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Influence of adsorption on the diffusion selectivity for mixture permeation across mesoporous membranes

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ABSTRACT

Molecular dynamics (MD) simulations were carried out to determine the self-diffusivities, $D_{1,\mathrm{self}}$, and $D_{2,\mathrm{self}}$ for a variety of binary mixtures: methane (C1)–ethane (C2), C1–propane (C3), C1–n-butane (nC4), C1–n-hexane (nC6), C2–nC4, C2–nC6, Ar–C1, Ar–C2, Ar–C3, Ar–nC4, Ar–nC6, and Ar - Kr in a cylindrical silica mesopores. The diffusion selectivity, defined by ($D_{1,\mathrm{self}}/D_{2,\mathrm{self}}$) was found to be significantly different from the Knudsen selectivity, $\sqrt{M_2/M_1}$, where M_i is the molar mass of species *i*. For mixtures in which component 2 is more strongly adsorbed than component 1, $(D_{1,\mathrm{self}}/D_{2,\mathrm{self}})/\sqrt{M_2/M_1}$ has values in the range 1.5–4; the departures from the Knudsen selectivity increased with increasing differences in adsorption strengths of the constituent species.

1. Introduction

The proper modeling of diffusion of guest molecules inside mesoporous materials such as SBA-15, MCM-41, and Vycor glass is important in the development of a variety of membrane separation applications. For membrane processes the permeation selectivity, S_{perm}, is defined by

$$S_{\mathrm{perm}} = \frac{N_1/N_2}{f_1/f_2} \tag{1}$$

where the N_i are the permeation fluxes across the membrane for partial gas phase fugacities, f_i, in the upstream membrane compartment. The permeation selectivity can be expressed as the product [1]:

$$S_{\mathrm{perm}} = S_{\mathrm{ads}} \times S_{\mathrm{diff}} \tag{2}$$

where the adsorption selectivity, S_{ads}, is defined by:

$$S_{\mathrm{ads}} = \frac{c_1/c_2}{f_1/f_2} \tag{3}$$

where the c_i represent the pore concentrations in equilibrium with a bulk fluid phase with partial fugacities f_i at the upstream face of the membrane.

The main focus of the present communication is the estimation of the diffusion selectivity, S_{diff}. Diffusion inside mesopores is governed by a combination of molecule–molecule and molecule–pore wall interactions. For binary mixture diffusion, for example, the fluxes N_i are related to the chemical potential gradients $\nabla \mu_i$ by use of the Maxwell–Stefan (M–S) equations [2–8]:

$$-\phi \frac{c_i}{RT} \nabla \mu_i = \sum_{\substack{j=1 \\ j \neq i}}^{2} \frac{x_j N_i - x_j N_i}{Đ_{ij}} + \frac{N_i}{Đ_i}; \quad i = 1, 2 \tag{4}$$

where ϕ represents the fractional pore volume of the porous material, and the concentrations c_i are defined in terms of moles per m^3 of accessible pore volume. The x_i in Eq. (4) is the component mole fractions of the adsorbed phase within the micropores:

$$x_i = \frac{c_i}{c_t}; \quad i = 1, 2, \ldots n \tag{5}$$

The $Đ_i$ characterize species *i*-pore wall interactions in the broadest sense. The $Đ_{ij}$ are exchange coefficients representing interaction between components *i* with component *j*. For diffusion within mesopores, the $Đ_{ij}$ can be identified with the corresponding M–S diffusivity for a *fluid phase* mixture [5–7]. Conformity with the Onsager reciprocal relations prescribes

$$Đ_{ij} = Đ_{ji} \tag{6}$$

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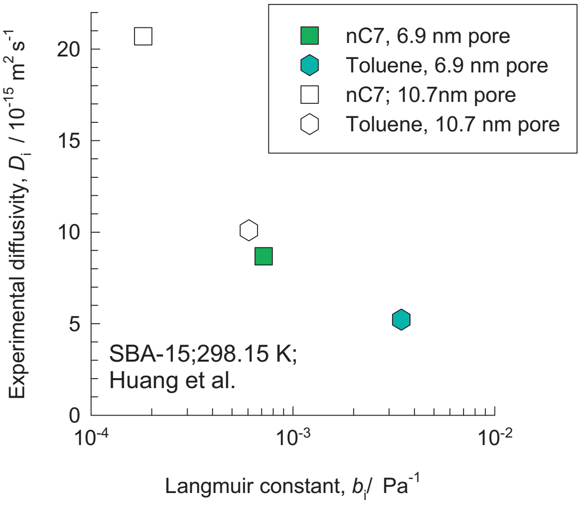

