Simulation of Diffusion in Zeolitic Structures

Leo J. P. van den Broeke
Dept. of Chemical Engineering, University of Amsterdam, 1018 WV Amsterdam, The Netherlands

Using Maxwell–Stefan equations, experimental and computational results of binary diffusion in pore- and cage-type zeolitic structures are described. In the generalized Maxwell–Stefan (GMS) formulation, the Fick diffusivity is written as the product of two separate contributions, the GMS or corrected diffusivity and the thermodynamic factor. The concentration dependence of the GMS diffusivity for one- and two-component diffusion in zeolitic structures is investigated. From the Maxwell–Stefan equations, different models for the Fick diffusion coefficient matrix for the description of binary mass transport in molecular sieve materials are derived. Various models used predict binary diffusion in zeolitic structures. First, theoretical predictions of binary apparent diffusivities as a function of the occupancy are compared to results from Monte Carlo simulations. Second, theoretical results of binary uptake profiles are compared to experimental results for the system ethylbenzene/benzene/ZSM-5. For different zeolitic structures, that is, pore- and cage-type structures, results of the Monte Carlo simulations agree well with the theoretical predictions. In cage-type structures, the effect of counterexchange between sorbed molecules is demonstrated. Experimental results of transient uptake profiles of a mixture of benzene and ethylbenzene in ZSM-5 follow predictions of the theoretical single-file diffusion model.

Introduction

The concentration dependence of the one-component Fick diffusion coefficient in molecular sieve materials shows a wide range of variety. The Fick diffusivity of gases in different molecular sieve materials has been found to increase with increasing occupancy, to be almost independent of occupancy, and to decrease with increasing surface occupancy for monolayer adsorption and isothermal conditions (Chen and Yang, 1991; Xiao and Wei, 1992b; Kärger and Ruthven, 1992). A number of theoretical approaches have been presented for the modeling of one-component mass transfer in molecular sieve materials, such as zeolites and carbon molecular sieves.

Chen and Yang (1991) proposed a unified model for diffusion in molecular sieve materials based on a random-walk, or hopping, mechanism. By introducing a blocking parameter, which takes blockage by other sorbed molecules on the transport process into account, the different observed behaviors of the Fick diffusivity as a function of the occupancy θ can be described. A distinction is made between surface and zeolitic diffusion. Surface diffusion is ascribed to the situation when there is no hindrance at all by other sorbed molecules on the transport process. For one-component surface diffusion like, for example, in activated carbons, the generalized Maxwell-Stefan or corrected diffusivity is then constant and the Fick diffusivity increases according to the thermodynamic factor. For Langmuir adsorption this is given by $(d \ln p / d \ln \theta) = (1 - \theta)^{-1}$. However, for zeolitic structures often a deviation from the thermodynamic factor is found (Chen and Yang, 1991). This can be attributed to the concentration dependence of the Maxwell–Stefan diffusivity. In the case of mass transfer in zeolites the transport processes are always retarded by the presence of other sorbed molecules in the zeolite structure. Therefore, the Fick diffusion coefficients of gases in zeolites increase less rapidly with occupancy as compared to the surface diffusion coefficient, under the condition of no interactions between adsorbed molecules.

Tsikoyiannis and Wei (1990) used the theory of Markov processes to model diffusion and reaction in zeolites. The Markov theory was applied to a system where only one molecule can occupy a site. For different site–site and transition–site interactions the different dependencies of the one-component Fick diffusivity on occupancy can be described. In addition to the three different behaviors of the diffusivity just mentioned, two other dependencies of the Fick diffusivity on occupancy were found. For repulsive interactions it was found

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L. J. P. van den Broeke is currently at the Dept. of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands.

that the diffusivity first increases and then decreases with increasing occupancy and for attractive interactions it is possible to have a diffusivity that first decreases and then increases with occupancy. Xiao and Wei (1992a) developed a unified approach to describe diffusion processes, including one-component diffusion in zeolites. They also extended the work of Tsikoyiannis and Wei (1991) to systems where two molecules per site can be adsorbed.

A description of diffusion in cage-type structures was developed by Fiedler and Gelbin (1978). In their approach it is taken into account that the loading per cage is not constant inside the zeolite crystals and as a consequence the diffusivity will vary locally; see also Gelbin and Fiedler (1980). They are able to describe the increasing diffusivity of *n*-heptane as function of the amount adsorbed for 13X and 5A zeolite.

For practical applications a proper description of mass transfer of multicomponent mixtures in molecular sieve materials is of great interest. For the description of diffusion in microporous materials the main problem is to relate the transport process to the amount adsorbed, and several effects need to be taken into account. First, the diffusion in molecular sieve materials shows a strong concentration dependence. For one-component sorption kinetics the dependence of the diffusivity on the sorbate concentration varies with the pore structure (Chen and Yang, 1991). For the same zeolite, different behaviors have been found for the Fick diffusivity. For the concentration dependence of the one-component Fick diffusivity of benzene in zeolite ZSM-5, different behaviors are reported by Xiao and Wei (1992b).

Second, the one-component diffusion coefficients determine the mass-transfer rates of the individual components in the mixture. In the recently introduced approach to describe multicomponent diffusion in molecular sieve materials with the Maxwell–Stefan equations, this is the starting point (Krishna, 1990, 1993). So far, only the generalized Maxwell–Stefan (GMS) equations give a unified diffusion theory for mass transfer of multicomponent mixtures. The GMS description uses for the predictions of multicomponent mass-transfer rates of sorbed molecules the one-component diffusivities, a model for the counterexchange between the mixture components, and the binary absorption isotherm. In this work we extend the GMS description by taking the concentration dependence of the GMS diffusivity into account. Also, the contribution of counterexchange between sorbed molecules to binary diffusion is studied.

For the theoretical description of multicomponent diffusion in zeolites a number of models for the Fick diffusion coefficient matrix have been examined with considerable success. Using the Onsager formalism with a vanishing cross-coefficient L_{12} binary diffusion in zeolites has been investigated by Habgood (1958), Round et al. (1966), and Kärger and Bülow (1975). Yang et al. (1991) also included the cross-coefficient L_{12} in the description of binary diffusion in zeolites based on the Onsager formalism. Krishna (1990, 1993) described multicomponent diffusion in molecular sieve adsorbents using the Maxwell–Stefan equations. A Vignes relation was used to describe the Maxwell–Stefan diffusion coefficients $\mathfrak{D}_{12}$. Qureshi and Wei (1990a,b) described binary apparent diffusivities in ZSM-5 with a single-file diffusion model.

Other approaches to the description of sorption kinetics of mixtures in molecular sieve materials involve a numerical solution of the mass balance equations. This has been done by Round et al. (1966) and Yang et al. (1991). Using the inverse method of sorption kinetics of multicomponent mixtures, Marutovsky and Bülow (1989), and references therein, are able to evaluate the multicomponent Fick diffusion coefficient matrix from uptake profiles.

A number of studies on multicomponent diffusion based on a computational approach have also been reported. Using Monte Carlo methods the dependence of the diffusivity on occupancy in the case of mass transfer of one- and multicomponent systems can be studied by a random-walk mechanism. Palekar and Rajadhyaksha (1985) have studied binary sorption in zeolites with parallel and nonintersecting channels by a Monte Carlo method. From uptake simulations it was concluded that the apparent diffusivity of the fast-moving component decreases with increasing occupancy of the slower diffusing component, with a constant total occupancy of one-half.

Dahlke and Emig (1991) have presented results of Monte Carlo simulations of binary codiffusion in cage-type zeolites. The molecules in the cages are not fixed and the maximum loading of a cage is two molecules. For a binary mixture, with a ratio of the jump frequency of four, the dependence of the apparent diffusivities on the occupancy has been investigated. For the two apparent diffusivities the highest values were found if a small amount of the other component is present in the zeolite particle. The cross-elements D_{ij} of the Fick diffusion matrix become of the same order of magnitude as the straight elements D_{ii} if the surface occupancy is greater than one-half.

Van den Broeke et al. (1992) used Monte Carlo simulations to study one- and multicomponent diffusion in pore-type zeolitic structures, with intersecting channels. The one-component Fick diffusivity with Langmuir adsorption has been found to be independent of occupancy. Uptake profiles for co- and counterdiffusion of a binary mixture are in agreement with a single-file diffusion model. In this work the same computational model is used to study apparent binary diffusivities.

The main objective of this work is to use the generalized Maxwell–Stefan theory to describe results of binary diffusion in zeolitic structures. Especially, the influence of the pore structure of the molecular sieve, pore or cage type, on the concentration dependence of the (one-component) GMS diffusivity $\mathfrak{D}_i$ and on the GMS counterexchange coefficient $\mathfrak{D}_{ij}$ will be investigated. The counterexchange between sorbed molecules will contribute to the straight and cross-elements in the Fick diffusion coefficients matrix. In the GMS description the Fick diffusivity is described as the product of two separate contributions, a contribution from drag effects and a contribution from nonideality effects. The contribution to the drag or kinetic effects is by the GMS diffusivity. The contribution to the nonideality effects is given by the thermodynamic factor, which can be determined from independent equilibrium experiments. It will be shown that the different theoretical models for multicomponent diffusion in molecular sieve materials can be derived from the Maxwell–Stefan equations with the gradient of the chemical potential taken as the driving force for diffusion. The different theoretical models for multicomponent diffusion will be compared with experimental and computational results. The latter involve Monte Carlo simulations based on the random-walk principle.

