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Verification of the Maxwell–Stefan theory for mixture diffusion in zeolites by comparison with MD simulations

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Abstract

The Maxwell–Stefan formulation for mixture diffusion, in principle, allows us to predict the diffusion characteristics of mixtures on the basis of information of the pure component Maxwell–Stefan diffusivities at zero loading. The interaction between the diffusing, sorbed, species is taken into account by introduction of an interchange coefficient $Đ_{ij}$, which is estimated using a logarithmic interpolation formula. In the recent work of Kapteijn et al. [Chem. Eng. Sci. 55 (2000) 2923], the Maxwell–Stefan formulation has been extended to take account of differences in the saturation capacities of the constituents in the mixture. In this paper we use published molecular dynamics simulations for diffusion of mixtures of methane–perfluoromethane, methane–xenon, and methane–*n*-butane in silicalite to obtain direct verification of Maxwell–Stefan formulation. It is shown that ignoring either differences in the saturation capacities or diffusional interchange lead to significantly poorer predictions of mixture diffusion behaviour. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Maxwell–Stefan theory; Zeolites; Mixture diffusion; MD simulation

1. Introduction

The proper description of diffusive transport within zeolitic materials is of considerable importance in practice because of the many applications in catalytic reaction and separation processes [1–4]. A variety of models and techniques have been used to describe diffusion within zeolites, ranging from phenomenological models such as Fick's law of diffusion [1,2,5,6], irreversible thermodynamics [7,8] and the Maxwell–Stefan (MS) formulation [9–20] to Monte Carlo (MC) simulations [21–29] and molecular dynamics (MD) [30–42]. While MC and MD simulations are essential tools for gaining insights into diffusive transport within zeolites, such techniques are too computationally expensive to use in routine process simulations of say membrane transport or adsorber breakthrough. For process simulations, we still need to rely on phenomenological models [5–20].

The phenomenological models available in the literature for mixture diffusion in zeolites vary considerably in their complexity. The formulation of Habgood [5,6], for example, ignores the diffusional interaction, or interchange, between the constituent species. Recent experimental data on permeation of binary hydrocarbon mixtures across a silicalite membrane have emphasised the need for including the diffusional interchange [43]. Earlier formulations of the MS theory [11–16] do not account for the differences in the saturation capacities of the constituents. In a more recent paper, the MS model has been extended to include the influence of differences in saturation sorbate loadings [18].

The objectives of the present communication are twofold. Firstly, we aim to show that the published MD simulation results for mixture diffusivities obey simple mixture rules which can be derived from MS diffusion formulation. Secondly, we underline the influence of differences in saturation sorbate loadings on mixture diffusion.

We begin with a refresher of the MS theory and derive simple formula to describe self-diffusivities in mixtures; these formula are later compared with MD simulation results.

2. The MS theory of diffusion in zeolites

The essential concepts behind a general constitutive relation for diffusion in multicomponent mixtures were already available more than a century ago following the pioneering works of Maxwell [9] and Stefan [10]. These ideas have been applied to describe diffusion of *n* species within a zeolite matrix using the following set of equations [11–20]:

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Nomenclature

$[B]$	square matrix of inverse Maxwell–Stefan coefficients (m^{-2} s)
$[D]$	matrix of Fick diffusivities ($m^2\,s^{-1}$)
D_1	Fick diffusivity of component 1 in zeolite ($m^2\,s^{-1}$)
D_{12}	Fick diffusivity of 1–2 binary in fluid mixture ($m^2\,s^{-1}$)
$Đ_i$	Maxwell–Stefan diffusivity of species i in zeolite ($m^2\,s^{-1}$)
$D_{i,\mathrm{eff}}$	effective Fick diffusivity for component i diffusing in a zeolite ($m^2\,s^{-1}$)
$Đ_{ij}$	Maxwell–Stefan diffusivity describing interchange between i and j ($m^2\,s^{-1}$)
f_i	fugacity of species i; $f_i = p_i$ for ideal gases (Pa)
n	number of diffusing species (dimensionless)
$\mathbf{N}_i$	molar or molecular flux of species i (molecules $m^{-2}\,s^{-1}$)
p_i	partial pressure of species i (Pa)
$[R]$	matrix defined by Eq. (14) ($m^2\,s^{-1}$)
$\mathbb{R}$	gas constant (8.314 J $mol^{-1}\,K^{-1}$)
T	absolute temperature (K)
z	number of nearest neighbour sites (dimensionless)

Greek letters

Γ	thermodynamic correction factor (dimensionless)
$[\Gamma]$	matrix of thermodynamic factors (dimensionless)
θ_i	fractional surface occupancy of component i
Θ_i	molecular loading (molecules per unit cell or per cage)
$\Theta_{i,\mathrm{sat}}$	saturation loading (molecules per unit cell or per cage)
$\Theta_{i,\mathrm{sat\,A}}$	maximum loading of site A (molecules per unit cell)
$\Theta_{i,\mathrm{sat\,B}}$	maximum loading of site B (molecules per unit cell)
λ	lateral displacement (m)
μ_i	molar chemical potential (J mol^{-1})
ν	jump frequency (s^{-1})
π	spreading pressure (Pa m)
ρ	density of zeolite (number of unit cells per m^3)

