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Hindering effects in diffusion of CO_2/CH_4 mixtures in ZIF-8 crystals

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ABSTRACT

Cage-type micro-porous materials such as LTA, CHA, SAPO-34, DDR, ERI, ZIF-7, and ZIF-8 have significant potential for use in membrane technologies for CO_2 capture. The permeation selectivities are governed by a combination of adsorption and diffusion selectivities, each of which can be separately manipulated. In this study we have investigated the characteristics of CO_2/CH_4 mixture diffusion in ZIF-8 by monitoring the uptake within crystals using infra-red microscopy (IRM). The uptake profiles were fitted to determine the "effective" Fick diffusivities of the individual components in the mixture. The diffusivity measurements, conducted for a range of loadings, clearly demonstrate that the preponderance of CO_2 at the window regions of ZIF-8 hinders the inter-cage transport of partner CH_4 molecules. Such hindering effects serve to enhance the CO_2/CH_4 permeation selectivities across ZIF-8 membranes for high mixture loadings within the membrane above values anticipated on the basis of unary permeances.

1. Introduction

Micro-porous materials such as zeolites (crystalline aluminosilicates), metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs) are of potential use in a variety separation applications. Membrane-based technologies, using thin micro-porous layers of the order of a few micrometers, are of particular interest in applications such as CO_2 capture [1–9], H_2 purification [10,11], pervaporation [12,13], and alkane/alkene separations [14–17]. The permeation selectivities in such processes are dictated by both adsorption and intra-crystalline diffusion. For a given separation application, both adsorption and diffusion selectivities can be *separately* manipulated in order to enhance the overall separation performance. In this regard, cage-type microporous materials such as LTA, CHA, SAPO-34, DDR, ZIF-7, and ZIF-8, with the sizes of the window apertures separating the cages in the 3.2–4.1 Å range, offer significant advantages. Diffusion selectivities can be significantly enhanced, by up to two orders of magnitude, by appropriate choice of the sizes of the window aperture [18–20].

In modeling mixture diffusion in cage-type structures, it is commonly assumed that the inter-cage hopping of molecules occurs one-at-a-time and are *uncorrelated* [6,7,11,21,22]. In the event that correlation effects can be ignored, the diffusivities of each of the species in the mixture can be identified with those of the pure components. As illustration, Fig. 1 presents data on the effective Fick diffusivities, $D_{i,\mathrm{eff}}$, of individual components in mixtures of ethane and ethene in ZIF-8, determined by fitting the uptake profiles within a single ZIF-8 crystal using infra-red microscopy (IRM). The details of the IRM experimental technique and the methodology for determination of the Fick diffusivities are presented as Supplementary material accompanying this publication; these are the same as described in earlier works [23–26]. The component diffusivities in the mixture are practically the same as that obtained from unary diffusion measurements, when compared at the same total mixture loading, Θ_t. As a consequence, the component permeances for mixture permeation across ZIF-8 membranes should be expected to be the same as those obtained from unary permeation [27,28]. Experimental data on ethane/ethene permeation across ZIF-8 membrane confirm this expectation [14].

There are, however, situations in which the inter-cage hopping of one of the species in the mixture is profoundly influenced by the partner molecules. Molecular simulations of adsorption of CO_2/CH_4, CO_2/N_2, and CO_2/H_2 mixture in LTA, DDR, and ERI zeolites have revealed segregation effects; CO_2 molecules have been found to prefer locating at the window regions [29–31]. As illustration, Fig. 2 a shows a snapshot showing the location of CH_4 and CO_2 molecules in DDR. Molecular dynamics (MD) simulations have shown that the preferential perching of CO_2 at the windows hinders the inter-cage hopping of partner molecules CH_4, N_2, and H_2 [29–31]. Such hindering effects need to be taken into account in order to interpret experimental data for CO_2/CH_4, and CO_2/Air permeation experiments across DDR membranes [32,33]. Fig. 2b