Fig. 1. Diffusivities of nC7 and toluene in SBA-15 materials with pore sizes of 6.9 nm (SBA-15-80) and 10.7 nm (SBA-15-130), determined at 298.15 K by Huang et al. [18].

Starting with Eq. (4), the following expression for S_{diff} can be derived [1]:

$$S_{\text{diff}} = \frac{Đ_1}{Đ_2}\frac{\left(1+Đ_2/Đ_{12}\right)}{\left(1+Đ_1/Đ_{12}\right)} \tag{7}$$

In the limit of vanishingly small pore concentrations, $c_i \to 0$, the zero-loading diffusivity value $Đ_i(0)$ is dictated primarily by molecule-wall collisions. When the reflections are purely *diffuse* in nature, i.e. the angle of reflection bears no relation to the angle of incidence at which the molecule strikes the pore wall, the $Đ_i(0)$ value corresponds to that obtained by the classic Knudsen formula

$$D_{i,Kn} = \frac{d_p}{3}\sqrt{\frac{8RT}{\pi M_i}} \tag{8}$$

When Eq. (8) applies, S_{diff} equals the Knudsen selectivity:

$$S_{\text{diff}} = \frac{D_{1,Kn}}{D_{2,Kn}} = \sqrt{\frac{M_2}{M_1}} \tag{9}$$

Strictly speaking, Eq. (8) holds only in the limiting case when the molecule does not adsorb at pore walls. Adsorption causes the molecules to “stick” to the wall, and perhaps hop to a neighboring adsorption site, rather than return to the bulk after collision [8–17]. Consequently, adsorption at the pore wall introduces a *bias* that makes a molecule hop to a neighboring site on the surface rather than return to the bulk; this bias increases with increasing adsorption strength. Molecular Dynamics (MD) simulations for diffusion of a variety of guest molecules with significant adsorption strength in silica pores have shown that the zero-loading diffusivity value $Đ_i(0)$ can be substantially lower than that the predictions of the Knudsen formula [5–9,14–16]. Indeed, MD simulations show a direct, reducing, influence of adsorption strength on the pore diffusivity. To illustrate the influence of pore adsorption Fig. 1 presents the experimental data of Huang et al. [18] for nC7 (n-heptane) and toluene in SBA-15 materials of two different pore sizes. The molar masses of the two species are nearly equal, 0.1 and 0.092 kg mol^{-1}, respectively. However, the diffusivities of Toluene are found to be significantly lower than that of nC7, because of its higher adsorption strength. Indeed, the data of Huang et al. [18] indicate that the diffusivity correlates not only with the average pore size, but also with the adsorption strength, quantified by the Langmuir adsorption constant. Bhatia and Nicholson [17] have shown that when a component is weakly adsorbed the diffusivity scales linearly with $\sqrt{T/M_i}$, whereas if a component is strongly adsorbed, its diffusivity does not scale linearly with $\sqrt{T/M_i}$. As a consequence we should expect the diffusion selectivity does not scale linearly with $\sqrt{T/M_i}$.

Ruthven and co-workers [19,20] have questioned the conclusions reached in the MD simulations regarding the influence of pore adsorption, and have re-analysed available experimental data [4,21] to conclude that Knudsen formula remains valid even for gases that have strong adsorption. This debate on the validity of the Knudsen formula is further complicated by the fact that, in practice, the tortuosity factors are not known precisely and there is still disagreement on what tortuosity factors can be considered to be reasonable [17]. Furthermore, there is often a distribution of pore diameters that makes the application of Eq. (8) not entirely clear-cut.