Subscripts

1	component 1 in binary mixture
2	component 2 in binary mixture
eff	effective parameter
i, j	components in mixture
max	referring to maximum loading
sat	referring to saturation conditions

Superscripts

0	pure component parameter

Vector and matrix notation

()	component vector
[ ]	square matrix

Operators

∇	gradient or nabla

$$-\rho\frac{\theta_i}{\mathbb{R}T}\nabla\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\Theta_j\mathbf{N}_i-\Theta_i\mathbf{N}_j}{\Theta_{i,\mathrm{sat}}\Theta_{j,\mathrm{sat}}Đ_{ij}}+\frac{\mathbf{N}_i}{\Theta_{i,\mathrm{sat}}Đ_i},\quad i=1,2,\ldots,n \tag{1}$$

where ρ is the zeolite matrix density expressed as unit cells per m^3, θ_i represents the loading expressed in molecules of sorbate per unit cell of zeolite, $\theta_{i,\mathrm{sat}}$ is the saturation loading of species i, $\mathbb{R}$ the gas constant and T the temperature. $\nabla\mu_i$ is the gradient of the chemical potential of species i, which is the fundamental driving force for diffusion. The fractional occupancy θ_i of the sorbate within the zeolite matrix is defined as

$$\theta_i \equiv \frac{\Theta_i}{\Theta_{i,\mathrm{sat}}},\quad i=1,2,\ldots,n \tag{2}$$

In general the saturation loadings of the various species $\Theta_{i,\mathrm{sat}}$ in the mixture will be different from one another. $\mathbf{N}_i$ are the molecular fluxes expressed in terms of molecules transported per square meter per second.

In the MS formulation for zeolite diffusion, Eq. (1), we have to reckon in general with two types of MS diffusivities: $Đ_{ij}$ and $Đ_i$. The $Đ_i$ are the diffusivities which reflect interactions between species i and the zeolite matrix. Mixture diffusion introduces an additional complication due to sorbate–sorbate interactions. This interaction is embodied in the coefficients $Đ_{ij}$. We can consider this coefficient as representing the facility for counter-exchange, i.e. at a sorption site the sorbed species j is replaced by the species i. The net effect of this counter-exchange is a slowing down of a faster moving species due to interactions with a species of lower mobility. Also, a species of lower mobility is accelerated by interactions with another species of higher mobility.

The MS formulation of single component diffusion, can be derived from Eq. (1) by setting $n = 1$:

$$\mathbf{N}_1 = -\rho\Theta_{\mathrm{sat}}Đ_1\left(\frac{\theta_1}{\mathbb{R}T}\nabla\mu_1\right) \tag{3}$$

where μ_1 is the chemical potential of the sorbed species 1. Assuming equilibrium between the sorbed species and the bulk fluid phase we have the following relationship for the chemical potential μ_1:

$$\mu_1 = \mu_1^0 + RT\ln(f_1) \tag{4}$$

where μ_1^0 is the chemical potential in the chosen standard state and f_1 the fugacity. For not too high system pressures the component partial pressure, p_1, can be used in place of the component fugacity, f_1, i.e. $f_1 \approx p_1$. The chemical potential gradients may be expressed in terms of the gradients of the fractional occupancy, $\nabla\theta_1$,

$$\frac{1}{RT}\nabla\mu_1 = \frac{1}{\theta_1}\Gamma\nabla\theta_1, \quad \Gamma \equiv \theta_1\frac{\partial \ln p_1}{\partial\theta_1} \tag{5}$$

where Γ is the thermodynamic correction factor. Introducing Eq. (5) into Eq. (3) we obtain:

$$\mathbf{N}_1 = -\rho\Theta_{1,\mathrm{sat}}D_1\nabla\theta_1 = -\rho\Theta_{1,\mathrm{sat}}\text{Đ}_1\Gamma_1\nabla\theta_1 \tag{6}$$

D_1 is termed the transport or the Fick diffusivity. Đ_1 is variously called the MS, "corrected" or "jump" diffusivity [1,16]. These two diffusivities are inter-related:

$$D_1 = \text{Đ}_1\Gamma \tag{7}$$

Mechanistically, the MS diffusivity Đ_1 may be related to the displacement of the adsorbed molecular species, λ, and the jump frequency, ν, which in general can be expected to be dependent on the total coverage [21]

$$\text{Đ}_1 = \frac{1}{z}\lambda^2\nu \tag{8}$$

where z represent the number of nearest neighbour sites. The jump frequency ν can be expected to decrease with occupancy. If we assume that a molecule can migrate from one site to another only when the receiving site is vacant, the chance that this will occur will be a function of the fraction of unoccupied sites. A general form of the MS diffusion equation is therefore

$$\text{Đ}_1 = \text{Đ}_1(0)f(1-\theta_1) \tag{9}$$

where $\text{Đ}_1(0)$ represents the MS diffusivity in the limit of zero loading and $f(1-\theta_1)$ is some function of the fraction of unoccupied sites.

The simplest model for the dependence of the MS diffusivity Đ_1 with occupancy is that it is independent of molecular loading within the zeolite:

$$\text{Đ}_1 = \text{Đ}_1(0) \tag{10}$$

This is indeed found experimentally to be true in several cases [1].