In this work results of apparent diffusivities obtained with Monte Carlo simulations will be presented. From binary uptake simulations in a pore-type structure, a square lattice, the two apparent diffusion coefficients have been evaluated. Monte Carlo results of apparent diffusivities of binary diffusion in cage-type [results presented by Dahlke and Emig (1991)] and pore-type zeolitic structures (this study) have been compared with theoretical predictions.

In the last section of this article experimental results of uptake of a binary mixture in zeolite ZSM-5 (Niessen, 1991; Niessen et al. 1993; Niessen and Karge, 1993) will be compared with theoretical predictions. Karge and Niessen (Karge and Niessen, 1991; Niessen and Karge, 1991) developed a new method, based on Fourier transform infrared spectroscopy (FTIR), to measure both one-component and multicomponent transient uptake profiles in zeolites.

To investigate the relation between the concentration dependence of the Fick diffusion coefficient matrix and the type of the pore structure of the molecular sieve, different models will be used to predict the transient uptake profiles of binary mixtures. The GMS diffusion coefficients are evaluated from the one-component uptake profiles. Using the GMS diffusivities and the binary adsorption isotherm, a direct comparison is made between binary uptake profiles obtained from theory and those measured experimentally. Binary uptake profiles, both co- and counterdiffusion, obtained for a mixture of benzene and ethylbenzene in ZSM-5, have been predicted using two different models for the Fick diffusion coefficient matrix. The uptake profiles of the binary mixture in ZSM-5 follows the predictions of the single-file model.

It can be concluded that with the knowledge of the concentration dependence of the one-component diffusivities and a model for the counterexchange coefficient $\mathcal{D}_{12}$ binary mass transfer in molecular sieve materials can be described with high accuracy using the generalized Maxwell-Stefan equations.

Concentration Dependence of the Fick Diffusion Coefficient Matrix

In the description of multicomponent diffusion in molecular sieve materials the objective is to relate the mass-transfer rate of a mixture to the one-component mass-transfer rates. This means that the one-component diffusion behavior determines to a great extent the diffusion behavior of the mixture. The diffusion process in microporous media is strongly influenced by the type of pore structure, the amount adsorbed, and the nonlinearity of the isotherm. The various dependencies of one-component diffusion in microporous media on the amount adsorbed are described in the Introduction. For different adsorbents a different dependence of the Fick diffusivity on the amount adsorbed has been observed, Chen and Yang (1991). Due to the molecular sieve effect of the pore structure and the presence of other sorbed molecules the mobility of molecules is restricted. In addition to these effects there will be extra contributions to the mass transfer of mixtures due to the coupling between the mixture components. The mixture components are coupled through the multicomponent adsorption isotherm as well as through a counterexchange coefficient.

In this work we will look at two different zeolitic structures. The first structure has only one adsorption site at the intersections of the micropores. This is referred to as the pore-type structure. For the second structure it is possible to have two (or more) adsorption sites at the pore intersections. This is referred to as the cage-type structure. The former structure corresponds to, for example, zeolite ZSM-5, the latter structure corresponds to, for example, zeolite A (cf. Figure 3 of Xiao and Wei, 1992a).

Maxwell–Stefan equations for micropore diffusion

If we follow the mechanistic Maxwell–Stefan description, the Fick diffusivity can be considered to consist of two separate contributions (see Krishna (1993)). The first contribution is from drag effects, represented by the inverse of the Maxwell–Stefan diffusivity. The second contribution is from thermodynamic nonideality effects, represented by a thermodynamic correction factor.

For the general case of mass transfer of a multicomponent mixture the Fick diffusion coefficient matrix can be expressed in terms of an inverted matrix of Maxwell–Stefan diffusivity $[B]^{-1}$ and a matrix of thermodynamic factors $[\Gamma]$. For surface, or micropore, diffusion of an n-component mixture, we can define the following GMS equations

$$-\frac{\theta_i}{R_g T}\nabla\mu_i = \sum_{j=1,\, i\neq j}^{n} \frac{\theta_j N_i - \theta_i N_j}{n_{\text{tot}}\,\mathcal{D}_{ij}} + \frac{N_i}{n_{\text{tot}}\,\mathcal{D}_i}. \tag{1}$$

Equation 1 has been obtained by introducing a GMS surface diffusivity according to

$$\mathcal{D}_i = \frac{\mathcal{D}_{iV}}{\theta_V}$$

$$v_V = 0. \tag{2}$$

In this equation θ is the surface occupancy and $v_V = v_{n+1}$ is the velocity of the fixed sites. In the GMS formulation the sorption sites are considered as the $(n+1)$ component in the mixture. The fractional surface occupancy is related to the amount adsorbed by

$$\theta_i = \frac{n_i}{n_{S,i}},$$

and satisfies

$$\sum_{i=1}^{n+1} \theta_i = 1 \qquad \theta_{n+1} \equiv \theta_V.$$

These relations, Eqs. 1 and 2, are in complete analogy with the description of Knudsen diffusion in the dusty-gas model (Krishna, 1993). The definition of the GMS equations according to Eqs. 1 and 2 has been motivated by the results of Monte Carlo simulations (Van den Broeke et al., 1992), and descriptions of multicomponent diffusion presented in literature, as will be discussed below.

The Maxwell–Stefan diffusivity $\mathfrak{D}_{ij}$ describes the simultaneous counterexchange of the molecules i and j, adsorbed at two nearest neighbor sites. The counterexchange coefficients satisfy

$$\mathfrak{D}_{ij} = \mathfrak{D}_{ji}.$$

The Maxwell–Stefan diffusivity $\mathfrak{D}_i$ describes the movement of adsorbed molecules i between the adsorption sites. The dependence of the surface diffusivity $\mathfrak{D}_i$ on the amount adsorbed will be studied below. The Fick diffusion coefficient matrix $[D]$ can be related to the Maxwell–Stefan diffusivities. Rewriting Eq. 1 gives

$$n_{\text{tot}}[\Gamma](\nabla\theta) = [B](N).$$

From a comparison with Fick's law, $(J) = n_{\text{tot}}[D](\nabla\theta)$, we see that

$$[D] = [B]^{-1}[\Gamma]. \tag{3}$$

The two separate contributions to the Fick diffusivity are as follows. For the drag or kinetic effects we have

$$B_{ii} = \frac{1}{\mathfrak{D}_i} + \sum_{j=1, i \neq j}^{n} \frac{\theta_j}{\mathfrak{D}_{ij}}$$

$$B_{ij} = -\frac{\theta_i}{\mathfrak{D}_{ij}}. \tag{4}$$

For the thermodynamic effects we have

$$\Gamma_{ij} = \theta_i \frac{\partial \mu_i}{\partial \theta_j}. \tag{5}$$

The chemical potential can be related to the fugacity according to

$$\mu_i = \mu_i^0 + R_g T \ln(f_i). \tag{6}$$

It is noted that for a given adsorbate–adsorbent system the thermodynamic factor matrix can be determined from independent equilibrium measurements.

For the description of the binary sorption kinetics of microporous adsorbents, a model needs to be established for the kinetics contributions, the $[B]^{-1}$ matrix. In the following, three models, based on the one-component mass-transfer rates, will be discussed.

One-component diffusion

For one-component sorption we have the scalar form of Eq. 3

$$D_1(\theta) = \mathfrak{D}_1(\theta)\Gamma(\theta). \tag{7}$$

Equation 7 is also known as the Darken equation (Darken, 1948; Ruthven, 1984). In the original derivation of Darken, the GMS (or corrected) diffusivity is given in terms of a mobility, B, which is a function of the occupancy.

In the following we will focus on the concentration dependence of the one-component GMS diffusivity, and the contribution of this to the binary mass-transfer rates. To illustrate some features of diffusion and adsorption in micropores the Langmuir isotherm will be used.

$$bp = \frac{\theta}{1-\theta}. \tag{8}$$

The Langmuir isotherm leads to the following thermodynamic factor, with for an ideal system the pressure equal to the fugacity

$$\Gamma = \frac{1}{1-\theta}. \tag{9}$$

In the random-walk model the GMS diffusivity can be related to the jump frequency of the adsorbed molecules in the following way

$$\mathfrak{D}_1(\theta) = \frac{1}{z}\lambda^2\nu(\theta), \tag{10}$$

with λ the jump distance, which is equal to the distance between two nearest neighbor adsorption sites. The parameter z is the lattice coordinate number, and gives the number of nearest neighbor sites. It accounts for the fact that we have an isotropic medium in which the diffusivity in any direction is the same. The number of nearest neighbor sites z can be related to the dimension d of the zeolite pore structure according to $d = z/2$.