There are several examples in the published literature [22–25] where S_{diff} of binary mixtures in the same host material, determined experimentally for mesoporous membranes, are at variance with the predictions of Eq. (9). For example, Choi and Tsapatsis [24] obtain H_2/N_2 selectivities for a MCM22/Silica nanocomposite membranes that are significantly higher than the Knudsen selectivities. These authors have not, however, attributed this departure to the failure of the Knudsen formula for calculating the diffusivity of the more strongly adsorbed N_2.

Bhatia and Nicholson [16,17] have shown that when there is a distribution of pore sizes, the apparent tortuosity is not a medium property, but depends also on the temperature and on the diffusing molecule. As a consequence, the diffusion selectivity will not follow the Knudsen prescription, given by Eq. (9), even when the influence of adsorption is negligible.

The major objective of the present communication is to undertake a systematic investigation of the validity of Eq. (9) for estimation of the diffusion selectivity, S_{diff}, for binary mixture diffusion inside cylindrical mesopores, and tortuosity issues are not relevant. To achieve this objective, MD simulations were carried to determine the $D_{1,\text{self}}$, and $D_{2,\text{self}}$, for a variety of binary mixtures: methane (C1)–ethane (C2), C1–propane (C3), C1–n-butane (nC4), C1–n-hexane (nC6), C2–nC4, C2–nC6, Ar–C1, Ar–C2, Ar–C3, Ar–nC4, Ar–nC6, and Ar–Kr in cylindrical silica mesopores.

As shown in our previous work [1], the right member of Eq. (7) can be taken equal to the ratio of the self-diffusivities $D_{i,\text{self}}$ in the mixture, determined from MD:

$$S_{\text{diff}} = \frac{D_{1,\text{self}}}{D_{2,\text{self}}} \tag{10}$$

The S_{diff} values, determined from Eq. (10) using MD simulations, are compared with the estimations of Eq. (9) to draw conclusions regarding the validity of the Knudsen formula for varying degrees of adsorption of guest molecules.

The MD simulation strategy used is the same as that described in our previous work [5–8]. For convenience and easy reference, the simulation methodology, specification of force fields, and simulation data on diffusivities are provided in the Supplementary Material accompanying this publication.

2. MD simulation results and discussion

Consider, for example, the diffusion of an equimolar ($c_1 = c_2$) binary mixture of C1 (1) and nC6 (2) in a 3 nm cylindrical mesopore at 300 K. Fig. 2a presents the data on the self-diffusivities $D_{i,\text{self}}$ for the constituents as a function of the total pore concentration, $c_t = c_1 + c_2$. The corresponding values of S_{diff} are presented in Fig. 2b. We note that the MD simulations yield S_{diff} values that vary from a value of 9 in the limit of low pore concentrations c_t, to a value of about 6 for $c_t \approx 5$ kmol m^{-3}. The decrease in the S_{diff} value with increasing c_t is attributable to diffusional correlations that tend to slow down the more mobile methane molecules [1,7].