Often in experiments and simulations, the self- or tracer diffusivity of species 1 is determined under conditions where there is no net gradient, $\nabla\theta_1 \equiv 0$. The self-diffusivity shows a decreasing trend with molecular loading, see Fig. 1(a) and (b) for MD simulation results of CH_4, CF_4 and xenon in silicalite [32,33]. Monte Carlo simulations have been used recently to show the inter-relationship between self-, MS and transport diffusivities [29], see Fig. 1(c). The self-diffusivity is influenced by correlation effects whereas such correlation effects do not affect the MS and Fick diffusivities. We note that the MS diffusivities follow the simple linear relationship:

$$\text{Đ}_1 = \text{Đ}_1(0)(1-\theta_1) \tag{11}$$

where $\text{Đ}_1(0)$ represents the MS diffusivity in the limit of zero loading. At zero loading, all three diffusivities, self-, MS and Fick are equal to one another. This zero loading diffusivity can be determined experimentally or by use of transition state theory [44–46].

For a binary mixture, $n = 2$, Eq. (1) may be cast into two-dimensional matrix notation to give

$$\mathbf{N} = -\rho[\Theta_{\mathrm{sat}}][B]^{-1}[\Gamma]\nabla(\theta) = -\rho[\Theta_{\mathrm{sat}}][D]\nabla(\theta) \tag{12}$$

where $[D]$ is the two-dimensional Fick diffusivity matrix and $[\Theta_{\mathrm{sat}}]$ is a diagonal matrix with the saturation loadings $\Theta_{i,\mathrm{sat}}$. The matrix $[B]$ has the elements

$$B_{ii} = \frac{1}{\text{Đ}_i} + \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\theta_j}{\text{Đ}_{ij}}, \qquad B_{ij} = -\frac{\theta_i}{\text{Đ}_{ij}},$$
$$i, j = 1, 2, \ldots, n \tag{13}$$

Taking the inverse of matrix $[B]$ and denoting this as $[R]$, we obtain

$$[B]^{-1} \equiv [R] = \frac{1}{(1+\theta_1(\text{Đ}_2/\text{Đ}_{12}) + \theta_2(\text{Đ}_1/\text{Đ}_{12}))} \times \begin{bmatrix} \text{Đ}_1 + \theta_1\dfrac{\text{Đ}_1\text{Đ}_2}{\text{Đ}_{12}} & \theta_1\dfrac{\text{Đ}_1\text{Đ}_2}{\text{Đ}_{12}} \\ \theta_2\dfrac{\text{Đ}_1\text{Đ}_2}{\text{Đ}_{12}} & \text{Đ}_2 + \theta_2\dfrac{\text{Đ}_1\text{Đ}_2}{\text{Đ}_{12}} \end{bmatrix} \tag{14}$$

A procedure for the estimation of the counter-exchange coefficient Đ_{12} has been suggested by Krishna and Wesselingh [16]:

$$\text{Đ}_{12} = [\text{Đ}_1]^{\theta_1/(\theta_1+\theta_2)}[\text{Đ}_2]^{\theta_2/(\theta_1+\theta_2)} \tag{15}$$

The matrix $[\Gamma]$ is the thermodynamic correction factor matrix, which can be determined from the mixture isotherm:

$$\Gamma_{ij} \equiv \left(\frac{\Theta_{j,\mathrm{sat}}}{\Theta_{i,\mathrm{sat}}}\right)\frac{\Theta_i}{p_i}\frac{\partial p_i}{\partial\Theta_j}, \quad i, j = 1, 2, \ldots, n \tag{16}$$

When the saturation loadings of the two components, $\Theta_{i,\mathrm{sat}}$, are equal to each other, and the isotherms of the pure components can be described by a single-site Langmuir isotherm, the matrix of thermodynamic correction factors can be determined from

$$[\Gamma] = \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} = \begin{bmatrix} 1-\theta_2 & \theta_1 \\ \theta_2 & 1-\theta_1 \end{bmatrix}(1-\theta_1-\theta_2)^{-1} \tag{17}$$

In the general case, when the saturation loadings of the two components are different we must use the ideal adsorbed solution theory to calculate the mixture isotherms [18]. However, we have established after several numerical computations that Eq. (17) can also be used with acceptable accuracy for the general case where the saturation loadings of the constituents are different, provided the fractional occupancies are calculated using Eq. (2).

