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Predicting transport diffusivities of binary mixtures in zeolites

R. Krishna *

Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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Abstract

We test the Maxwell–Stefan formulation for diffusion of multicomponent mixtures in zeolites and show that the mixture transport behaviour can be predicted on the basis of information of the pure component jump diffusivities at zero loading. The interaction between the diffusing, adsorbed, species is taken into account by introduction of interchange coefficients $Đ_{ij}$; these encapsulate the correlations in the molecular jumps. A logarithmic-interpolation formula is suggested for estimating these interchange coefficients from information on the pure component jump diffusivities. To verify the developed Maxwell–Stefan formulation we use published molecular dynamics simulation results for transport diffusivities of CH_4 and CF_4 in Faujasite at 300 K. The predictions of the Maxwell–Stefan model are in very good agreement with the MD simulation results. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In the design of zeolite based adsorption or catalytic processes, it is essential to have a proper description of diffusion of mixtures within the crystals of a zeolite (e.g. faujasite) [1–3]. For 2-component diffusion the fluxes $\mathbf{N}_i$, expressed in molecules m^{-2} s^{-1}, are related to the gradients of the fractional occupancies $\nabla\theta_i$ by the following relation:

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

where $[D]$ is the 2-dimensional square matrix of Fick diffusivities, ρ is the zeolite matrix density expressed as the number of supercages per m^3 for say faujasite, $[\Theta_{\mathrm{sat}}]$ is a diagonal matrix with elements $\Theta_{i,\mathrm{sat}}$, representing the saturation loading of species i. The fractional occupancies θ_i are defined as

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

where Θ_i represent the loading of species i expressed in molecules of sorbate per supercage.

For estimation of the fluxes $\mathbf{N}_i$ we need to estimate the 2×2 elements of $[D]$. The elements of $[D]$ are influenced not only by the species mobilities but also by the sorption thermodynamics [4]. For design purposes it is important to have a mixture diffusion theory with the capability of predicting the elements of $[D]$ from pure component transport data. Such mixture diffusion theories are almost invariably based on the theory of irreversible thermodynamics (IT) [4–7]. In the Onsager IT formulation, a linear relation is postulated between the fluxes and the chemical potential gradients

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* Fax: +31-20-525-5604.
E-mail address: krishna@science.uva.nl (R. Krishna).

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$$(\mathbf{N}) = -\rho[\Theta_{\mathrm{sat}}][L]\frac{1}{RT}(\nabla\mu), \tag{3}$$

where R is the gas constant, T is the temperature, $(\nabla\mu)$ the column matrix of chemical potential gradients, $\nabla\mu_i$, which represent the correct driving forces for diffusion, $[L]$ is the square matrix of Onsager coefficients having the units ($\mathrm{m}^2\ \mathrm{s}^{-1}$). The Onsager matrix $[L]$ is non-diagonal, in general, and the cross-coefficients portray the coupling between species diffusion. The Onsager reciprocal relations demand that the matrix $[L]$ be symmetric, i.e.,

$$L_{ij} = L_{ji}, \quad i = 1,2. \tag{4}$$

The chemical potential gradients in Eq. (3) may be expressed in terms of the gradients of the occupancies by introduction of the matrix of thermodynamic correction factors $[\Gamma]$

$$\frac{\theta_i}{RT}\nabla\mu_i = \sum_{j=1}^{n}\Gamma_{ij}\nabla\theta_j, \quad \Gamma_{ij} \equiv \frac{\theta_i}{\theta_j}\frac{\partial \ln f_i}{\partial \ln \theta_j}, \quad i,j = 1,2, \tag{5}$$

where f_i is the fugacity of component i in the bulk gas phase. Knowledge of the sorption isotherm is sufficient to allow estimation of $[\Gamma]$ and $(\nabla\mu)$. If the 2-component sorption can be described by the multicomponent Langmuir isotherm, the elements of $[\Gamma]$ are given by

$$\Gamma_{ij} = \delta_{ij} + \frac{\theta_i}{1-\theta_1-\theta_2}, \quad i,j = 1,2, \tag{6}$$

where δ_{ij} is the Kronecker delta.