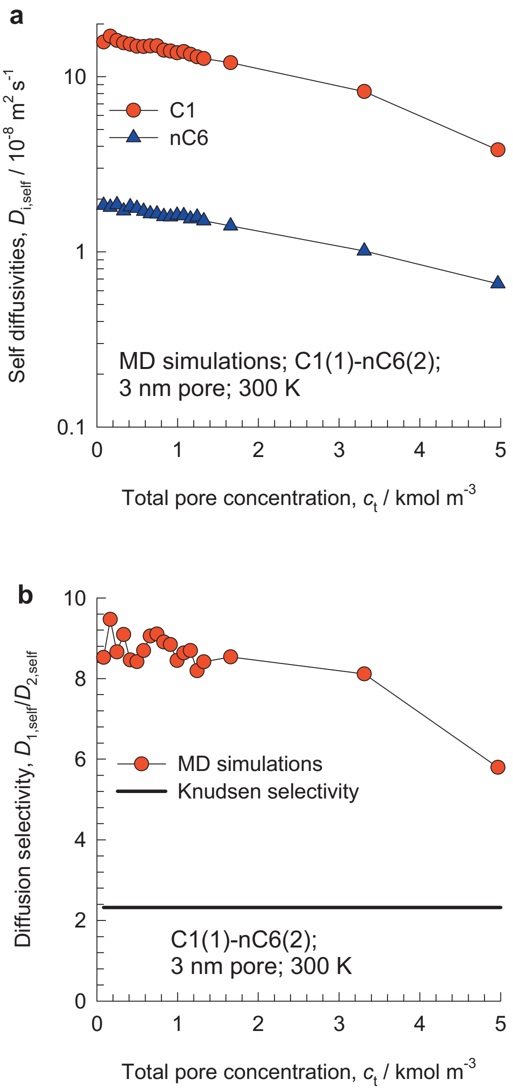

Fig. 2. (a) Self-diffusivities $D_{1,self}$, and $D_{2,self}$ in equimolar ($c_1 = c_2$) binary mixture of C1 (1) and nC6 (2) in the 3 nm cylindrical mesopore at 300 K as a function of the total pore concentration, $c_t = c_1 + c_2$. (b) The corresponding values of $S_{diff} = D_{1,self}/D_{2,self}$ are compared with the Knudsen selectivity value from Eq. (9).

Over the entire range of pore concentrations, the S_{diff} from MD are found to be significantly higher than the Knudsen selectivity value of 2.3, obtained from using Eq. (9). The higher S_{diff} is attributable to the fact that nC6 adsorbs more strongly than C1 at the pore walls. Consequently, the diffusivity of nC6 is lowered below the Knudsen prescription, given by Eq. (8), to a greater extent than is the case for C1 [8].

Data analogous to that presented in Fig. 2 were obtained for all binary mixtures investigated, and are available in the Supplementary Material accompanying this publication. From the data sets we determined that ratio of the MD simulated S_{diff} value to that of the Knudsen selectivity, given by Eq. (9); these data are presented in Fig. 3a–c for binary mixtures of C1, Ar, and C2, respectively, with different partner species.

Let us consider mixtures containing C1 with alkanes of varying chain length; see Fig. 3a. With increasing alkane chain lengths the adsorption strength increases, and consequently, the corresponding diffusivities fall increasingly below the Knudsen prescription [8]. As a consequence the S_{diff} for methane with respect with respect to its partners increases with increasing chain length of partner alkanes.