Two special cases

Using the Langmuir isotherm two models for the GMS diffusivities can be considered. In the first model we assume that the diffusion process is described by a constant GMS diffusivity, equal to the zero-coverage value. This corresponds to the situation of maximum mobility, also referred to as surface diffusion. For this case we have the highest possible Fick diffusivity as a function of the occupancy.

In the second model we assume that the adsorbed molecules are not able to pass another in the zeolite channels, and this corresponds to the situation of single-file diffusion (SFD). For this situation the probability of a molecule being moved is proportional to the probability of an empty nearest neighbor site. This means that under the conditions of single-file diffusion the jump frequency decreases with the vacancy

$$\theta_V = 1 - \theta.$$

This gives for the GMS diffusivity the following two possibilities

$$\mathfrak{D}_1(\theta) = \mathfrak{D}_1(0) \qquad \text{(GMS model)}, \tag{11a}$$

$$\mathfrak{D}_1(\theta) = \mathfrak{D}_1(0)(1-\theta) = \mathfrak{D}_1(0)\theta_V \qquad \text{(SFD model)}. \tag{11b}$$

For the first model, the GMS model, the Fick diffusivity increases with the thermodynamic factor

$$D_1(\theta) = \mathfrak{D}_1(0)\frac{1}{1-\theta}. \tag{12}$$

The SFD model leads to a constant Fick diffusivity

$$D_1(\theta) = \mathfrak{D}_1(0). \tag{13}$$

The fact that in a Langmuir layer with single-file diffusion the Fick diffusivity is independent of the amount adsorbed has been derived before theoretically by Riekert (1971). The zero-coverage GMS diffusivity follows from Eq. 10 and can be interpreted as the movement of one molecule in an otherwise empty lattice. One of the first to apply the hopping model, Eqs. 10 and 12, to the description of transport of molecules in zeolitic lattices were Barrer and Jost (Barrer, 1941; Barrer and Jost, 1949).

A constant Fick diffusivity has been confirmed by a number of experimental results. The single-file diffusion mechanism for one- and multicomponent systems is applicable to, for example, zeolite ZSM-5. Xiao and Wei (1992b) have found that the Fick diffusion coefficient of a number of hydrocarbons in ZSM-5 is indeed independent of occupancy, with the condition of less than four molecules sorbed per unit cell.

Two-component diffusion

For the description of binary diffusion we can follow the same approach as for one-component diffusion. The one-component diffusivities D_1 as given by Eqs. 12 and 13 can easily be extended to the binary case by using for the vacancy

$$\theta_V = 1 - \theta_1 - \theta_2. \tag{14}$$

However, in this binary situation the extra interaction between the sorbed molecules represented by the counterexchange $\mathfrak{D}_{12}$ should be taken into account. For the description of binary diffusion in molecular sieve materials the evaluation of the counterexchange coefficient $\mathfrak{D}_{12}$ is the main point. In the following three models for binary diffusion with different models for the (one-component) GMS diffusivity and with different models for the counterexchange coefficient will be compared.

Complete GMS Model. The most general model for the description of binary sorption and diffusion in microporous media follows from Eq. 4. From the relation for the $[B]$ matrix the following matrix of GMS diffusion coefficients is obtained

$$[B]^{-1} = \frac{1}{\theta_1\mathfrak{D}_2 + \theta_2\mathfrak{D}_1 + \mathfrak{D}_{12}}\begin{pmatrix} \mathfrak{D}_1[\theta_1\mathfrak{D}_2 + \mathfrak{D}_{12}] & \theta_1\mathfrak{D}_1\mathfrak{D}_2 \\ \theta_2\mathfrak{D}_1\mathfrak{D}_2 & \mathfrak{D}_2[\theta_2\mathfrak{D}_1 + \mathfrak{D}_{12}] \end{pmatrix}. \tag{15}$$

For the counterexchange coefficient $\mathfrak{D}_{12}$ the empirical Vignes relation (Vignes, 1966) can be taken

$$\mathfrak{D}_{12} = [\mathfrak{D}_1]^{\theta_1/(\theta_1+\theta_2)}[\mathfrak{D}_2]^{\theta_2/(\theta_1+\theta_2)}. \tag{16}$$

From Eqs. 15 and 16 two points should be noted. In these equations the GMS diffusivity $\mathfrak{D}_i$ can be a function of the amount adsorbed. For binary diffusion the counterexchange coefficient needs to be specified. The most simple situation is the one where we can neglect the counterexchange between sorbed molecules.

Onsager Formalism with $L_{12} = 0$. For certain zeolite systems counterexchange cannot take place. The advantage of the definition of the GMS equations as given in Eqs. 1 and 2 becomes clear if we take an infinite counterexchange coefficient, or equivalently, a vanishing drag coefficient

$$\frac{1}{\mathfrak{D}_{ij}} = 0 \quad (i \neq j). \tag{17}$$

In that case the $[B]^{-1}$ matrix is diagonal, and Eq. 4 reduces to

$$B_{ii} = \frac{1}{\mathfrak{D}_i(\theta)}$$

$$B_{ij} = 0. \tag{18}$$

For Eq. 18, again two special cases can be considered. We see that we can take the expressions for the one-component GMS diffusivities, given by Eqs. 11a or 11b, on the diagonal elements of the $[B]^{-1}$ matrix. For the concentration dependence of the GMS diffusivity, Eq. 11a, we have to use the binary vacancy given by Eq. 14.

Two special cases

For the situation where we have constant GMS diffusivities, the $[B]^{-1}$ matrix, with a vanishing drag coefficient between the sorbed species, becomes

$$[B]^{-1} = \begin{pmatrix} \mathfrak{D}_1(0) & 0 \\ 0 & \mathfrak{D}_2(0) \end{pmatrix}. \tag{19}$$

Equations 18 and 19 correspond to the Onsager formalism of irreversible thermodynamics with a vanishing cross-element L_{12}.

This model with a constant GMS diffusivity, Eq. 19, in combination with the Langmuir adsorption isotherm is often used for the description of the adsorption process (Habgood, 1958; Round et al., 1966; Kärger and Bülow, 1975).

From a comparison with the Onsager formulation, $(J) = [L](\nabla\mu)$, we have for binary diffusion

$$[L]^{-1} = \begin{pmatrix} \theta_1 & 0 \\ 0 & \theta_2 \end{pmatrix}[B].$$

Single-File Diffusion. If we use instead of a constant one-component GMS diffusivity the decreasing diffusivity, given by Eq. 11b with Eq. 14 for the vacancy, we obtain the binary diffusion matrix for the single-file diffusion model

$$[B]^{-1} = \begin{pmatrix} \mathfrak{D}_1(0)\theta_V & 0 \\ 0 & \mathfrak{D}_2(0)\theta_V \end{pmatrix}. \qquad (20)$$

Equation 20 with the Langmuir isotherm has been used by Qureshi and Wei (1991) to describe diffusion of a mixture of benzene and toluene in ZSM-5, which showed good agreement between theory and experiment.

The three models, derived previously, will be used to compare experimental and computational results of diffusion of a binary mixture in microporous sorbents with theory:

- *GMS Model.* Equations 15 and 16
- *$L_{12} = 0$ Model.* Equation 19 (or Eq. 18 for a concentration-dependent GMS diffusivity)
- *SFD Model.* Equation 20.

It is clear that the results for the $L_{12} = 0$ and the SFD model for binary diffusion are in complete analogy with the two special one-component cases, as given by Eqs. 11 to 13. For the two models with variable GMS diffusivities, respectively, Eqs. 15 and 16 and Eq. 18, the concentration dependence of the GMS diffusivities need to be specified.

Multicomponent Diffusion in the Configurational Regime

In the following the different theoretical models will be used to investigate the influence of the pore structure on mass transfer in molecular sieve materials. Also, the contribution of a constant GMS diffusivity and a variable one to the mass transfer will be compared, for both one- and two-component diffusion. For the three multicomponent models the time dependence of the transient uptake profiles and the dependence of the apparent diffusivities on occupancy will be different.

Single-file diffusion

For a number of molecular sieve materials, sorbed molecules are not able to pass one another inside the pore structure. If we take as an indication that everywhere in the molecular sieve we have the following condition for the minimum kinetic diameters of the adsorbed molecules

$$(d_{\text{molec},i} + d_{\text{molec},j}) > d_{\text{pore}},$$

we say that mass transfer takes place by a single-file diffusion mechanism. For this condition two molecules are not able to pass one another in the zeolite channels, and as a consequence we have a vanishing counterexchange coefficient $\mathfrak{D}_{ij}$ $(i \neq j)$. For a number of zeolitic systems, the ratio of the effective (micro)pore diameter, d_{pore}, to the Lennard-Jones kinetic diameter are known, see, for example, Ruthven (1984) and Xiao and Wei (1992a).

Apparent diffusion coefficient

To be able to compare the results of the Monte Carlo simulations with theory we introduce apparent diffusivities. The apparent diffusion coefficient for a binary mixture can be obtained from the surface flux in the following way

$$D_{A,1}(\theta_1,\theta_2) = \frac{J_1}{|\nabla\theta_1|} = D_{11} + D_{12}\frac{|\nabla\theta_2|}{|\nabla\theta_1|}, \qquad (21)$$

with a similar expression for the second component.