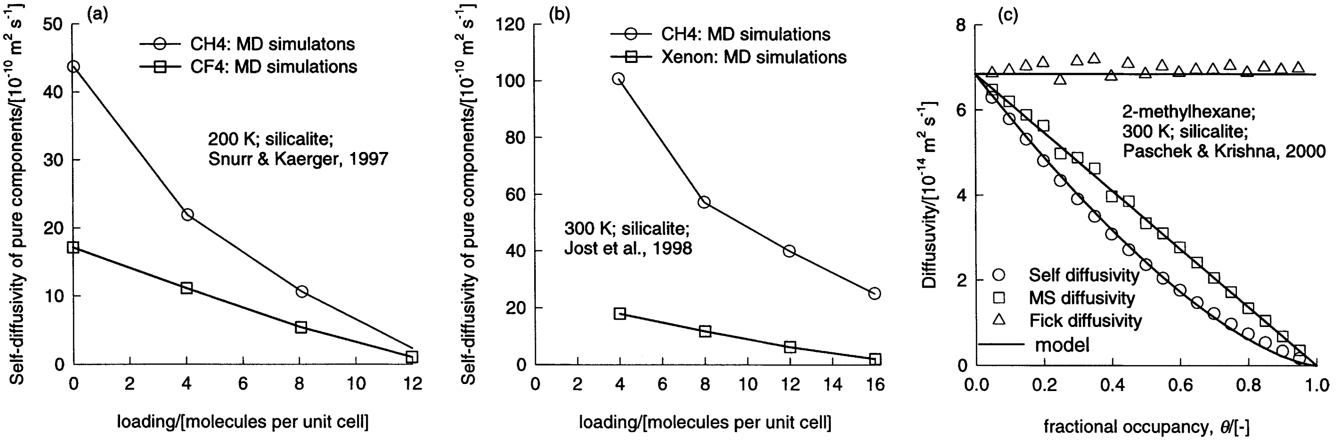


Fig. 1. (a) Self-diffusivities of pure components CH_4 and CF_4 in silicalite-1 at 200 K. MD simulations of Snurr and Kärger [32]. (b) Self-diffusivities of pure components CH_4 and xenon in silicalite-1 at 300 K. MD simulations of Jost et al. [33]. (c) Monte Carlo simulations of self-, MS and Fick diffusivities of 2-methylhexane (2MH) in silicalite at 300 K [29]. The saturation capacity of 2MH is 4 molecules per unit cell.

We could force-fit Eq. (12) for the two fluxes $\mathbf{N}_i$ into the form of Fick's law for each species with effective diffusivities:

$$\mathbf{N}_i = -\rho\Theta_{\text{sat}} D_{i,\text{eff}} \nabla\theta_i, \quad i = 1, 2 \tag{18}$$

where the effective Fick diffusivities of components 1 and 2 are given by

$$D_{1,\text{eff}} = D_{11} + D_{12}\frac{\nabla\theta_2}{\nabla\theta_1} \tag{19}$$

$$D_{2,\text{eff}} = D_{21}\frac{\nabla\theta_1}{\nabla\theta_2} + D_{22} \tag{20}$$

For self-diffusivity measurements or simulations, the sum of the gradients vanishes, i.e.

$$\nabla\theta_1 + \nabla\theta_2 = 0 \tag{21}$$

and therefore the expression for the self-diffusivities of components 1 and 2 simplify to

$$\begin{aligned}\begin{pmatrix} D_{1,\text{eff}} \\ D_{2,\text{eff}} \end{pmatrix} &= \begin{pmatrix} D_{11} - D_{12} \\ D_{22} - D_{21} \end{pmatrix} \\ &= \begin{pmatrix} R_{11}\Gamma_{11} + R_{12}\Gamma_{21} - R_{11}\Gamma_{12} - R_{12}\Gamma_{22} \\ R_{21}\Gamma_{12} + R_{22}\Gamma_{22} - R_{21}\Gamma_{11} - R_{22}\Gamma_{21} \end{pmatrix}\end{aligned} \tag{22}$$

For the situation in which Eq. (17) applies, Eq. (22) further simplifies, yielding

$$\begin{aligned}\begin{pmatrix} D_{1,\text{eff}} \\ D_{2,\text{eff}} \end{pmatrix} &= \begin{pmatrix} R_{11} - R_{12} \\ R_{22} - R_{21} \end{pmatrix} \\ &= \frac{1}{1 + \theta_1(Đ_2/Đ_{12}) + \theta_2(Đ_1/Đ_{12})}\begin{pmatrix} Đ_1 \\ Đ_2 \end{pmatrix}\end{aligned} \tag{23}$$

Eq. (23) represents a remarkably simple result which shows that the self-diffusivities in a binary mixture are not affected by thermodynamic factors and can be determined purely from the knowledge of $Đ_1$, $Đ_2$ and $Đ_{12}$. Extending Eq. (11) to binary mixtures we take

$$\begin{aligned} Đ_1 &= Đ_1(0)(1 - \theta_1 - \theta_2), \\ Đ_2 &= Đ_2(0)(1 - \theta_1 - \theta_2) \end{aligned} \tag{24}$$

and use Eq. (15) for determination of the counter-exchange coefficient $Đ_{12}$.

If the interactions between the diffusing species are ignored and the Habgood formulations [5,6] are used we obtain the following simplified expressions for the self-diffusivities in the mixture

$$\begin{pmatrix} D_{1,\text{eff}} \\ D_{2,\text{eff}} \end{pmatrix} = \begin{pmatrix} Đ_1 \\ Đ_2 \end{pmatrix} \tag{25}$$

3. Verification of Eq. (23) using MD mixture simulations

We first consider the MD simulations of Snurr and Kärger [32] for CH_4 (1) and CF_4 (2) at 200 K in silicalite at a total mixture loading of 12 molecules per unit cell. They performed MD simulations for mixtures in which the methane loading is varied from 0–12 molecules per unit cell; their simulation data are shown in Fig. 2. We will try to predict the mixture behaviour from pure component data. The pure component self-diffusivities are shown in Fig. 1(a). Methane being a smaller molecule has a higher saturation loading than that of CF_4; we therefore take $\Theta_{1,\text{sat}} = 22$ and $\Theta_{2,\text{sat}} = 12$ on the basis of information on mixture isotherms [35]. The pure component diffusivities at zero loading are estimated from Fig. 1(a) as $Đ_1(0) = 6 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$, $Đ_2(0) = 3 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}$. The calculations of the diffusivities $D_{1,\text{eff}}$ and $D_{2,\text{eff}}$ using Eqs. (15), (23) and (24) show excellent agreement with the MD simulations of Snurr and Kärger [32], see Fig. 2(a). The use of Eq. (15) for the interchange

