux in one-dimension can be rewritten using Eq. (2):

$$N = -\rho q^{sat} D \frac{1}{1-\theta} \frac{\partial \theta}{\partial z} \quad (3)$$

Here we considered the fluxes with three different single-component M-S surface diffusivities. In the weak confinement scenario the M-S diffusivity is taken to be independent of the occupancy and equal to the zero-loading molecular diffusivity:

$$D = D(0) \quad (4)$$

In the strong confinement scenario the M-S diffusivity shows linear relations with the occupancy:

$$D = D(0)(1-\theta) \quad (5)$$

However, Eq. (5) does not reflect a wide variety of the observed loading dependence on M-S surface diffusivity. Reed and Ehrlich [4] suggested the more general loading dependence model for the M-S surface diffusivity as follows:

$$D(\theta) = D(0) \frac{(1+\varepsilon)^{\gamma-1}}{(1+\varepsilon/f)^\gamma} \quad (6)$$

where γ is the coordination number, representing the maximum number of nearest neighbors, and the other parameters are given by

$$f = \exp(\delta E / RT); \quad \gamma = \sqrt{1 - 4\theta(1-\theta)(1-1/f)}; \quad \varepsilon = \frac{(\gamma-1+2\theta)f}{2(1-\theta)} \quad (7)$$

The approach reflects the diffusion influenced by each of the neighboring molecules with the pair interaction factor f , where δE represents the reduction in the energy barrier.

The transient surface occupancy in membrane for a single component is described by

$$\frac{\partial \theta}{\partial t} = -\frac{1}{\rho q^{sat}} \frac{\partial N}{\partial z} \quad (8)$$

When the membrane is initially empty, the initial and boundary conditions are:

$$\text{I.C.: } \theta(z,0)=0, \quad N(z,0)=0 \quad (9)$$

$$\text{B.C.: } \theta(0,t) = \frac{b p_{feed}}{1+b p_{feed}}, \quad \theta(\delta_M, t) = \frac{b p_{perm}}{1+b p_{perm}} \quad (10)$$

where δ_M is the membrane thickness, and p_{feed} and p_{perm} are the pressures at the feed and permeate sides, respectively.

결과 및 토론

Since all three different kinds of M-S surface diffusivities include the zero-loading molecular diffusivity as described in Eqs. (4) to (6), we need to get the zero-loading molecular diffusivities for CO₂ and CH₄. The quasi-chemical theory in Eq. (6) describes occupancy-dependent diffusivities more extensively than the weak or the strong confinement scenario. Krishna et al. [5] and Krishna and van Baten [6] obtained some parameter values available for the quasi-chemical approach for CO₂ and CH₄. Their data were used to our CO₂/CH₄ permeation system treating occupancy-dependent surface diffusion. The CH₄ data at 298 from the work of Krishna et al. [5] could be directly used to our model system, but only the CO₂ data at 300 K was available from the work of Krishna and van Baten [6]. Thus the zero-loading molecular diffusivity of CO₂ at 298 K was estimated from van't Hoff equation with assumption that its diffusivity activation energy is the same as that of M-S surface diffusivity. The pair interaction factor f at 298 K was estimated with the assumption that the change in energy of system, δE of Eq. (7) is constant around the temperature.

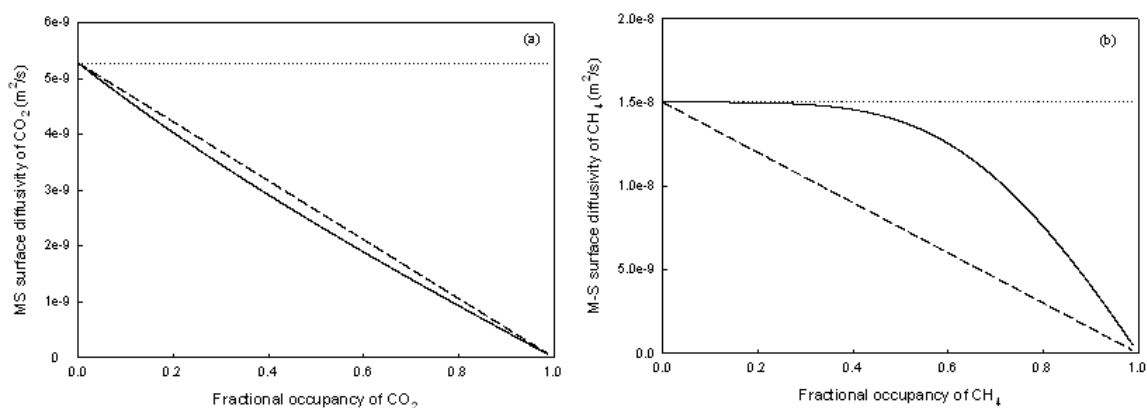


Fig. 1. Occupancy dependencies of M-S surface diffusivity for (a) CO₂ and (b) CH₄. (.....: weak confinement scenario, -----: strong confinement scenario, —: quasi-chemical approach)

Fig. 1a and 1b show the calculated M-S surface diffusivities of CO₂ and CH₄ as a function of fractional surface occupancy of each species, respectively. The calculated M-S surface diffusivity of CO₂ from the quasi-chemical approach is a little lower than that from the strong confinement scenario, while the calculated M-S surface diffusivity of CO₂ from the weak confinement scenario was somewhat higher than the other cases. In the case of CH₄, the calculated M-S surface diffusivity from the quasi-chemical approach was almost equal to that from the weak confinement at the fractional surface occupancy less than 0.4, but it decreased with the fractional occupancy rapidly at higher occupancies.