If the gradients of the surface occupancies are known, the apparent diffusivities can be evaluated from one of the models for the binary Fick diffusion matrix, as given by Eqs. 15 to 20. In the Monte Carlo simulations the gradients of the surface occupancies are taken as finite differences, $\Delta\theta/\Delta x$. Furthermore, at the beginning of every simulation the two gradients are equal.

We see from Eq. 21 that the apparent diffusivity is a function of the GMS diffusivities, the surface occupancies, and the surface occupancy gradients. We can introduce dimensionless diffusivities by considering the quantity $D_{A,i}(\theta_1,\theta_2)/\mathfrak{D}_i(0)$. For all the models the zero-coverage value of the apparent diffusivity equals the one-component GMS diffusivity

$$D_{A,i}(0,0) = \mathfrak{D}_i(0). \qquad (22)$$

Binary Langmuir sorption

In the following the binary Langmuir isotherm will be used in the description of binary mass transfer in molecular sieve materials. The matrix of thermodynamic factors for Langmuir adsorption is given by

$$[\Gamma] = \frac{1}{1-\theta_1-\theta_2}\begin{pmatrix} 1-\theta_2 & \theta_1 \\ \theta_2 & 1-\theta_1 \end{pmatrix}. \qquad (23)$$

Transient uptake profiles: linearized theory and numerical solution

To investigate sorption kinetics of mixtures in molecular sieve materials binary uptake profiles have been simulated. For the prediction of the transient uptake profiles of a binary mixture the linearized theory of multicomponent mass transfer has been used, see Krishna (1990).

In Figure 1a an example is given of the uptake profiles for a binary mixture in a spherical particle calculated with the GMS model, the $L_{12} = 0$ model, and the SFD model. In Figure 1b a comparison is made for the GMS model between the results of the numerical solution of Fick's second law of diffusion and the linearized theory. The input conditions for Figure 1a and 1b are given in Table 1.

The influence of the concentration dependence of the Fick diffusion coefficient matrix can be compared with the linearized theory by solving

$$\frac{\partial\theta_i}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_{ij}(\theta)\frac{\partial\theta_j}{\partial r}\right) \qquad (i,j = 1,2). \qquad (24)$$

For codiffusion we start with a clean adsorbent particle and perform a step in the concentration at time zero. This gives as initial condition

$$\theta_i(r, t<0) = 0 \qquad (i = 1,2). \qquad (25)$$

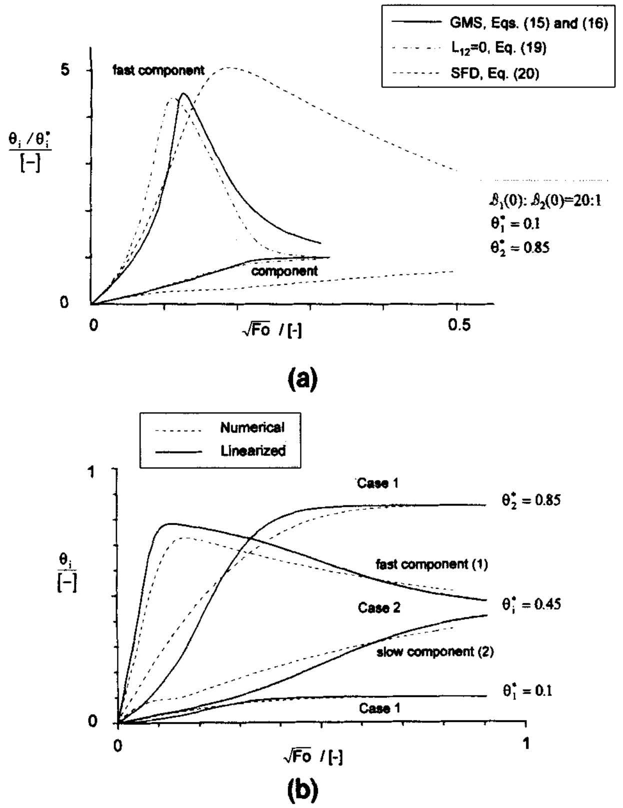

Figure 1. Analytical results for binary uptake profiles (equal to the normalized surface occupancy θ_i/θ_i^*) for a spherical particle, as function of the square root of the Fourier number ($F_o = \mathfrak{D}_1(0)t/R^2$).

The input parameters are given in Table 1. (a) Comparison of the GMS model, Eqs. 14 and 15, the $L_{12} = 0$ model, Eq. 18, and the SFD model, Eq. 19. The matrix of thermodynamic factors is given by the Langmuir model, Eq. 22. (b) Single-file diffusion results for binary uptake; Case 1, with only a difference in the equilibrium occupancies; Case 2, with only a difference in the GMS diffusivities.

For the boundary conditions the following equilibrium values are taken

$$\theta_1^* = \theta_1(r = R) = 0.10$$

$$\theta_2^* = \theta_2(r = R) = 0.85$$

$$\frac{\partial \theta_i(r = 0)}{\partial r} = 0, \tag{26}$$

The solution of the set of Eqs. 24–26 is calculated with the NAG routine D03PGF (NAG, 1991), which solves a system of nonlinear parabolic partial differential equations using the method of lines and Gear's method.

Table 1. Parameters for Theoretical Results of the Transient Uptake of a Binary Mixture*

	$\mathfrak{D}_1(0)$: $\mathfrak{D}_2(0)$	θ_1^*	θ_2^*
Figure 1a	20:1	$0 \rightarrow 0.10$	$0 \rightarrow 0.85$
Figure 1b, Case 1	1:1	$0 \rightarrow 0.10$	$0 \rightarrow 0.85$
Figure 1b, Case 2	20:1	$0 \rightarrow 0.45$	$0 \rightarrow 0.45$

*Results are shown in Figure 1.

The linearized theory uses the solution of Eqs. 24–26 for the one-component case with a constant diffusivity. The solution is computed by taking small steps in the Fourier number. The one-component fractional uptake is for this problem given by (Crank, 1975)

$$\frac{\theta(t) - \theta(t_0)}{\theta(t_\infty) - \theta(t_0)} = 1 - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp\left(-m^2\pi^2 \frac{Dt}{R^2}\right), \tag{27}$$

with the one-component Fick diffusivity D equal to $\mathfrak{D}(0)$, for a constant diffusivity, or to $\mathfrak{D}(\theta)\Gamma$, for the most general case.

The Fourier number is defined as

$$Fo = \frac{\mathfrak{D}_1(0)t}{R^2} \quad \text{with} \quad \mathfrak{D}_1(0) < \mathfrak{D}_2(0).$$

The matrix analog of Eq. 27 has been used as a description of the multicomponent transient uptake (see Krishna (1990)). We see that for binary codiffusion, that is, with $\theta_i(t_0) = 0$, the fractional uptake reduces to the normalized surface occupancy $\theta_i(t)/\theta_i(t_\infty)$.

In Figure 1a an example is given of the uptake profiles as functions of the Fourier number, for a binary mixture in a spherical particle using the three different models for the Fick diffusion coefficient matrix. The binary mixture consists of a fast-moving weakly adsorbed component and a slow-moving strongly adsorbed component; the Langmuir model has been taken for the adsorption isotherm. The uptake of the mixture is specified by the ratio of the GMS diffusivities $\mathfrak{D}_1(0)/\mathfrak{D}_2(0) = 20$, the initial occupancies $\theta_1 = 0 = \theta_2$, and the equilibrium occupancies $\theta_1^* = 0.10$ and $\theta_2^* = 0.85$.

For small Fourier numbers there is a small difference in the uptake of the fast-moving weakly adsorbed component, as given by the three models. However, after the maximum in the uptake profile has occurred, the SFD model gives a different behavior for the occupancy of the fast-moving component. The GMS and the $L_{12} = 0$ model show a rapid decrease in the surface occupancy. For these two cases the dependence on the vacancies θ_V influence the uptake behavior considerably and the effect of the counterexchange makes a minor contribution. In the SFD model, that is, in pore-type where we have no counterexchange, it takes much longer to reach equilibrium. For the slow-moving strongly adsorbed component the GMS and the $L_{12} = 0$ model show a more rapid uptake than the SFD model.

The difference between the GMS and the $L_{12} = 0$ model on the one hand and SFD model on the other hand is a consequence of the different dependences of the diffusivities on the vacancy $(\theta_V)^{-1}$. In the GMS and the $L_{12} = 0$ model the diffusivity increases rapidly with a decrease in the vacancies; in the SFD model this dependence is not that strong (see Eqs. 20 and 23). It is noted that for a constant Fick diffusion coefficient matrix $[D]$ both the uptake profiles increase monotonously to their equilibrium values.

Chen and Yang (1992) also solved the set of Eqs. 24 to 25 numerically. They have included the off-diagonal elements of the matrix of phenomenological coefficients in their description of the Fick diffusion coefficient matrix. The Fick diffusivity is a function of the occupancy and a function of a blocking parameter λ. The latter is equal to the ratio of the sticking probability of one molecule to another molecule to the sticking probability of a molecule to a vacant site. For $\lambda_i = 0$ (cf. Eqs. 39 to 42 of their article) the $L_{12} = 0$ model is obtained.