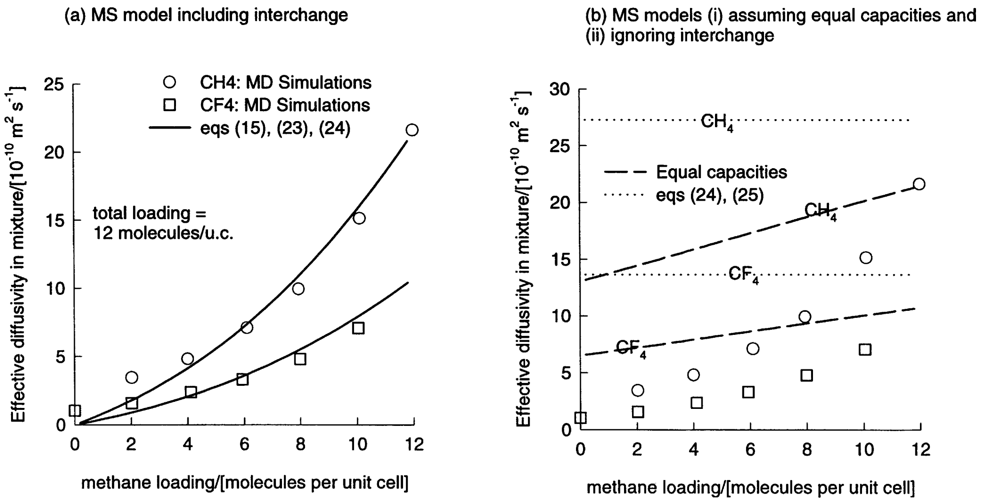


Fig. 2. Comparison of MD mixture simulations of Snurr and Kärger [32] for CH_4 and CF_4 in silicalite-1 at 200 K with estimations using MS theory.

coefficient, as suggested by Krishna and Wesselingh [16] is therefore justified. In Fig. 2(b) the calculations are repeated wherein the saturation capacities are forced to be equal to 22. The calculations of $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$ are much worse than in (a). This underlines the influence of differences in saturation capacities on mixture diffusion. Also shown in Fig. 2(b) are calculations in which the interchange coefficient is ignored; in this case $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$ are given by Eq. (25). The agreement with the MD simulations are very poor. Clearly, it is important to take the interchange into account.

Jost et al. [33] have published MD simulations for the self-diffusivities in mixtures of CH_4 (1) and xenon (2) at 300 K. Their MD data for a total mixture loading of eight are shown in Fig. 3. We now attempt to use the MS theory to predict the mixture behaviour. The pure component self-diffusivities are shown in Fig. 1(b). The saturation loadings are estimated as $\Theta_{1,\mathrm{sat}} = 22$ and $\Theta_{2,\mathrm{sat}} = 16$. The pure component diffusivities at zero loading are estimated from Fig. 1(b) as $Đ_1(0) = 12 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$, $Đ_2(0) = 4 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$. The calculations of the diffusivities $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$ using Eqs. (15), (23) and (24) show good agreement with the MD simulations of Jost et al. [33], see Fig. 3(a). The use of Eq. (15) for the interchange coefficient, as suggested by Krishna and Wesselingh [16] is therefore justified. In Fig. 3(b) the calculations are repeated wherein the saturation capacities are forced to be equal to 22. The calculations of $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$ are much worse than in (a). This underlines the influence of differences in saturation capacities on mixture diffusion. Also shown in Fig. 3(b) are calculations in which the interchange coefficient is ignored; in this case $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$ are given by Eq. (25). The agreement with the MD simulations are again much poorer.

Gergidis and Theodorou [38] have performed two sets of MD simulations for the self-diffusivities in the mixture of