Combining Eqs. (1), (5) and (6) we obtain

$$(\mathbf{N}) = -\rho[\Theta_{\mathrm{sat}}][L]\begin{bmatrix} 1/\theta_1 & 0 \\ 0 & 1/\theta_2 \end{bmatrix}[\Gamma](\nabla\theta). \tag{7}$$

Comparing Eqs. (1) and (7) we obtain the inter-relation

$$[D] = [L]\begin{bmatrix} 1/\theta_1 & 0 \\ 0 & 1/\theta_2 \end{bmatrix}[\Gamma]. \tag{8}$$

The Fick matrix $[D]$ can be estimated from knowledge of the Onsager matrix $[L]$. Unfortunately, the IT theory provides no fundamental guidelines for estimating $[L]$ from data on pure component transport coefficients. For estimation purposes, the Maxwell–Stefan (MS) approach [4,7,10,11] is the most convenient approach.

The objectives of the present communication are:

1. To demonstrate how to parameterize the MS approach from single component diffusion data, and multicomponent adsorption data.
2. To test the Maxwell–Stefan theory for estimating $[L]$ and $[D]$ by comparing with the published MD simulation results of Sanborn and Snurr [8,9] for diffusion of a binary mixture of CH_4 and CF_4 in faujasite at 300 K.

We begin with a review of the Maxwell–Stefan theory for zeolite diffusion.

2. The Maxwell–Stefan theory of diffusion in zeolites

In the Maxwell–Stefan formulation, entirely consistent with the theory of IT, the chemical potential gradients are written as linear functions of the fluxes [4,7,10,11]

$$-\rho\frac{\theta_i}{RT}\nabla\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\Theta_j\mathbf{N}_i - \Theta_i\mathbf{N}_j}{\Theta_{i,\mathrm{sat}}\Theta_{j,\mathrm{sat}}Đ_{ij}} + \frac{\mathbf{N}_i}{\Theta_{i,\mathrm{sat}}Đ_i}, \quad i = 1,2. \tag{9}$$

We have to reckon in general with two types of MS diffusivities: $Đ_i$ and $Đ_{ij}$. The $Đ_i$ are the diffusivities that reflect interactions between guest species i and the zeolite matrix; they are also referred to as jump or 'corrected' diffusivities in the literature [3,4]. For weakly confined guest molecules in a zeolite host, such as CH_4 in silicalite-1, the MS diffusivities are practically independent of molecular loading [12], and can be estimated from the zero-loading diffusivity data

$$Đ_i = Đ_i(0); \quad \text{weakly confined guest molecules.} \tag{10}$$

For tightly confined guest molecules in zeolitic hosts, the MS diffusivities decrease with molecular loading, following [13]:

$$Đ_i = Đ_i(0)(1-\theta_1-\theta_2); \quad \text{strongly confined guest molecules.} \tag{11}$$

Mixture diffusion introduces an additional complication due to sorbate–sorbate interactions.

This interaction is embodied in the coefficients $Ð_{ij}$. We can consider this coefficient as representing the facility for counter-exchange. The Onsager reciprocal relations require $Ð_{ij} = Ð_{ji}$. 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. As shown by Paschek and Krishna [14], $Ð_{ij}$ encapsulates the correlation effects associated with molecular jumps. The interchange coefficient $Ð_{ij}$ can be estimated by the logarithmic interpolation formula that has been suggested by Krishna and Wesselingh [4]

$$Ð_{ij} = [Ð_i]^{\Theta_i/(\Theta_i+\Theta_j)}[Ð_j]^{\Theta_j/(\Theta_i+\Theta_j)}. \tag{12}$$

It is convenient to define a 2-dimensional square matrix $[B]$ with elements

$$B_{ii} = \frac{1}{Ð_i} + \sum_{\substack{j=1 \\ j\neq i}} \frac{\theta_j}{Ð_{ij}}, \qquad B_{ij} = -\frac{\theta_i}{Ð_{ij}}, \quad i,j = 1,2. \tag{13}$$

With this definition of $[B]$, Eq. (9) can be cast into n-dimensional matrix form

$$(\mathbf{N}) = -\rho[\Theta_{\text{sat}}][B]^{-1}[\Gamma]\nabla(\theta) \tag{14}$$

which gives the following expressions for the Onsager and Fick matrices

$$[L] = [B]^{-1}\begin{bmatrix}\theta_1 & 0 \\ 0 & \theta_2\end{bmatrix}, \quad [D] = [B]^{-1}[\Gamma]. \tag{15}$$