We see from Figure 1a that there is a small difference between the $L_{12} = 0$ and the GMS model when the same solution technique is used. In Figure 1b a further comparison is made between the linearized theory (Krishna, 1990) and the numerical solution to investigate the competition effect between different sorbed molecules.

Diffusion competition effect

To study the displacement of the faster moving component in more detail the uptake of a binary mixture with different conditions has been calculated (linearized theory and numerical solution). The conditions for the simulations shown in Figure 1b are given in Table 1.

We see from Figure 1b that if there is no difference between the GMS diffusivities, Case 1, the amount adsorbed increases monotonously with time for both components, and there is no maximum in either of the profiles. However, when the GMS diffusivities are different a maximum in the uptake profile of the faster moving component always occurs, irrespective of the equilibrium values of the occupancies. In the second case the equilibrium occupancies are equal, and are given by $\theta_i^* = 0.45$. This indicates that the maximum is a consequence of a diffusion-induced competition effect, and the maximum arises because the uptake of the individual components takes place at different rates.

Results and Discussion

There exist no clear criteria for the concentration dependence of the Fick diffusion coefficient matrix for mass transfer in molecular sieve materials. In the following an attempt is made to classify diffusion in different zeolites systems based on the type of pore structure.

In the first part the random-walk approach is applied to study, by means of Monte Carlo simulations, apparent diffusion coefficients in pore-type and cage-type zeolitic structures. In the second part the GMS equations are used to predict experimental results of transient uptake of a binary mixture in zeolite ZSM-5. The one-component diffusivities and the binary isotherm are used to describe the binary mass-transfer rates.

Apparent Fick Diffusion Coefficient

One way to obtain apparent diffusivities is from uptake experiments. For short times the uptake is linear with the square root of time. To obtain from the Monte Carlo simulations the binary apparent diffusivities in the pore-type structure, the following equation has been used

$$\frac{\theta_i(t) - \theta_i(t_0)}{\theta_i(t_\infty) - \theta_i(t_0)} = \alpha \sqrt{\frac{D_{A,i} t}{R^2}} \,. \tag{28}$$

Another way to evaluate the apparent diffusivities is from the surface fluxes; this has been done for the cage-type structures by Dahlke and Emig (1991) using Monte Carlo simulations.

Monte Carlo scheme for sorption kinetics

In the Monte Carlo simulations two different models are frequently used. In the first model an activated molecule does not have to leave the site. This means that after a direction is selected at random the molecule will move if the nearest neighbor site is vacant. If the receiving site is occupied, the activated molecule will not move and stays at the site. In the second model the activated molecule has to leave the site; it remains on the site only if all the nearest neighbor sites are occupied. In the latter model we can say that the adsorbed molecule is forced off the host site. The following two models have been used to study one- and two-component diffusion in zeolitic structures:

- *Model 1.* An activated molecule can move in one (random) direction ($z = 1$).
- *Model 2.* An activated molecule can move in z directions, selected at random.

The Monte Carlo simulations for the pore-type structure have been performed on a (25×25) square lattice. On the square lattice the adsorption sites are uniformly distributed and are placed at the pore intersections. In this way an energetically homogeneous surface with four nearest neighbor sites is formed.

In the Monte Carlo simulations the mass transfer on a lattice is modeled as a sequence of elementary steps and conditions, according to the conditions given earlier.

The main step is the activation of an adsorbed molecule and the selection of a nearest neighbor site. A random number generator is used to select a molecule on the lattice. This molecule is activated to execute a jump. The next step is the random selection of a nearest neighbor site. The molecule will then be moved according to the model implemented. The jump frequency can be evaluated from the number of activations.

For more details of the computational models, see Dahlke and Emig (1991) and Van den Broeke et al. (1992).

In general the jump frequency of an activated molecule is determined by the rate of adsorption on the nearest neighbor sites. The adsorption of an activated molecule is proportional to the probability of finding an empty nearest neighbor site. For the pore-type structures this probability is given by $(1 - \theta^z)$. The surface occupancy θ is equivalent to the probability of a site being occupied.

The random-walk mechanism can be applied to pore-type as well as to cage-type structures. The dependence of the jump frequency on the occupancy θ for the two models can be written as

$$\begin{aligned} \mathfrak{D}_1(\theta) &= \frac{1}{mz} \lambda^2 \nu_1(\theta) \\ &= \frac{1}{mz} \lambda^2 \nu_1^0(\theta) \exp(-E/R_g T) \\ &= \mathfrak{D}_1(0)(1 - \theta^{mz}). \end{aligned} \tag{29}$$

Equation 29 is the generalization of Eq. 10, which resulted in Eqs. 11a and 11b for diffusion in a Langmuir layer.

For cage-type structure we have to replace z with mz where m is the maximum number of molecules per cage. The factor mz represents the maximum number of vacant nearest neighbor sites per cage and the term $(1-\theta^{mz})$ is the probability that at least one of the nearest neighbor sites is vacant.

Diffusion in zeolites is an activated process, where molecules move in a potential energy field. The diffusivity can be related to the activation energy E for migration in micropores, according to Eq. 29. It has been found that the activation energy depends strongly on the ratio of the pore size to the molecular size (Xiao and Wei, 1992a; Kärger and Ruthven, 1992).

For a description of the two Monte Carlo models, we have to use a modified isotherm and thermodynamic factor. We will use the quasi-chemical approximation for the description of sorption kinetics of molecules in pore-type structures and a statistical model isotherm for the description of sorption kinetics in cage-type structures.

Quasi-chemical approximation

For the description of diffusion in pore-type structures with interactions between molecules adsorbed on nearest neighbor sites, the quasi-chemical approximation (QCA) can be used. For a discussion of this see, for example, Hill (1962) and Reed and Ehrlich (1981). For the thermodynamic factor we have

$$\Gamma_{QCA}=\frac{1}{1-\theta}\left(1+\frac{z}{2}\,\frac{1-\beta}{\beta}\right), \tag{30}$$

with β given by

$$\beta=\sqrt{1-4\theta(1-\theta)[1-\exp(-\epsilon/R_gT)]}\,, \tag{31}$$

and in the expression for the GMS diffusivity, Eq. 29, we have $m=1$ and $z=4$. The thermodynamic factor in the quasi-chemical approximation reduces to the Langmuir form for $\epsilon=0$. The thermodynamic factor is then independent of the coordinate number z, see Eq. 9.

Statistical isotherm

Ruthven (1976, 1984) derived an isotherm for cage-type structures using statistical mechanics. For a maximum of two molecules per cage, $m=2$, the relation between the amount adsorbed and the pressure is given by

$$n=\frac{bp+(bp)^2(1-2\beta/V)^2}{1+bp+\frac{1}{2}(bp)^2(1-2\beta/V)^2}. \tag{32}$$

For this isotherm the following assumptions hold:

- Molecules in a cage are not adsorbed at localized sites
- The molecular interactions are represented as reduction in free volume
- Interactions between molecules in neighboring cages are neglected.

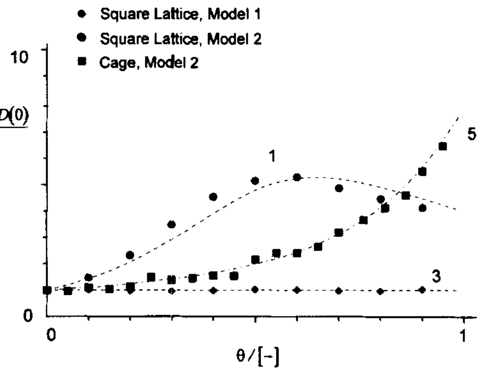

Figure 2. One-component Fick diffusivity $D(\theta)/D(0)$ as a function of the occupancy.

Results of the Monte Carlo simulations and theoretical predictions. Monte Carlo results for the cage structure are adapted from Dahlke and Emig (1991). The parameters used for the theoretical results are given in Table 2.

If we assume that in the Monte Carlo simulations for diffusion in a cage-type structure (Dahlke and Emig, 1992), where we have nonlocalized sorbed molecules, the only interaction between sorbed molecules takes place as a reduction in free volume, we can put $\beta=V/2$. We see that for this situation, the Langmuir isotherm is also obtained for $m=2$. The thermodynamic factor is again given by Eq. 9. In the expression for the GMS diffusivity, Eq. 29, we have to take $m=2$ and $z=4$.

One-component diffusivities

The results of the Monte Carlo simulations with the two models for the one-component Fick diffusivities in pore- and cage-type zeolites and the theoretical predictions are shown in Figure 2. The model parameters are given in Table 2.

Using Monte Carlo simulations, the one-component Fick diffusivity in pore-type zeolites has been found to be independent of surface occupancy for model 1, see Aust et al. (1989) and Van den Broeke et al. (1992). The ideal Langmuir model is obtained for $z=1=m$, which corresponds to the assumptions made for Model 1, curve 3 in Figure 2. For diffusion in pore-type structures with Model 2 assumptions the interaction energy ϵ equals R_gT. The behavior is shown in Figure 2 by curve 1. In cage-type structures the one-component diffusivity increases monotonously with increasing occupancy, curve 5 in Figure 2. For the different pore structures good agreement is obtained between the theoretical predictions and the results of the Monte Carlo simulations.