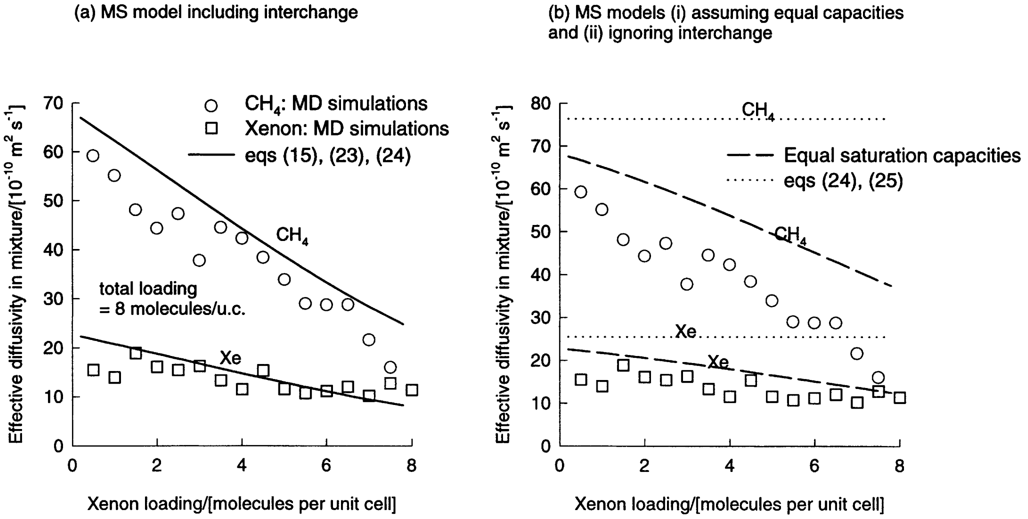
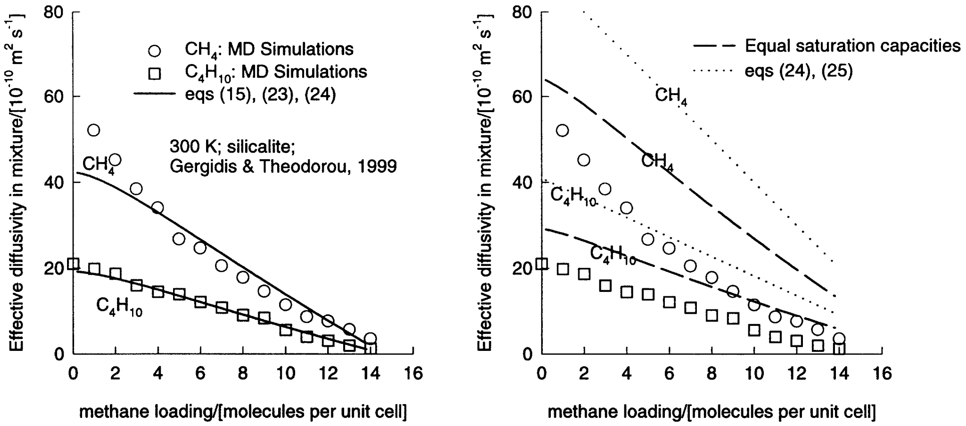
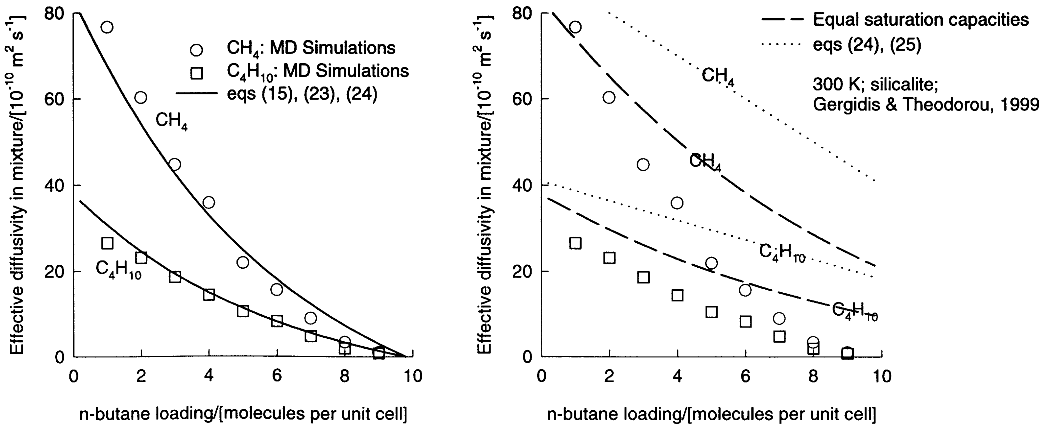


Fig. 3. Comparison of MD mixture simulations of Jost et al. [33] for CH_4 and xenon in silicalite at 300 K with estimations using MS theory.


(a) n-butane loading = 4;
MS model including interchange

(b) n-butane loading = 4;
MS models (i) assuming equal capacities
and (ii) ignoring interchange


(c) methane loading = 4;
MS model including interchange

(d) methane loading = 4;
MS models (i) assuming equal capacities
and (ii) ignoring interchange

Fig. 4. Comparison of MD mixture simulations of Gergidis and Theodorou [38] for the mixture of CH_4 (1) and *n*-butane (2) in silicalite with estimations using MS theory.

CH_4 (1) and *n*-butane (2) at 300 K in silicalite, see Fig. 4. In the first set (Fig. 4(a) and (b)) the *n*-butane loading is kept constant at 4 molecules per unit cell and the methane loading is varied. In the second set (see Fig. 4(c) and (d)) the methane loading is kept constant at 4 molecules per unit cell and the *n*-butane loading is varied. We now attempt to model the self-diffusivities using the MS formulations developed above. The saturation loadings are estimated as $\Theta_{1,\mathrm{sat}} = 22$ and $\Theta_{2,\mathrm{sat}} = 12$. The pure component diffusivities at 300 K are taken as $\text{Đ}_1(0) = 11 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ and $\text{Đ}_2(0) = 5 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ on the basis of the data presented by Gergidis and Theodorou [38]. The calculations of the diffusivities in the mixture, $D_{1,\mathrm{eff}}$ and $D_{2,\mathrm{eff}}$, using Eqs. (15), (23) and (24) show excellent agreement with the MD simulations of Gergidis and Theodorou [38] for the both sets of simulations reported, see Fig. 4(a) and (c). In Fig. 4(b) and (d), we test simpler models in which (i) the saturation capacities are both taken to be 22 and (ii) the interchange is ignored. Both these simplifications lead to substantially poorer predictions of the mixture diffusion behaviour.