For single component diffusion, Eq. (15) simplifies to

$$L_1 = Ð_1\theta_1, \quad D_1 = \frac{Ð_1}{1-\theta_1}. \tag{16}$$

If the MS diffusivity is independent of loading (cf. Eq. (10)), the Fick diffusivity D_1 increasing strongly with occupancy

$$D_1 = \frac{Ð_1(0)}{1-\theta_1}; \quad \text{weak confinement.} \tag{17}$$

The strong increase in Fick D_1 is typically observed for weakly confined guest molecules; this is exemplified by the MD simulation results for diffusion of CH_4 in silicalite-1 [11]. On the other hand, if the MS diffusivity follows the loading dependence given by Eq. (11) the Fick diffusivity will be independent of the occupancy

$$D_1 = Ð_1(0); \quad \text{strong confinement.} \tag{18}$$

Eq. (15) is the result that we have sought; it allows prediction of the elements of the Fick matrix from pure component transport data.

3. Verification of Eq. (15) using MD simulation results

Sanborn and Snurr [8] have performed MD simulations to determine the elements D_{ij} of the Fick matrix $[D]$ for the binary mixture of CH_4 (component 1) and CF_4 (component 2) in Faujasite at 300 K. A variety of total mixture loadings, 1, 2, 4 and 6 molecules per supercage were investigated for a range of mixture compositions.

The first step in the prediction procedure outlined above is to determine the saturation sorption capacities of CH_4 and CF_4. This information is contained in the MD simulation results for $\partial \ln f_i/\partial \ln \theta_j$ at a mixture loading $\Theta = \Theta_1 + \Theta_2 = 6$ molecules per supercage, see Fig. 1. The continuous lines in Fig. 1 were drawn using eqs. (5) and (6) taking the saturation capacities $\Theta_{1,\text{sat}} = 10$ and $\Theta_{2,\text{sat}} = 6.1$, respectively, for CH_4 and CF_4. The agreement of the MD simulations with the multicomponent Langmuir calculations for the thermodynamics is very good.

The next step is to determine the M-S diffusivities $Ð_i$ as a function of loading. Sanborn and Snurr [8, Table 4] report fits of the MD simulations for pure component Fick diffusivities, see Fig. 2a. The Fick diffusivity of CH_4 appears to follow the weak confinement scenario described by Eq. (17). We therefore take the MS diffusivity for CH_4 to be independent of loading (cf. Eq. (10)) with the value $Ð_1(0) = 35 \times 10^{-9}$ m²/s. The behaviour of CF_4 is more closely in line with the strong confinement scenario of Eq. (18). For *CF_4* we take the zero-loading diffusivity $Ð_2(0) = 20 \times 10^{-9}$ m²/s and assume the loading dependence given by Eq. (11). These two distinct behaviours can also be rationalized on the basis of the differences in their molecular sizes.