Table 2. Parameters for One-Component Diffusion*

Curve	Structure	$\mathfrak{D}_1(\theta)/\mathfrak{D}_1(0)$	Thermody. Factor Γ
1	$m=1,\ z=4$	$(1-\theta^4)$	QCA, $\epsilon=R_gT$
2	$m=1,\ z=4$	$(1-\theta^4)$	QCA, $\epsilon=0.5\,R_gT$
3	$m=1,\ z=1$	$(1-\theta)$	QCA, $\epsilon=0,\ \Gamma\rightarrow(1-\theta)^{-1}$
4	$m=2,\ z=1$	$(1-\theta^2)$	$(1-\theta)^{-1}$
5	$m=2,\ z=4$	$(1-\theta^8)$	$(1-\theta)^{-1}$
6		1	$(1-\theta)^{-1}$

*See Figures 2 and 3; QCA refers to Eqs. 30 and 31; and $\mathfrak{D}=(\lambda^2\nu)/(zm)$.

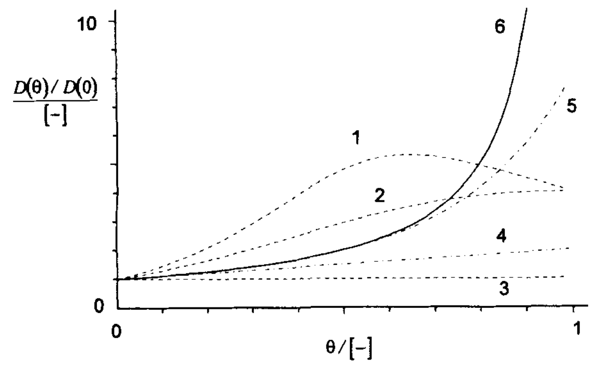

Figure 3. Theoretical results for the one-component Fick diffusivity $D(\theta)/D(0)$ as a function of the occupancy for different models.

The model parameters are given in Table 2.

Experimental results of Xiao and Wei (1992b) for one-component diffusion of benzene in ZSM-5 show a transition from a constant Fick diffusivity, for occupancies of less than four molecules per unit cell, to an increasing diffusivity, for more than four molecules per unit cell (cf. Figures 6 and 11 of their article). Also results are reported for benzene with a small maximum in the Fick diffusivity as a function of the amount adsorbed (cf. Figure 8 of their article). For the latter results a different (Si/Al) ratio was used, as compared to the zeolite sample with a constant and an increasing diffusivity.

For the situation of an increasing diffusivity the sorbed molecules also reside at the center of the channels and interactions between the sorbed molecules have an influence on the diffusion process.

The Monte Carlo simulations performed with the pore-type structure have a strong resemblance to the cases of a constant diffusivity and the diffusivity with a maximum as studied by Xiao and Wei (1992a,b). These results are for the situation of a maximum of four molecules per unit cell and the molecules are sorbed at the sites at the channel intersections.

In Figure 3 predictions are depicted for different values of m and z and a constant GMS diffusivity with the two isotherms given earlier. The parameters are again given in Table 2. For the localized adsorption in pore-type structures the dependence of the diffusivity on the occupancy varies strongly with the interaction energy. For the situation with a repulsive interaction, both the theory and the Monte Carlo simulation give a diffusivity with a maximum. This behavior is shown in Figures 2 and 3 by curve 1.

We also see from Figure 3 that there is small difference between surface diffusion, curve 6, and diffusion in cage-type zeolites, curve 5. For both situations the Langmuir adsorption isotherm ($m = 2$, $z = 4$) has been used. For an occupancy up to about 0.75, the difference between the two models is less than 10%. From Eq. 29 it follows that surface diffusion occurs for $z \gg 1$. This further means that for cage-type zeolites, for example, zeolite X and zeolite A, which can host a number of molecules per cage, the GMS or corrected diffusivity is (almost) constant and the Fick diffusivity increases monotonously with increasing concentration.

In a number of experimental studies, on the one-component mass transfer in cage-type zeolitic structures, these behaviors of the diffusivities are indeed observed. These behaviors have been found for the diffusion of light hydrocarbons in zeolite 5A by Ruthven et al. (1973) and for the diffusion of C8 aromatic hydrocarbons in zeolite NaX by Goddard and Ruthven (1986).

Two-component diffusivities

In the following (Figures 4 and 5), results of Monte Carlo simulations performed with a binary mixture in pore- and cage-type zeolites are compared with the theoretical models. The mixture components are distinguished by a difference in the jump frequency. The fast-moving component is denoted component 2.

In Figure 4 the result of the dimensionless apparent diffusion coefficient for the fast-moving component, $D_{A,2}(\theta_1, \theta_2)/D_{A,2}(0,0)$, in a pore-type zeolite as a function of the surface occupancies is presented. For the ratio of the GMS diffusivities, $\mathfrak{D}_2(0)/\mathfrak{D}_1(0) = 5$ has been taken. Compared with the result for the one-component diffusivity, curve 3 in Figure 2, we see that the presence of a second component greatly influences the apparent diffusivities. Three essentially different behaviors are found for the apparent diffusivity of the fast-moving component in the case of binary codiffusion.

The apparent diffusivity of component 2 decreases, at low occupancies of component 2, with increasing occupancy of the slow-moving component, component 1. The apparent diffusivity of component 2 is almost constant if the two components are present in the same amount, that is, if $\theta_1 = \theta_2$. In this situation the apparent diffusivity is of the same order of magnitude as the one-component diffusivity. For low occupancies of component 1 the apparent diffusivity of component 2 increases with increasing occupancy of component 2. These three situations are considered in more detail in Figure 5.

In Figure 5a a comparison is made between the results of diffusion of a binary mixture in a cage-type zeolitic structure, as presented by Dahlke and Emig (1991), a pore-type zeolitic structure, this study, and the three theoretical models, Eqs. 15 to 20.

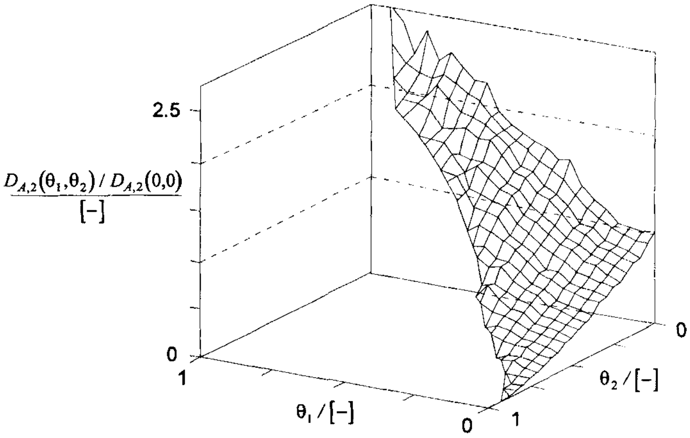

Figure 4. Normalized apparent diffusivity $D_{A,2}(\theta_1, \theta_2)/D_{A,2}(0, 0)$ as function of the occupancies θ_i.

Result of Monte Carlo simulations, for the fast-moving component in a binary mixture, obtained with Model 1 assumptions for a channel-type structure.

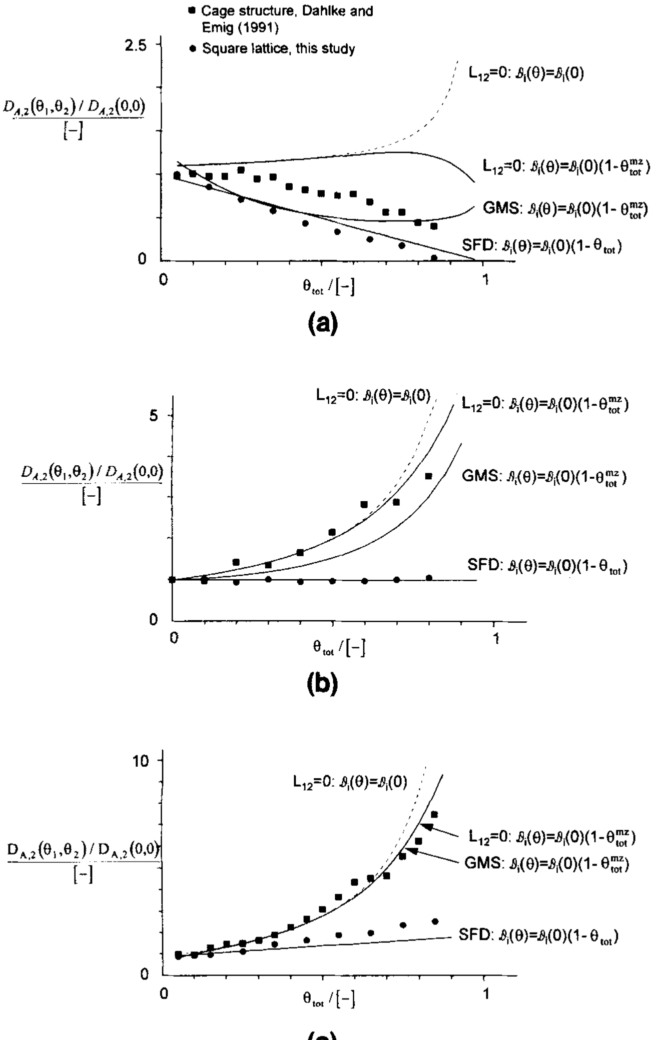

Figure 5. Apparent diffusivity $D_{A,2}(\theta_1,\theta_2)/D_{A,2}(0,0)$, as a function of the total occupancy, normalized on the zero-coverage diffusivity.