4. Conclusions

Using the MS theory for binary mixture diffusion in zeolites we have developed explicit formulae, Eqs. (19) and (20), for calculation of the diffusivities of the components in the mixture. For situations in which the sum of the gradients of the two species is maintained as zero, these expressions simplify considerably to yield Eq. (23) which, when used in conjunction with Eq. (15) for estimation of the counter-exchange coefficient Đ_{12}, allows the estimation of the mixture diffusivities purely on the basis of the zero-loading diffusivities $\text{Đ}_i(0)$. The validity of Eq. (23) has been demonstrated by comparing with published MD mixture simulations for mixtures of methane–xenon, methane–perfluoromethane and methane–*n*-butane in silicalite.

We have also established the importance of taking proper account of the differences in the saturation capacities of the constituents; taking these to be equal leads to significantly poorer predictions of mixture diffusion performance. Ignoring the interchange coefficient, embodied in $Đ_{12}$, also leads to much poorer predictions. We conclude that the MS formulations, including interchange, are sufficiently accurate for use in chemical process design.

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References

[1] J. Kärger, D.M. Ruthven, Diffusion in Zeolites, Wiley, New York, 1992.

[2] D.M. Ruthven, S. Farooq, K.S. Knaebel, Pressure Swing Adsorption, VCH Publishers, New York, 1994.

[3] R. Krishna, B. Smit, T.J.H. Vlugt, Sorption-induced diffusion-selective separation of hydrocarbon isomers using silicalite, J. Phys. Chem. A 102 (1998) 7727–7730.

[4] T.J.H. Vlugt, R. Krishna, B. Smit, Molecular simulations of adsorption isotherms of linear and branched alkanes and their mixtures in silicalite, J. Phys. Chem. B 103 (1999) 1102–1118.

[5] H.W. Habgood, The kinetics of molecular sieve action. Sorption of nitrogen–methane mixtures by Linde molecular sieve 4A, Can. J. Chem. 36 (1958) 1384–1397.

[6] G.F. Round, H.W. Habgood, R. Newton, A numerical analysis of surface diffusion in a binary adsorbed film, Separation Sci. 1 (1966) 219–244.

[7] R.T. Yang, Y.D. Chen, Y.T. Yeh, Predictions of cross-term coefficients in binary diffusion: diffusion in zeolite, Chem. Eng. Sci. 46 (1991) 3089–3099.

[8] N. Sundaram, R.T. Yang, Binary diffusion of unequal sized molecules in zeolites, Chem. Eng. Sci. 55 (2000) 1747–1754.

[9] J.C. Maxwell, On the dynamical theory of gases, Phil. Trans. R. Soc. 157 (1866) 49–88.

[10] J. Stefan, Über das Gleichgewich und die Bewegung, insbesondere die Diffusion von Gasmengen, Sitzungsber. Akad. Wiss. Wien 63 (1871) 63–124.

[11] R. Krishna, Multicomponent surface diffusion of adsorbed species. A description based on the generalized Maxwell–Stefan diffusion equations, Chem. Eng. Sci. 45 (1990) 1779–1791.

[12] R. Krishna, Problems and pitfalls in the use of the Fick formulation for intraparticle diffusion, Chem. Eng. Sci. 48 (1993) 845–861.

[13] R. Krishna, A unified approach to the modelling of intraparticle diffusion in adsorption processes, Gas Separation and Purification 7 (1993) 91–104.

[14] R. Krishna, L.J.P. van den Broeke, The Maxwell–Stefan description of mass transport across zeolite membranes, Chem. Eng. J. 57 (1995) 155–162.

[15] L.J.P. Van den Broeke, R. Krishna, Experimental verification of the Maxwell–Stefan theory for micropore diffusion, Chem. Eng. Sci. 50 (1995) 2507–2522.

[16] R. Krishna, J.A. Wesselingh, The Maxwell–Stefan approach to mass transfer, Chem. Eng. Sci. 52 (1997) 861–911.

[17] R. Krishna, T.J.H. Vlugt, B. Smit, Influence of isotherm inflection on diffusion in silicalite, Chem. Eng. Sci. 54 (1999) 1751–1757.

[18] F. Kapteijn, J.A. Moulijn, R. Krishna, The generalized Maxwell–Stefan model for diffusion in zeolites: sorbate molecules with different saturation loadings, Chem. Eng. Sci. 55 (2000) 2923–2930 .

[19] R. Krishna, D. Paschek, Permeation of hexane isomers across ZSM-5 zeolite membranes, Ind. Eng. Chem. Res. 39 (2000) 2618–2622.

[20] J.A. Wesselingh, R. Krishna, Mass Transfer in Multicomponent Mixtures, Delft University Press, Delft, 2000.

[21] E. Aust, K. Dahlke, G. Emig, Simulation of transport and self-diffusion in zeolites with the Monte Carlo method, J. Catal. 115 (1989) 86–97.

[22] L.J.P. Van den Broeke, S.A. Nijhuis, R. Krishna, Monte Carlo simulations of diffusion in zeolites and comparison with the generalized Maxwell–Stefan theory, J. Catal. 136 (1992) 463–477.