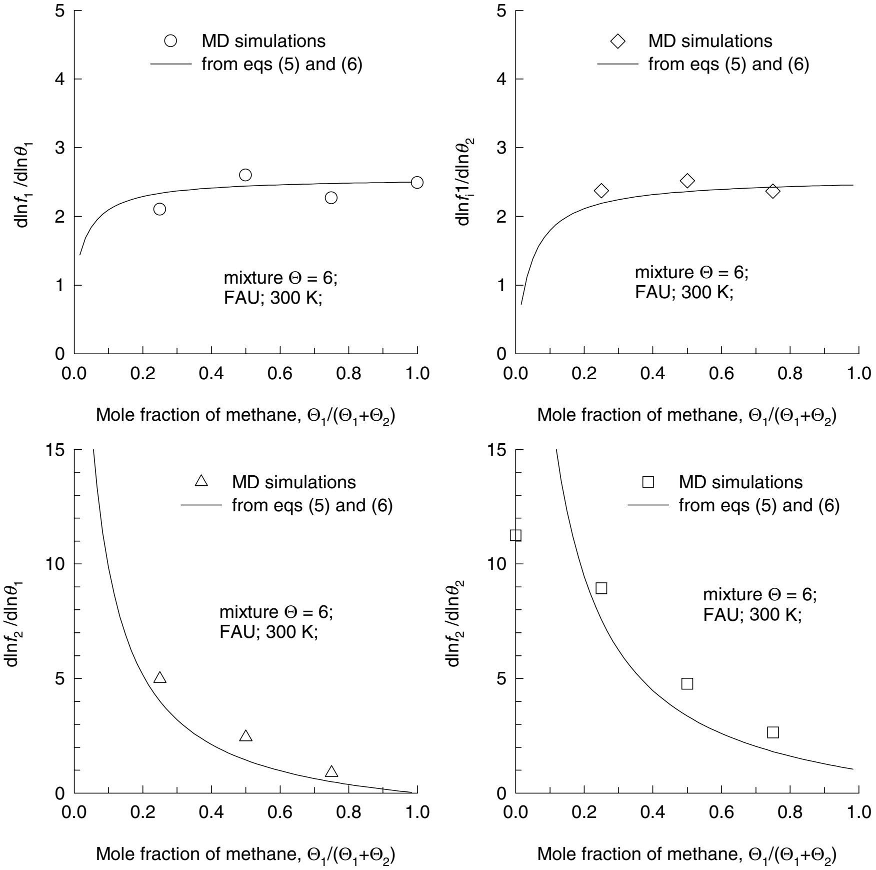

Fig. 1. Comparison of the MD simulated values of $\partial \ln f_i / \partial \ln \theta_j$ with calculations using Eqs. (5) and (6) taking $\Theta_{1,\text{sat}} = 10$ and $\Theta_{2,\text{sat}} = 6.1$ molecules.

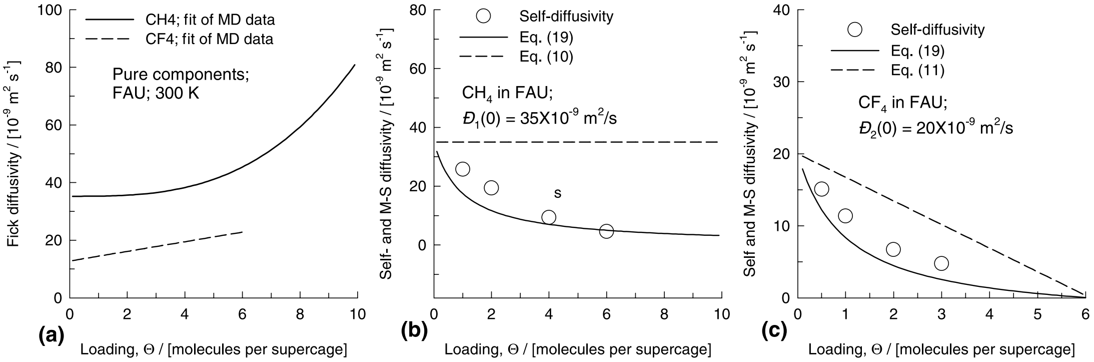

Fig. 2. (a) Pure component Fick diffusivities of CH_4 and CF_4 in faujasite at 300 K. The lines are drawn using the fitted parameters given in [8, Table 4], representing fits of MD simulations. (b) Self- and MS diffusivities of CH_4. (b) Self- and MS diffusivities of CF_4. Self diffusivity MD data from Sanborn and Snurr [9].

The self-diffusivities D_i^* of the two components, obtained from MD simulations by Sanborn and Snurr [9] in a companion publication, are shown in Fig. 2b, c. The MD simulated D_i^* values agree quite well with the relationship derived by Paschek and Krishna [14] using the MS theory

$$D_i^* = \frac{\text{Đ}_i}{1+\theta_i} = \frac{\text{Đ}_i}{1+\Theta_i/\Theta_{i,\mathrm{sat}}} \qquad (19)$$

and vindicates the chosen values of the saturation capacities $\Theta_{i,\mathrm{sat}}$; these values have been chosen to be 10 and 6.1 molecules per cage respectively for CH_4 and CF_4 on the basis of the MD data for $\partial \ln f_i / \partial \ln \theta_j$, see Fig. 1.