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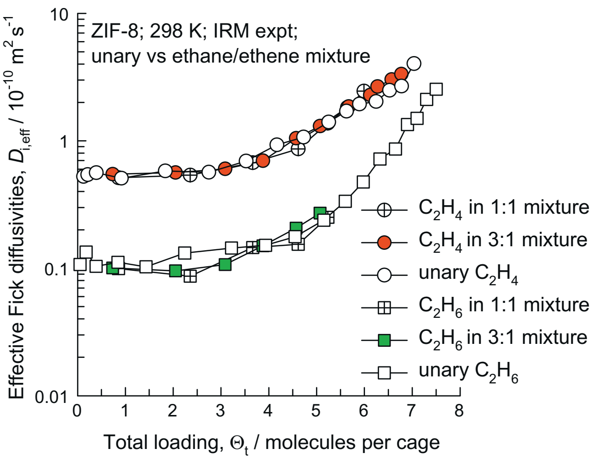

Fig. 1. Effective Fick diffusivities, $D_{i,\mathrm{eff}}$, of individual components in mixtures of ethane and ethene in ZIF-8 crystal at 298 K. The experimental diffusivity data, obtained from IRM, are from Bux et al. [14]. The values for two different ethane/ethene loadings within the crystal, 3:1, and 1:1, are compared to the unary diffusivities, D_i. The component loadings within the crystal are determined from ideal adsorbed solution theory (IAST) calculations using the pure component isotherm data fits reported in Table 1 of Bux et al. [14].

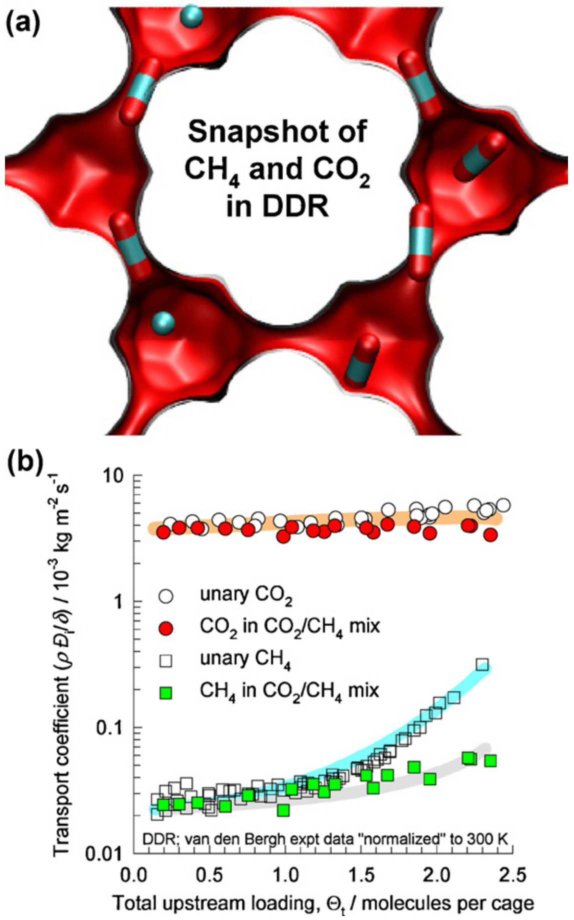

Fig. 2. (a) Snapshot showing the location of CO_2 and CH_4 molecules in DDR. (b) Comparison of transport coefficients, $(\rho Đ_i/\delta)$, for CO_2 and CH_4, backed out from unary and binary mixture permeation data across DDR membrane [32,33], plotted against the total mixture loading at the upstream face of the membrane. The details of the backing-out procedure are described in earlier works [29–31]. The data at different temperatures have been normalized to 300 K, by using the activation energy for diffusion. Video animations showing the inter-cage hopping of molecules across the windows of DDR are provided as Supplementary material accompanying this publication.