Results from Monte Carlo simulations and theoretical predictions for the fast-moving component in a binary mixture: (a) Surface occupancy: $\theta_1 = 0.05$ and $0 \leq \theta_2 \leq 0.9$. (b) Surface occupancy: $\theta_1 = \theta_2$ and $0 < \theta_i \leq 0.45$. (c) Surface occupancy: $0 \leq \theta_1 \leq 0.9$ and $\theta_2 = 0.05$.

In the predictions for the apparent binary diffusivities shown in Figure 5 results are given for a constant and a concentration-dependent GMS diffusivity. For the variable GMS diffusivity case Eq. 29 is inserted in the $[B]^{-1}$ matrix for the GMS model and the $L_{12} = 0$ model. For the occupancy in Eq. 29 we have taken the total amount adsorbed, that is, $\theta_1 + \theta_2$. It is noted that in the $L_{12} = 0$ model given by Eq. 19 the variable GMS diffusivity is given by Eq. 29. Results for the $L_{12} = 0$ model with a constant one-component GMS diffusivities $Ð_i(0)$ are also shown. Also, calculations have been performed with a constant GMS diffusivity in the GMS model; these results are not shown. However, the differences for the GMS model between a constant and a concentration-dependent GMS diffusivity are smaller than for the $L_{12} = 0$ model.

Pore-type zeolites

In Figure 5 results of Monte Carlo simulations of binary codiffusion in pore-type zeolitic structures are compared with a theoretical SFD model, Eq. 20, and the thermodynamic factor matrix obtained from the binary Langmuir adsorption isotherm, Eq. 23. We see that the maximum increase in the apparent diffusivity of the fast-moving component (component 2) as a function of the total occupancy is by a factor 2.8. This occurs when the slow-moving component is present in a small amount, $(\theta_1, \theta_2) = (0.05, 0.90)$. This is shown in Figure 5a. The SFD model predicts a maximum increase of 2.

Experimental results for the binary diffusion of benzene and toluene in ZSM-5 have been reported by Qureshi and Wei (1990b), with a diffusivity ratio of two. However, they have only considered the situation with the surface occupancies of the two components having the same value. Both the apparent diffusivities of benzene and toluene were found to be independent of the total surface occupancy. The values of the apparent diffusivities are of the same order of magnitude as the one-component Fick diffusivities. This is in agreement with the results found with the Monte Carlo simulations as depicted in Figure 5b.

From the results obtained with the Monte Carlo simulations it can be concluded that diffusion of a binary mixture in pore-type zeolitic structures can be described by a single-file diffusion model, that is, with a concentration-dependent GMS diffusivity.

Cage-type zeolites

Dahlke and Emig (1991) have performed Monte Carlo simulations of binary diffusion in cage-type zeolitic structures, with a ratio of GMS diffusivities $Ð_2(0)/Ð_1(0) = 4$. The surface occupancy gradients for the two components are the same at the beginning of the simulations (cf. Figure 1 of their article). Their results are also shown in Figure 5 and are compared with the GMS model, Eqs. 15 and 16, and the $L_{12} = 0$ model, Eq. 20. The ideal Langmuir model has been taken to evaluate the matrix of thermodynamic factors, Eq. 23. Also, results are shown for Eq. 18 using a variable GMS diffusivity given by Eq. 29.

For the situation with a small amount of the fast-moving component adsorbed, Figure 5a, the largest differences are found between the GMS and the $L_{12} = 0$ model. For this situation the $L_{12} = 0$ model is not capable of describing the observed decrease in the apparent diffusivity of the fast-moving component with increasing occupancy of the slow-moving component. The GMS model predicts a decreasing behavior of the apparent diffusivity. However, a somewhat lower value for the apparent diffusivity is obtained from the GMS model. We see that for this situation the counterexchange between sorbed molecules cannot be neglected.

For the case where we have a relatively large amount of the fast moving component adsorbed, Figure 5b and 5c, the differences between the GMS and $L_{12} = 0$ model are small. For these situations the results of the Monte Carlo simulations are in good agreement with the two theoretical models. For the situation shown in Figure 5c, the apparent diffusivity of the fast-moving component as a function of the total occupancy, which consists mainly of the fast component, the $L_{12} = 0$ model and the GMS model are almost identical.

To our knowledge only one other description of multicomponent diffusion in molecular sieve materials has included counterexchange between sorbed molecules. Yang et al. (1991) described diffusion in zeolites with the Onsager formalism of irreversible thermodynamics by including the cross-coefficients L_{12} in their derivation of the Fick diffusion coefficient matrix. However, if we consider the situation with both components adsorbed in the same amount, the result of Yang et al. (1991) (cf. relations 26 and 27 of their article) for the zero-coverage value of apparent diffusion coefficient varies with the interaction parameter and the GMS diffusivities. Therefore, their model does not satisfy Eq. 22. In a later article by the same authors (Chen et al., 1993) this has been solved by putting $\lambda = 0$ for the case of vanishing occupancies. However, in our opinion the interaction parameter should vanish identically for infinite diluted systems. This follows from Eq. 4, if we take for the occupancies the limit $\theta_k \to 0$ (with $k = 1, \ldots, n$) the $[B]^{-1}$ matrix becomes independent of the counterexchange coefficient $\mathfrak{D}_{ij}$.

It can be concluded from the comparison made between the results of the Monte Carlo simulations and the theoretical models that binary diffusion in cage-type zeolites is in agreement with predictions obtained from irreversible thermodynamics.

For most of the cases the differences between the $L_{12} = 0$ and the GMS model are small (Figure 1, Figure 5b, and Figure 5c). However, for some situations (Figure 5a) the $L_{12} = 0$ model gives the wrong dependence of the apparent diffusivity on the surface occupancy. Therefore, when counterexchange is important the generalized Maxwell-Stefan model should be used instead. Binary diffusion in cage-type structures is characterized by a strong dependence on the vacant sites as compared to diffusion in pore-type structures. In the SFD model the dependence on the vacant sites drops out of the relation for the Fick diffusion coefficient matrix in the case of Langmuir adsorption. By taking the product of Eq. 20 and Eq. 23, we see that the result is independent of θ_V.

From the Monte Carlo simulations of diffusion in the pore- and cage-type zeolitic structures a number of effects should be noted.

For the pore-type structure the apparent diffusivities are obtained from uptake simulations. During the uptake the surface occupancy gradients change, and this will affect the apparent diffusivities, according to Relation 21. This effect can explain the differences between the theoretical SFD model and the Monte Carlo simulation. This explanation is confirmed by the result obtained for the case where the two components are adsorbed in the same amount. For this situation the gradients in the occupancy will change in almost the same amount and the effect of the changes will cancel.

For diffusion in cage-type zeolitic structures, the effect of the maximum number of molecules per cage is not taken into account in the description of counterexchange, as given by the Vignes relation.

Transient Uptake Profiles in ZSM-5

In this section we present experimental and theoretical results for one- and two-component diffusion in zeolite ZSM-5. Based on the one-component mass-transfer rates of benzene and ethylbenzene in ZSM-5, co- and counterdiffusion experiments of the mixture benzene/ethylbenzene in ZSM-5 are described theoretically. A direct comparison is made between one- and two-component uptake profiles measured by Fourier transform IR spectroscopy and theoretical predictions obtained with the generalized Maxwell-Stefan theory. Uptake of benzene and ethylbenzene, and their mixture in a ZSM-5 sample were monitored by an FTIR technique (Karge and Niessen, 1990; Niessen and Karge, 1991; Niessen, 1991; Niessen et al., 1993a).

In the one-component case the partial pressure of benzene and ethylbenzene was increased from 0 to 115 Pa, respectively. In the codiffusion experiments the partial pressures of both components were changed from 0 to 115 Pa. In the counterdiffusion measurements benzene was preadsorbed at 115 Pa and ethylbenzene was admitted to the gas stream, with the pressure increasing from 0 to 115 Pa.

All the experimental results reported below are from the thesis of Niessen (Niessen, 1991). The numerical results presented below for the uptake curves are from independent fits performed in this study.