All the necessary data are now available to estimate the elements of the Fick matrix using Eq. (15). The calculations of D_{11}, D_{12}, D_{21} and D_{22} for a variety of compositions and loadings are presented in Fig. 3 along with the MD simulation results following Eq. (15) with the interchange coefficient being estimated using Eq. (12). The predictions of the MS theory are seen to be in good agreement with the MD simulations both with respect to the influence of mixture loading $\Theta(=1,2,4,6)$, and mixture composition $\Theta_1/(\Theta_1+\Theta_2)$. It is particularly encouraging to note that both the values and composition trends of the cross-terms D_{12} and D_{21} are predicted very well.

In order to appreciate the influence of the interchange coefficient Đ_{ij}, we consider a limiting case of facile molecule–molecule exchange, i.e., $\text{Đ}_{ij} \to \infty$. This signifies vanishing correlation ef-

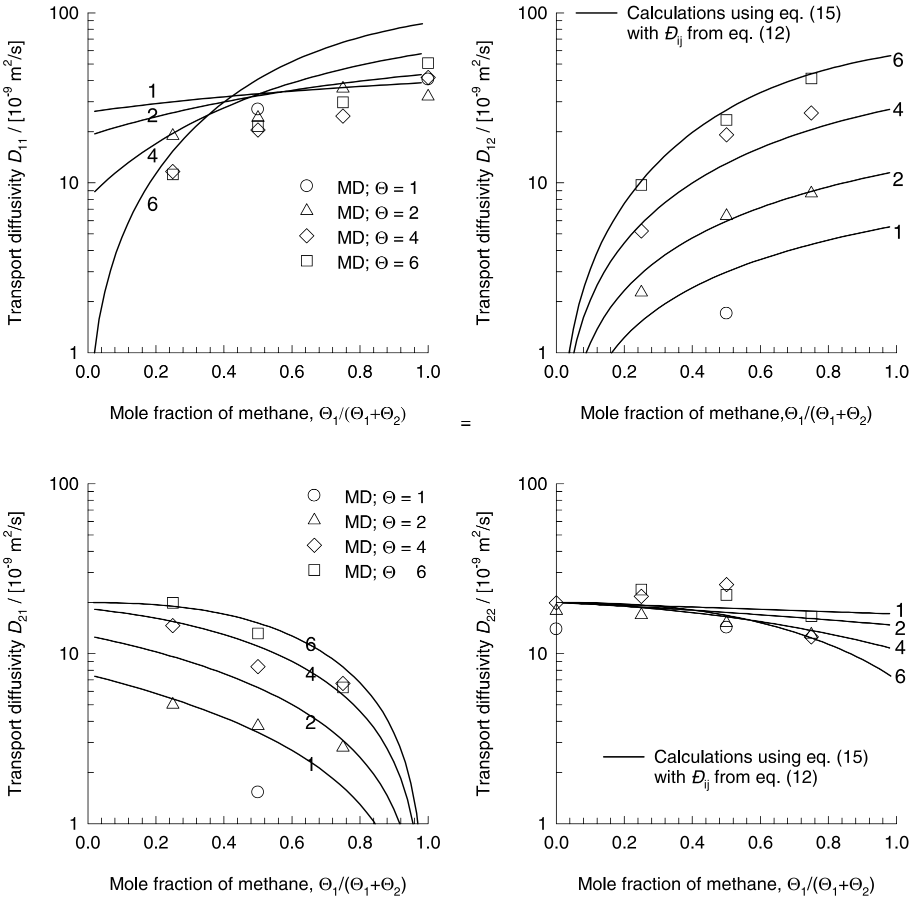

Fig. 3. Comparison of MD simulations of the Fick matrix [D] with calculations using Eq. (15). The interchange coefficients are calculated using Eq. (12).