[23] M.G. Palekar, R.A. Rajadhyaksha, Sorption in zeolites. I. Sorption of single component and binary sorbate systems, Chem. Eng. Sci. 40 (1985) 1085–1091.

[24] M.G. Palekar, R.A. Rajadhyaksha, Sorption in zeolites. III. Binary sorption, Chem. Eng. Sci. 41 (1986) 463–468.

[25] C. Saravanan, S.M. Auerbach, Modeling the concentration dependence of diffusion in zeolites. 2. Kinetic Monte Carlo simulations of benzene in Na-Y, J. Chem. Phys. 107 (1997) 8132–8137.

[26] S.M. Auerbach, Theory and simulation of jump dynamics, diffusion and phase equilibrium in nanopores, Int. Rev. Phys. Chem. 19 (2000) 155–198.

[27] M.O. Coppens, A.T. Bell, A.K. Chakraborty, Effect of topology and molecular occupancy on self-diffusion in lattice models of zeolites — Monte Carlo simulations, Chem. Eng. Sci. 53 (1998) 2053–2061.

[28] M.O. Coppens, A.T. Bell, A.K. Chakraborty, Dynamic Monte Carlo and mean-field study of the effect of strong adsorption sites on self-diffusion in zeolites, Chem. Eng. Sci. 54 (1999) 3455–3463.

[29] D. Paschek, R. Krishna, Monte Carlo simulations of self- and transport-diffusivities of 2-methylhexane in silicalite, Phys. Chem. Chem. Phys. 2 (2000) 2389–2394.

[30] R. Haberlandt, S. Fritzsche, G. Peinel, K. Heinzinger, Molecular Dynamics, Vieweg, Braunschweig, 1995 (in German).

[31] S.D. Pickett, A.K. Nowak, J.M. Thomas, B.K. Peterson, J.F.P. Swift, A.K. Cheetham, C.J.J. den Ouden, B. Smit, M.F.M. Post, Mobility of adsorbed species in zeolites — a molecular dynamics simulation of xenon in silicalite, J. Phys. Chem. 94 (1990) 1233–1236.

[32] R.Q. Snurr, J. Kärger, Molecular simulations and NMR measurements of binary diffusion in zeolites, J. Phys. Chem. B 101 (1997) 6469–6473.

[33] S. Jost, N.K. Bär, S. Fritzsche, R. Haberlandt, J. Kärger, Diffusion of a mixture of methane and xenon in silicalite: a molecular dynamics study and pulse field gradient nuclear magnetic resonance experiments, J. Phys. Chem. B 102 (1998) 6375–6381.

[34] S. Fritzsche, M. Gaub, R. Haberlandt, G. Hofmann, J. Kärger, M. Wolfsberg, Methane diffusion in zeolites of structure type LTA in dependence on physical and chemical parameters — an MD study, Stud. Surf. Sci. Catal. 105 (1997) 1859–1866.

[35] M. Heuchel, R.Q. Snurr, E. Buss, Adsorption of CH_4–CF_4 mixtures in silicalite: simulation, experiment, and theory, Langmuir 13 (1997) 6795–6804.

[36] R.C. Runnebaum, E.J. Maginn, Molecular dynamics simulations of alkanes in the zeolite silicalite: evidence for resonant diffusion effects, J. Phys. Chem. B 101 (1997) 6394–6408.

[37] D. Schuring, A.P.J. Jansen, R.A. Van Santen, Concentration and chainlength dependence of the diffusivity of alkanes in zeolites studied with MD simulations, J. Phys. Chem. B 104 (2000) 941–948.

[38] L.N. Gergidis, D.N. Theodorou, Molecular dynamics simulation of *n*-butane–methane mixtures in silicalite, J. Phys. Chem. B 103 (1999) 3380–3390.

[39] L.N. Gergidis, D.N. Theodorou, H. Jobic, Dynamics of *n*-butane–methane mixtures in silicalite, using quasielastic neutron scattering and molecular dynamics simulations, J. Phys. Chem. B 104 (2000) 5541–5552.

[40] N. Raj, G. Sastre, C.R.A. Catlow, Diffusion of octane in silicalite. A molecular dynamics study, J. Phys. Chem. B 103 (1999) 11007–11015.

[41] A. Bouyermaouen, A. Bellemans, Molecular dynamics simulation of the diffusion of *n*-butane and *i*-butane in silicalite, J. Chem. Phys. 108 (1998) 2170–2172.

[42] P. Demontis, G.B. Suffritti, Structure and dynamics of zeolites investigated by molecular dynamics, Chem. Rev. 97 (1997) 2845–2878.

[43] J. Van de Graaf, F. Kapteijn, J.A. Moulijn, Modeling permeation of binary mixtures through zeolite membranes, AIChE J. 45 (1999) 497–511.

[44] C. Tunca, D.M. Ford, A transition-state theory approach to adsorbate dynamics at arbitrary loadings, J. Chem. Phys. 111 (1999) 2751–2760.

[45] B. Smit, L.D.J.C. Loyens, G.L.M.M. Verbist, Simulation of adsorption and diffusion of hydrocarbons in zeolites, Faraday Discuss. 106 (1997) 93–104.

[46] R.L. June, A.T. Bell, D.N. Theodorou, Transition-state studies of xenon and SF_6 diffusion in silicalite, J. Phys. Chem. 95 (1991) 8866–8878.