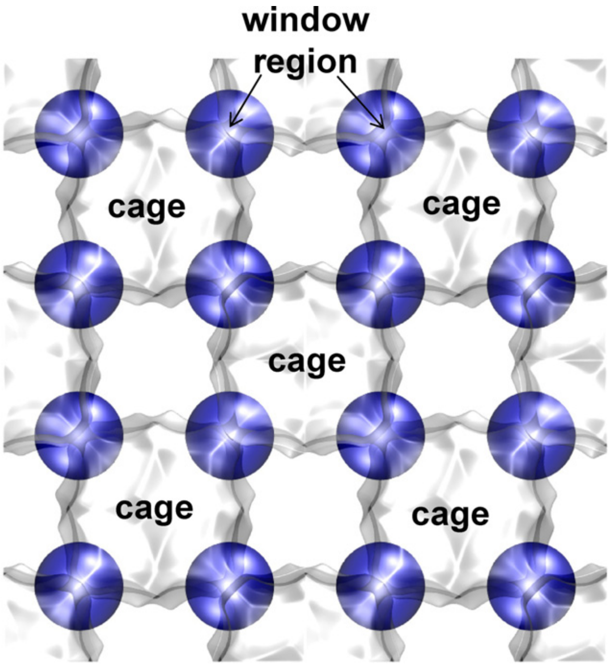

Fig. 3. Cartoon showing the definition of the window regions of ZIF-8 for sampling purposes. Video animations of the dynamics of the ZIF-8 are provided as Supplementary material.

compares the membrane transport coefficients, backed out from unary and binary mixture permeation data across DDR membrane. The transport coefficient for CO_2 in the mixture is the same as that determined from unary permeation, when compared at the same mixture loading, Θ_t. In sharp contrast, there is a dramatic reduction in the transport coefficient of CH_4 in the mixture, at higher loadings, when compared to the data from unary permeation; consequently the permeance of CH_4 in the mixture is significantly lower than that of the pure component. It must be emphasized that the reduction of the transport coefficient of CH_4 is *not* ascribable to correlation effects; such effects lower the mobility of the *more mobile partner* species [11,22]. The reduction of the mobility of tardier CH_4 in the mixture is a consequence of the blocking of window regions due to preferential location of CO_2 molecules. For DDR, window blocking by CO_2 is desirable in practice because the membrane permeation selectivities will be significantly enhanced above the values anticipated on the basis of pure component permeances.

The major objective of the present communication is to demonstrate that analogous window blocking effects also manifest for CO_2/CH_4 mixture diffusion in ZIF-8. For this purpose, we used IRM experiments to determine the diffusivities of CO_2 and CH_4 in binary mixtures, along with those for the individual pure components in a single ZIF-8 crystal at 298 K; see Supplementary material for experimental details.

2. Diffusivities of CO_2 and CH_4 in ZIF-8

The first task is to demonstrate that the window regions are preferentially populated by CO_2 molecules. We carried out configurational-bias Monte Carlo (CBMC) simulations for adsorption of CO_2/CH_4 mixtures, each with a partial pressure of 50 kPa, in $2 \times 2 \times 2 = 8$ unit cells of ZIF-8 (cf. Fig. 3). The CBMC simulations were carried out with the assumption of a rigid framework lattice. Comparisons of the CBMC simulated data, using the assumption of a fixed lattice, for adsorption isotherms for pure components are in very good agreement with IRM data on adsorption; details are provided in Supplementary material. In this context it is worth