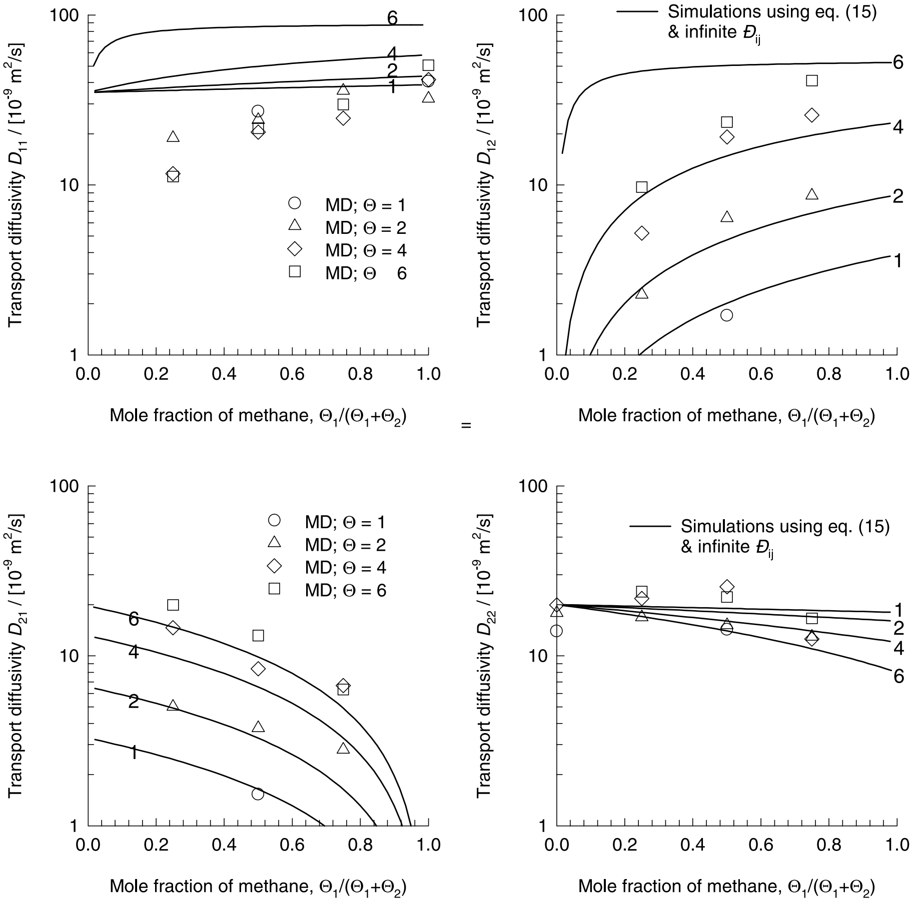

Fig. 4. Comparison of MD simulations of the Fick matrix [D] with calculations using Eq. (15), the interchange coefficient $Đ_{ij} \to \infty$.

fects during molecular jumps. We see from Eqs. (13) and (15) that if $Đ_{ij} \to \infty$, both [B] and [L] matrices reduce to diagonal matrices and the flux relations (9) simplify to give

$$\mathbf{N}_i = -\rho\Theta_{i,\mathrm{sat}}\frac{L_{ii}}{RT}\nabla\mu_i$$

$$\equiv -\rho\Theta_{i,\mathrm{sat}}Đ_i\frac{\theta_i}{RT}\nabla\mu_i, \quad i = 1,2,\ldots,n. \qquad (20)$$

The off-diagonal elements of the Onsager matrix are also a reflection of correlation effects and the assumption of vanishing off-diagonal elements of [L] signifies vanishing correlation effects. The predictions of the Fick matrix [D] for infinite $Đ_{ij}$ are shown in Fig. 4. These predictions are much worse than those witnessed in Fig. 3, with *finite* $Đ_{ij}$. In particular we note in Fig. 4 that the D_{11} values are much higher than those from MD simulations; signifying that the CH_4 is not being slowed down by CF_4 when we take $Đ_{ij} \to \infty$. Put another way, the MD simulation results of Sanborn and Snurr [8] point to a significant slowing down of CH_4, concomitant with speeding up of CF_4; these effects can only be accounted for by inclusion of a finite interchange coefficient $Đ_{ij}$.

4. Conclusions

We have tested the MS formulation for mixture diffusion in zeolites that allows the estimation of Fick transport coefficients on the basis of the pure component diffusivities at zero loading. This predictive capability has been verified by comparing with the MD simulations for diffusion of CH_4 and CF_4 in Faujasite at 300 K. The MD simulation results also underline the necessity of taking account of molecule–molecule interchange in predicting mixture diffusion. Our earlier work had performed a similar text for mixture diffusion within MFI zeolite [11]; it is heartening to note the same success with another zeolite topology, viz. faujasite. We conclude that the Maxwell–Stefan theory for multicomponent diffusion in zeolties can be used to predict mixture behaviour with good accuracy from pure component transport data.

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