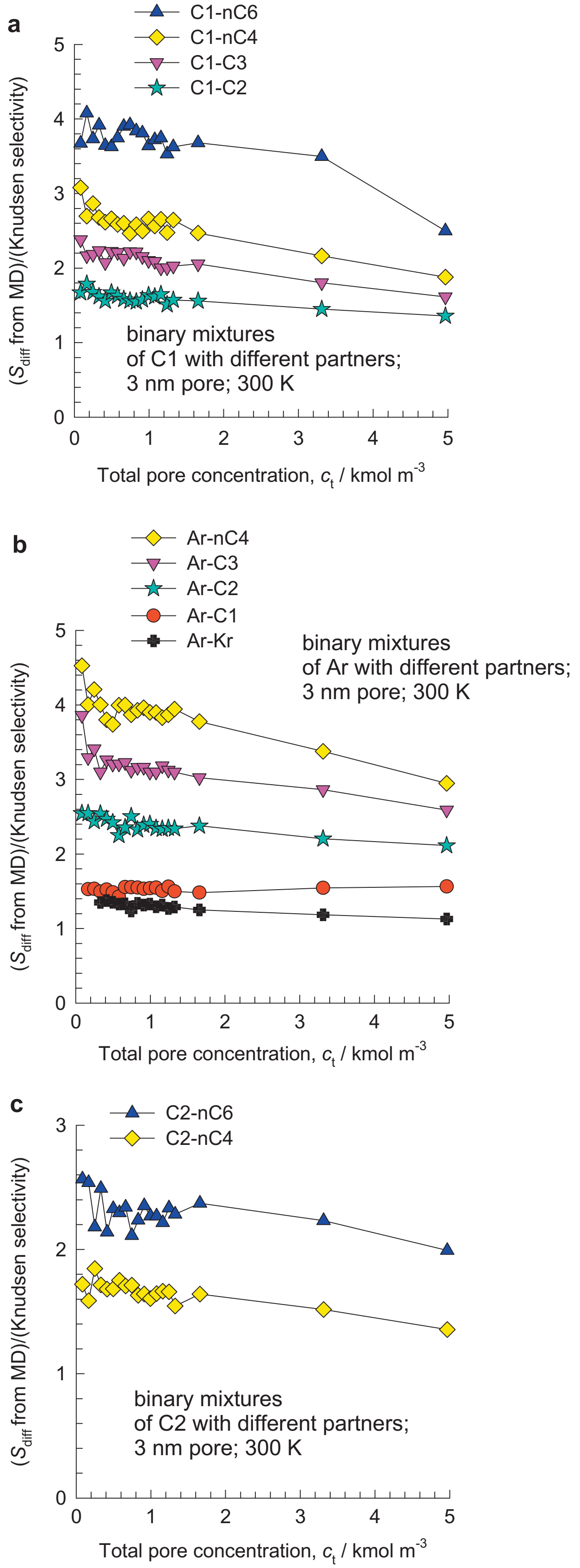

Fig. 3. The ratio of S_{diff}, obtained from MD simulations, to the Knudsen selectivity values, from Eq. (9), for (a) binary mixtures of C1, (b) Ar, and (c) C2 with a variety of partner molecules.

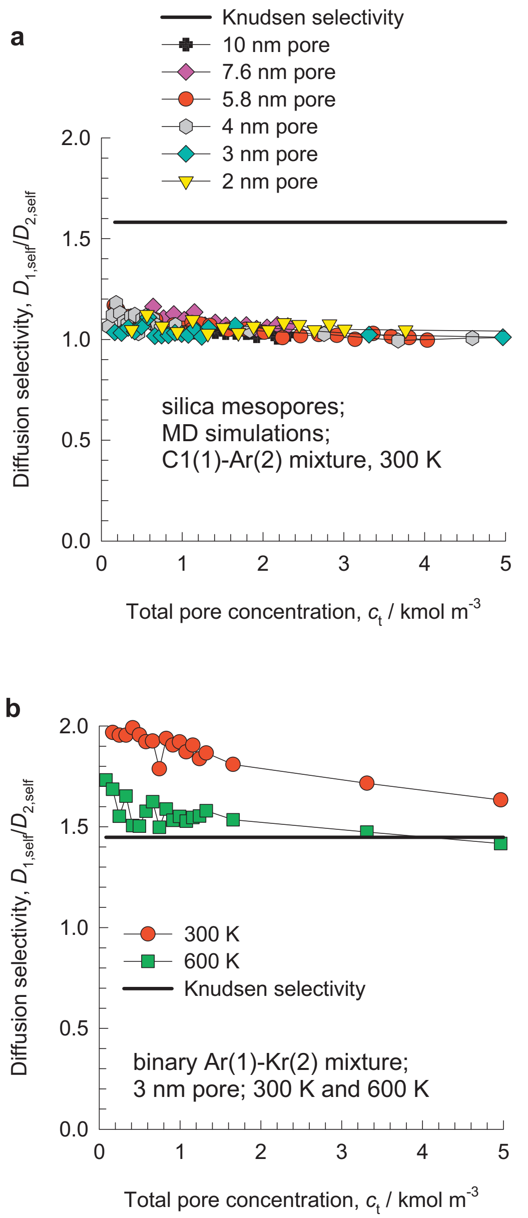

Fig. 4. (a) The diffusion selectivities, S_{diff}, for C1(1)–Ar(2) binary mixtures in silica mesopores of 2 nm, 3 nm, 4 nm, 5.8 nm, 7.6 nm and 10 nm are compared with the Knudsen selectivity value from Eq. (9). (b) The diffusion selectivities, S_{diff}, for Ar(1)–Kr(2) binary mixtures in 3 nm silica mesopore at 300 K and 600 K, compared with the Knudsen selectivity value.