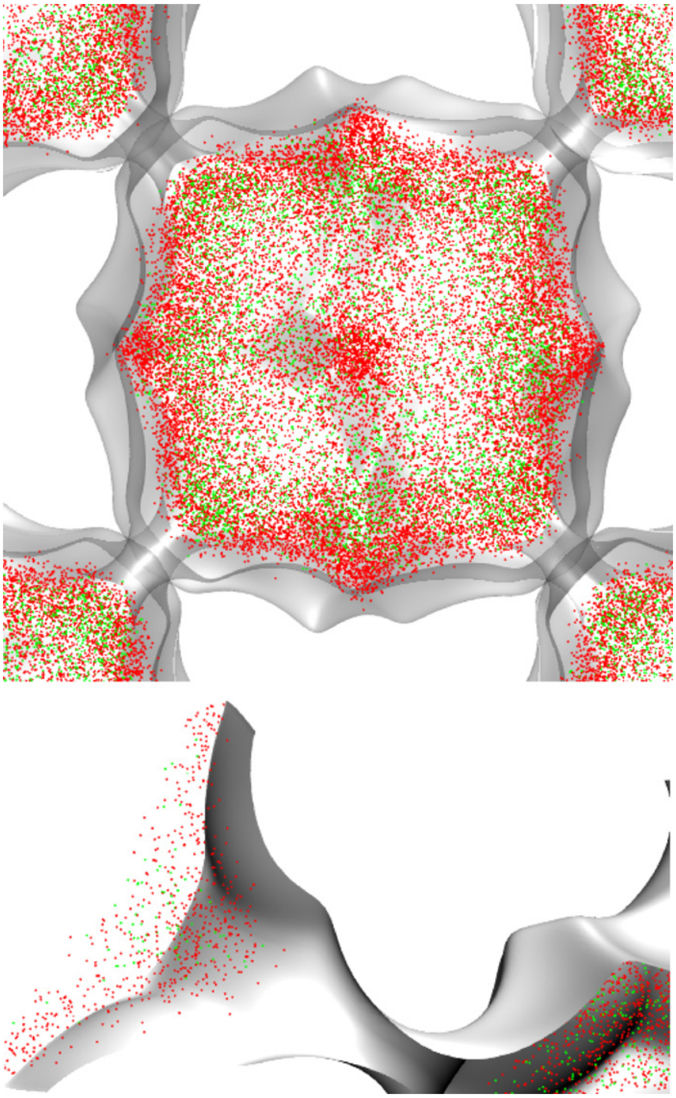

Fig. 4. Probability density plots showing the location of CO_2 (red) and CH_4 (green) molecules in ZIF-8. The chosen conditions are 300 K, with partial pressures of 50 kPa. The inset shows a zoomed-in probability density plot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

remarking that in a recent paper by Pantatosaki et al. [34] the adsorption isotherms were calculated using a flexible ZIF-8 framework; the agreement of their simulations with the experimental IRM data used here is less good than with a fixed framework. Our Monte Carlo simulations were run for a total of 10^7 cycles. These were sampled every 10^3 cycle to yield a total of 10^4 equilibrated samples that were analysed. For statistical analysis purposes, the regions circled in blue in Fig. 3 were considered to represent the window regions. In the 10^4 equilibrated samples, the window regions were detected to be populated with a total of 3272 CH_4 molecules and 5451 CO_2 molecules. The preponderance of CO_2 molecules at the window regions is visually evident in the probability density plots; see Fig. 4 in which CO_2 and CH_4 locations are indicated, respectively, in red and green. A close examination of each window region shows that population closest to the window is practically devoid of CH_4; see inset to Fig. 4. The preferential location of CO_2 at the windows can be expected to influence the diffusivity of CH_4. (For interpretation of the references to color in this text, the reader is referred to the web version of the article.)