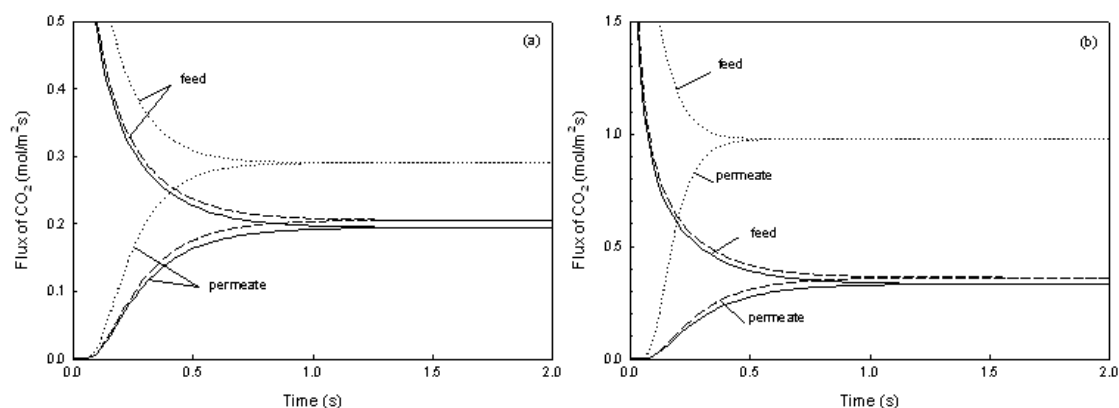


Fig. 2. Transient response to a step increase in feed CO₂ pressure to an empty zeolite membrane in a single-component permeation system. Feed and permeate fluxes for three different M-S diffusivities as a function of time at the feed pressures (a) 100 kPa and (b) 1000 kPa. (.....: weak confinement scenario, -----: strong confinement scenario, —: quasi-chemical approach)

Generally, the quasi-chemical approach presumes a real value of the occupancy-dependent M-S surface diffusivity the best among three methods for estimation of the M-S surface diffusivity, because it reflects a variety of occupancy dependences due to intermolecular interactions leading to various degrees of reduction in the energy barrier for diffusion [5]. The quasi-chemical approach was taken into consideration as the most ideal model for estimation of the permeation behavior through the zeolite membrane below.

To eliminate the effect of support resistance on permeation and ultimately analyze the permeation behavior using adsorption and occupancy-dependent diffusion within the membrane, we treated the zeolite membrane systems without support. In all of the membrane systems considered, the initial membrane was empty and the pressure at the permeate side was fixed at 0. The parameter values of the zeolite membrane used were 100 μm and 1780 kg/m³ for membrane thickness and density of zeolite,

respectively. Fig. 2 shows the transient permeation of pure CO₂ through the zeolite membrane varying the CO₂ pressure at the feed side. Before the transient fluxes at the feed and the permeate sides reached steady state, they decreased and increased with time monotonically regardless of the feed side pressure, respectively. As the feed side pressure was higher, there were larger differences among the transient fluxes calculated from the three methods for estimation of M-S surface diffusivity. However, even the highest feed side pressure did not make a big difference between the transient fluxes from the quasi-chemical approach and the strong confinement scenario, which is due to the very close values of M-S surface diffusivity between the two estimation methods as shown in Fig. 1a.

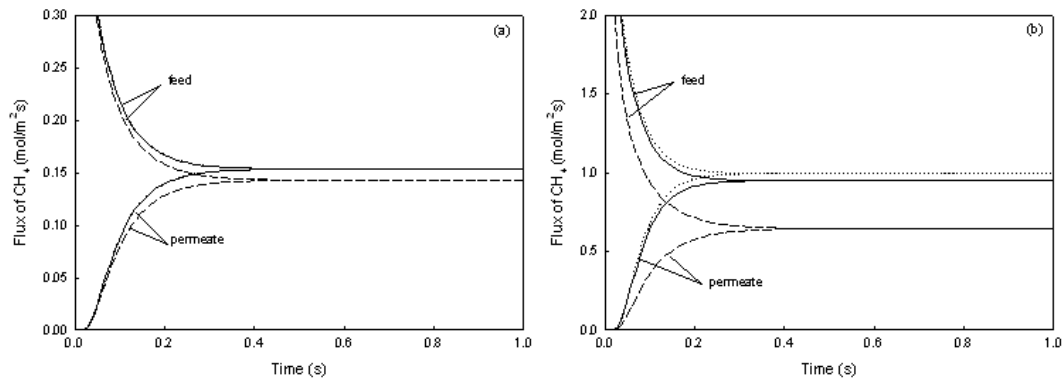


Fig. 3. Transient response to a step increase in feed CH₄ pressure to an empty zeolite membrane in a single-component permeation system. Feed and permeate fluxes for three different M-S diffusivities as a function of time at the feed pressures (a) 100 kPa and (b) 1000 kPa. (.....: weak confinement scenario, -----: strong confinement scenario, —: quasi-chemical approach)

Fig. 3 shows the transient permeation of pure CH₄ through the zeolite membrane varying the CH₄ pressure at the feed side. There were monotonic changes in transient flux of CH₄ with time in the same trend as displayed in the transient flux of CO₂, but CH₄ reached a steady state much earlier than CO₂ under the same condition. This is because the M-S surface diffusivity of CH₄ is higher than that of CO₂. The transient fluxes calculated with the quasi-chemical approach and the weak confinement scenario for estimation of M-S surface diffusivity were almost overlapped at the highest feed side pressure of 1000 kPa (Fig. 3b) as well as at the other feed pressure (Fig. 3a). This is supported by the fact that as shown in Fig. 1b the M-S surface diffusivities between the two estimation methods are very close at the fractional surface occupancy below 0.61, which is the fractional surface occupancy at the feed side pressure.

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