Fig. 3b presents data on the ratio of S_{diff} value to that of the Knudsen selectivity for mixtures of Ar with a variety of species. An analogous picture emerges; this ratio increases with the adsorption strength of partner molecules: Kr, C1, C2, C3 and nC4.

Fig. 3c presents the corresponding data for mixtures of C2 with nC4 and with nC6. For both mixtures S_{diff} is higher than the Knudsen selectivity. The increase is higher for C2–nC6 mixture when compared to C2–nC4 mixture because of the higher adsorption strength of nC6 compared to nC4.

Let us now consider diffusion of C1(1)–Ar(2) mixture in mesopores of a variety of diameters: 2 nm, 3 nm, 4 nm, 5.8 nm, 7.6 nm and 10 nm. Eq. (9) predicts a Knudsen selectivity of 1.58 for all these pore sizes. MD simulations yield values that are significantly lower because C1 is the more strongly adsorbing species; see data presented in Fig. 4a. It is also interesting to note that MD simulations yield S_{diff} values for C1–Ar mixtures that are practically independent of pore diameter. Put another way, the deviation of the diffusion selectivity from the Knudsen prescription holds for any mesopore size.

A different way to underline the influence of adsorption on the diffusion selectivity is to consider the influence of temperature. Fig. 4b presents the data on S_{diff} for Ar(1)–Kr(2) mixtures in a 3 nm silica mesopore at temperatures of 300 K and 600 K. We note that S_{diff} at 600 K is nearly the same as the value of the Knudsen selectivity, calculated from Eq. (9). This is because the influence of adsorption is significantly reduced with increasing temperature.

The data in Figs. 2–4 underline the fact that S_{diff} can be either higher or lower than that anticipated by Eq. (9), depending on whether the species 2 is more strongly or less strongly adsorbed, compared to species 1. For binary mixture diffusion in carbon nanotubes, Düren et al. [26] have also found similar deviations from Eq. (9). Besides the influence of adsorption, these authors have attributed this to additional drag between molecules.

3. Conclusions

Molecular Dynamics simulations have been used to investigate the diffusion selectivity S_{diff} for a variety of binary mixtures in a cylindrical silica mesopores. For all binary mixtures investigated the value of S_{diff} is significantly different from the predictions of Eq. (9). When component 2 has the higher adsorption strength, S_{diff} is significantly higher than the Knudsen selectivity.

The results of our study underline the failure of the Knudsen prescription, caused by adsorption phenomena. Furthermore, the deviations from the Knudsen selectivity values in several experimental works on membrane permeation [22–25] can be rationalized on the basis of the current work.

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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.2010.12.042.

Nomenclature

b_i	langmuir adsorption constant for species i (Pa^{-1})
c_i	concentration of species i (mol m^{-3})
c_t	total concentration in mixture (mol m^{-3})
d_p	pore diameter (m)
$D_{i,self}$	self-diffusivity of species i (m^2 s^{-1})
$Đ_i$	M–S diffusivity (m^2 s^{-1})
$Đ_i(0)$	zero-loading M–S diffusivity (m^2 s^{-1})
$Đ_{ij}$	M–S exchange coefficients (m^2 s^{-1})
$D_{i,Kn}$	knudsen diffusivity of species i (m^2 s^{-1})
f_i	fluid phase fugacity of species i (Pa)
M_i	molar mass of species i (kg mol^{-1})
N_i	molar flux of species i (mol m^{-2} s^{-1})
R	gas constant (8.314 J mol^{-1} K^{-1})
S_{ads}	adsorption selectivity (dimensionless)
S_{diff}	diffusion selectivity (dimensionless)
S_{perm}	permeation selectivity (dimensionless)

x_i	mole fraction of species i in the adsorbed phase (dimensionless)
T	temperature (K)

Greek letters

ϕ	fractional pore volume of material (dimensionless)
μ_i	molar chemical potential ($\mathrm{J\,mol^{-1}}$)

Subscripts

i	referring to component i
t	referring to total mixture
Kn	referring to Knudsen

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