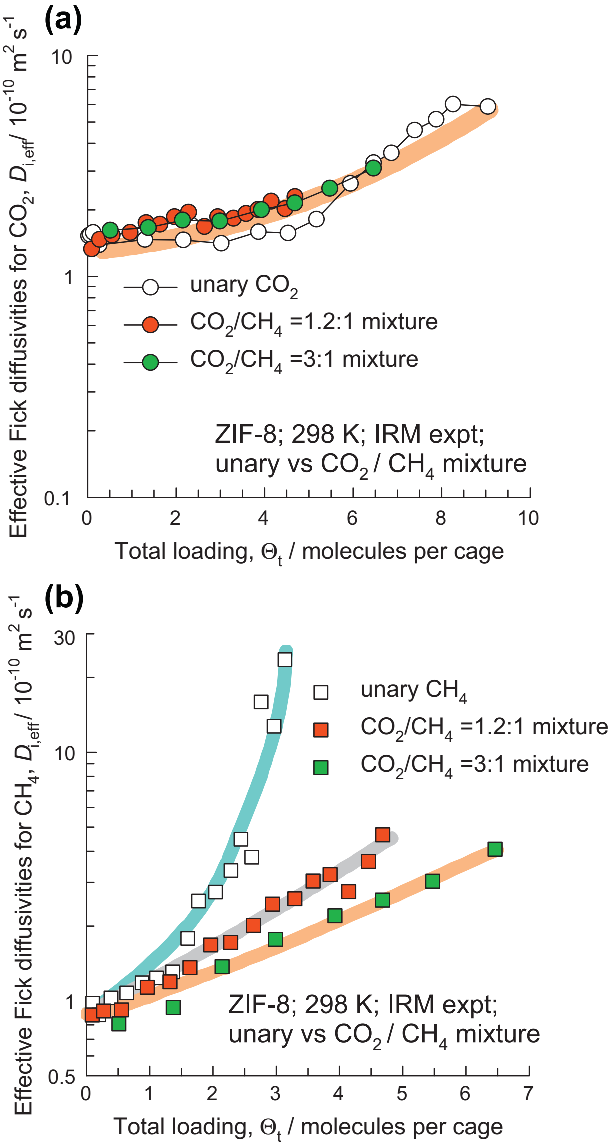

Fig. 5. Effective Fick diffusivities, $D_{i,\mathrm{eff}}$, of individual components in mixtures of CO_2 and CH_4 in ZIF-8 crystal as a function of the total mixture loading, Θ_t. The values for two different CO_2/CH_4 loadings within the crystal, 3:1, and 1.2:1, are compared to the unary diffusivities, D_i. The mixture experiments were carried out with constant gas phase compositions with CO_2/CH_4 ratios of 1.13 and 2.86, respectively. Consequently, the CO_2/CH_4 loadings within the crystal are not strictly constant, and increase slightly with increasing Θ_t. The loading ratios CO_2/CH_4 of 3:1 and 1.2:1 are *averaged* values. The component loadings within the crystal are determined from ideal adsorbed solution theory (IAST) calculations using fits of the pure component isotherms presented in Bux et al. [5].

The IRM data on the effective Fick diffusivities, $D_{i,\mathrm{eff}}$, are shown in Fig. 5. For CO_2, the diffusivity in the CO_2/CH_4 mixture is practically the same as for the pure component; see Fig. 5a. On the other hand, the CH_4 diffusivity in the CO_2/CH_4 mixtures is significantly lower, by about one order of magnitude, than the unary diffusivity values at high mixture loadings; see Fig. 5b. Another point to be noted in the data in Fig. 5 is that the Fick diffusivities of both components in the mixture increase with total mixture loading, Θ_t. This increase is typical of cage-type zeolites such as LTA, DDR, and CHA and such increases have been obtained in also verified by MD simulations for a wide variety of guest–host combinations [20,21]. Due to preferential adsorption of CO_2 in CO_2/CH_4 mixtures, the proportion of CH_4 in the mixture actually decreases with increasing Θ_t values. Put another way, the hindering effect that CO_2 exerts on CH_4

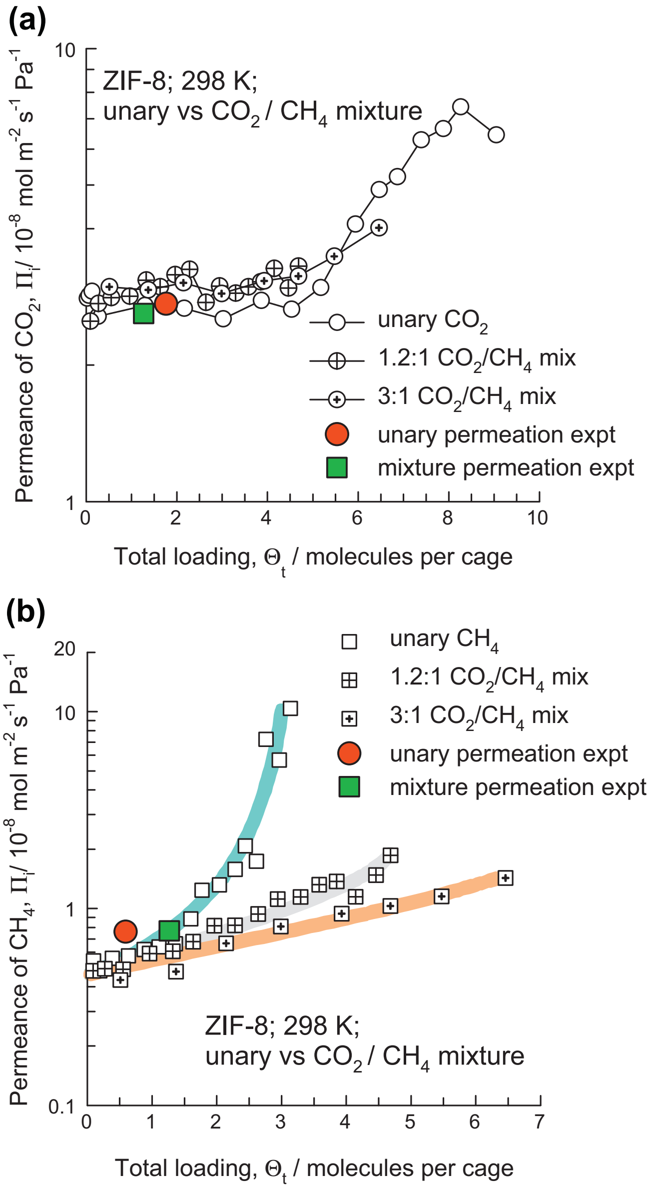

Fig. 6. Component permeances, Π_i, of individual components in mixtures of CO_2 and CH_4 in ZIF-8 crystal as a function of the total mixture loading, Θ_t, determined from IRM experiments compared with the corresponding data obtained by membrane permeation experiments. The calculations are based on Eq. (1), in which the component Henry coefficients are determined from IAST calculations using fits of the pure component isotherms. For ZIF-8, the framework density of $\rho = 924\ \mathrm{kg\,m^{-3}}$. The value of the effective membrane thickness δ was chosen to match the experimental data on permeances of Bux et al. [5]. The match was obtained taking $\delta = 70\ \mu\mathrm{m}$.

is attributable primarily to the relative increase in the proportion of CO_2 with increase in Θ_t. The IRM data in Fig. 5 are precisely analogous to the data on transport coefficients in the DDR membrane shown in Fig. 2.

From the IRM data on $D_{i,\mathrm{eff}}$, the component permeances for ZIF-8 membranes can be estimated from

$$\Pi_i = \frac{\rho}{\delta} D_{i,\mathrm{eff}} K_i \tag{1}$$

where the Henry coefficients, K_i, can be determined from the IAST calculations of mixture adsorption equilibrium. The accuracy and applicability of the IAST for calculation of adsorption loadings in mixtures were established by comparisons with IRM data on mixture adsorption; these comparisons are provided in Supplementary material. The estimates of the component permeances are shown in Fig. 6a and b for CO_2 and CH_4, respectively. Also shown in Fig. 6 are the experimental data of Bux et al. [5] in which the Θ_t values were lower than 2 molecules/cage. There is reasonably good agreement between the calculations following Eq. (1) and the experimental data. For CO_2, the component permeances in the mixture are practically the same as for the pure component over the entire range of loadings. For CH_4, the permeances in the mixture are anticipated to be significantly lower than the unary permeances as the mixture loading Θ_t increases to values higher than 2 molecules per cage.

3. Conclusions

IRM experiments of diffusivities of CO_2/CH_4 mixtures have revealed that there is a severe reduction in the inter-cage hopping of CH_4 molecules in ZIF-8. This reduction is attributable to hindering by CO_2 molecules that are preferentially located at the window regions. The important consequence of window blocking by CO_2 is that for high loadings, the permeance of CH_4 is significantly lower than unary permeance values. Such hindering effects are expected to be beneficial in CO_2 capture applications because of the permeation selectivities will be significantly higher than those anticipated from unary permeation data alone.

Supplementary material

This material includes a document containing the details of the IRM experimental set-up, and procedure for determination of diffusivities. Also included as supplementary material are video animations demonstrating the inter-cage hopping of molecules in DDR and ZIF-8.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2012.01.013.

Nomenclature Notation

D_i	unary Fick diffusivity of species i, $\mathrm{m^2\,s^{-1}}$
$D_{i,\mathrm{eff}}$	effective Fick diffusivity of species i in mixture, $\mathrm{m^2\,s^{-1}}$
$Đ_i$	M–S diffusivity of species i, $\mathrm{m^2\,s^{-1}}$
K_i	Henry coefficient for species i, $\mathrm{mol\,kg^{-1}\,Pa^{-1}}$

Greek letters

δ	thickness of membrane, m
Π_i	permeance of species i, $\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$
Θ_t	total mixture loading, molecules per cage
ρ	framework density of porous material, $\mathrm{kg\,m^{-3}}$

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