Adsorption isotherms

The adsorption isotherms for benzene and ethylbenzene in the ZSM-5 sample are given by the Langmuir-Freundlich relation, see Niessen (1991). For the one-component adsorption isotherm we have

$$n^* = n_0 \frac{bp^m}{1 + b_i p^m}, \tag{33}$$

and for the two-component adsorption isotherm

$$n_i^* = n_{0,i} \frac{b_i p_i^m}{1 + \sum_{j=1}^{2} b_j p_j^m}. \tag{34}$$

Equations 33 and 34 are solved to obtain the pressure and the relation for the surface occupancy $\theta = n/n_S$ is inserted. For the one-component adsorption, this gives

$$p = \left(\frac{1}{b} \frac{\theta}{1-\theta} \right)^{1/m}. \tag{35}$$

For the two-component adsorption the following relation for the partial pressure is obtained

$$p_1 = \left(\frac{1}{b_1} \frac{\theta_1}{1-\theta_1-\theta_2} \right)^{1/m}, \tag{36}$$

with a similar relation for the second component.

Using the definition for the thermodynamic factor, Eq. 5, and Eq. 35 for the pressure, we have for the one-component sorption

$$\Gamma_1 = \frac{1}{m_1} \frac{1}{1-\theta_1}. \tag{37}$$

Table 3. Data for the One-Component Adsorption Isotherm and the Amount Adsorbed in the One-Component Uptake Experiments, at a Temperature of $T = 375$ K*

One Comp.	m	b Pa^{-m}	n_0 mmol·g^{-1}	n mmol·g^{-1}	θ^*
Benzene	0.51	0.04	0.84	$0.0 \rightarrow 0.24$	0.29
Ethylbenzene	0.33	0.19	0.94	$0.0 \rightarrow 0.44$	0.47

*The experimental data and the fits are from Niessen (1991).

For the two-component sorption we have the following matrix of thermodynamic factors

$$[\Gamma] = \frac{1}{m}\frac{1}{1-\theta_1-\theta_2}\begin{pmatrix} 1-\theta_2 & \theta_1 \\ \theta_2 & 1-\theta_1 \end{pmatrix}. \tag{38}$$

The experimental data for the isotherms are from Niessen (1991). For the system benzene/ZSM-5, the system ethylbenzene/ZSM-5, and the system benzene/ethylbenzene/ZSM-5, the parameters for the isotherms at $T = 375$ K are given in the Tables 3 and 4.

One-component sorption kinetics

For the description of the diffusion process two models have been compared, the single-file diffusion model and the generalized Maxwell-Stefan model.

The one-component uptake in the spherical zeolite crystals, with a radius $R = 3.27 \times 10^{-6}$ m (Niessen, 1991), is described with the solution for a constant Fick diffusion coefficient. Due to the experimental setup there exists a time lag β in building up the surface concentration. For this situation the uptake is given by (Crank, 1975)

$$\frac{\theta(t)-\theta(t_0)}{\theta(t_\infty)-\theta(t_0)} = 1 - \frac{3D}{\beta R^2}\exp(-\beta t)\left(1-\sqrt{\frac{\beta R^2}{D}}\cot\sqrt{\frac{\beta R^2}{D}}\right) + \frac{6\beta R^2}{\pi^2 D}\sum_{m=1}^{\infty}\frac{1}{m^2\left(m^2\pi^2-\dfrac{\beta R^2}{D}\right)}\exp\left(-\frac{m^2\pi^2 Dt}{R^2}\right). \tag{39}$$

Again the Fick diffusivity can be constant or concentration-dependent. Using Eq. 39 in combination with the two different models, a constant Fick diffusivity equal to the zero-coverage value and a concentration-dependent Fick diffusivity, the one-component uptake can be fitted. The time lag β differs with the number of components adsorbed. For the one-component case a value of approximately $\beta = 0.07\ \text{s}^{-1}$ is obtained. For the binary situation a slightly higher value for β is obtained, $\beta = 0.15\ \text{s}^{-1}$. The offset time is between 4 and 5 s (see also Karge and Niessen (1991) for more details on the experimental setup).

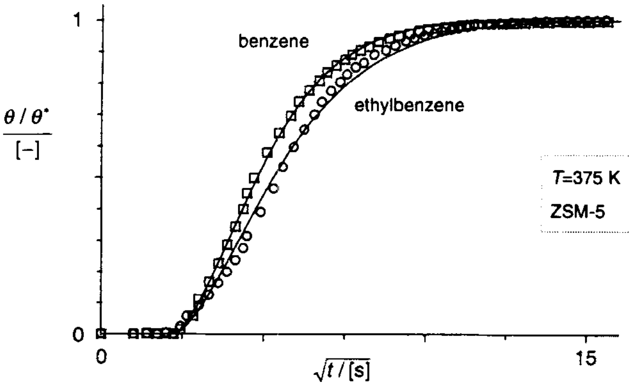

Figure 6. One-component uptake curve, of ethylbenzene and of benzene, in ZSM-5 as a function of the square root of time.

Experimental results obtained from FTIR measurements (Niessen, 1991), the solid lines are fits with Eq. 39 and the SFD model for the Fick diffusivity.

The results of the fits for the SFD model, Eq. 13, are shown in Figure 6. The values of the diffusivities are given in Table 5. The one-component uptake has also been fitted with a concentration-dependent diffusion coefficient, Eq. 11a, and the thermodynamic factor given by Eq. 37. The results of the profiles of these fits are on top of the results for the profiles obtained with a constant diffusivity and are therefore not shown. The Fick diffusivities are also given in Table 5, and the limited diffusivities, the zero-coverage GMS diffusivities, calculated from the one-component Fick diffusivities, are given in Table 6.

The concentration-dependent diffusivity can be evaluated, Eq. 39, with the linearized theory of diffusion (Krishna, 1990). The results for the one-component GMS diffusivities are used in the predictions for the binary diffusion processes.

Two-component sorption kinetics

In the SFD model the one-component Fick diffusivity equals $\mathfrak{D}_i(0)/m$. From this a ratio of the GMS diffusivities $\mathfrak{D}_1(0)/\mathfrak{D}_2(0) = 4.4$ is obtained for the benzene/ethylbenzene mixture. For the GMS model a ratio of $\mathfrak{D}_1(0)/\mathfrak{D}_2(0) = 4.3$ is obtained. These results are used to predict binary co- and counterdiffusion with the SFD model and the GMS model, and Eq. 38 for the matrix of thermodynamic factors. With the

Table 4. Experimental Data From Niessen (1991) for the Two-Component Adsorption Isotherm and the Amount Adsorbed in the Binary Uptake Experiments, at a temperature of $T = 375$ K*

Two-Comp.	m	b Pa^{-m}	n_0 mmol·g^{-1}	$n_{S,i}$ mmol·g^{-1}	Codiffusion n_i mmol·g^{-1}	Counterdiffusion n_i mmol·g^{-1}
Benzene	0.92	0.014	0.1	0.027	$0.0 \rightarrow 0.023$	$0.24 \rightarrow 0.0024$
Ethylbenzene	0.92	0.037	0.7	0.5	$0.0 \rightarrow 0.41$	$0.0 \rightarrow 0.37$

*The numerical results for the isotherms are obtained by fits with Eq. 36 performed in this work.

Table 5. Results for the One-Component Fick Diffusivity Obtained from Fits with Eq. 39*

One-Comp.	SFD Model $D = \mathfrak{D}_1(0)$ $m^2 \cdot s^{-1}$	GMS Model $\mathfrak{D} = \mathfrak{D}_1(0)\Gamma$ $m^2 \cdot s^{-1}$
Benzene	6.5×10^{-14}	2.6×10^{-14}
Ethylbenzene	2.4×10^{-14}	1.0×10^{-14}

*Results for the one-component Fick diffusivities. The experimental uptake data are from Niessen (1991). The SFD model refers to Eqs. 11b, the GMS model refers to the product of Eqs. 11a and 37.

use of the Fourier number $Fo[= \mathfrak{D}_1(0)t/R^2]$ and the ratio of the GMS diffusivities the multicomponent systems are completely specified.

It is clear that the kinetic effects are given by Eqs. 15 and 16 in the case of the GMS model and Eq. 20 in the case of the SFD model. In both models a constant GMS diffusivity $\mathfrak{D}_i[= \mathfrak{D}_i(0)]$ is used. The input conditions for the analytical simulations of the binary uptake profiles are given in Tables 4 and 6.

Codiffusion

The results from the theoretical predictions for the simultaneous uptake of the mixture of benzene and ethylbenzene in ZSM-5 are shown in Figure 7a. The uptake for binary codiffusion is equal to the normalized surface occupancies.

We see that the single-file diffusion model, over the whole range, gives a better result. Especially, the uptake of the fast-moving component is well-described by the SFD model. At the initial stage of the experiment both models differ from the uptake of the slow-moving component. The GMS model has a better result for short times but reaches equilibrium faster than the SFD model; for long times, the SFD model gives a better result. We also see that the height of the maximum varies with the ratio of the GMS diffusivities. For a large ratio of the diffusivities, the height of the maxima are of the same order for the GMS and the SFD model. This is shown in Figure 1a. However, for a small ratio of the diffusivities, there is a significant difference in the height of the maxima as predicted by the two models. This situation is shown in Figure 7a.

Predictions of the uptake profiles with the $L_{12} = 0$ model have also been performed. The results are not shown but are almost identical with the GMS model.

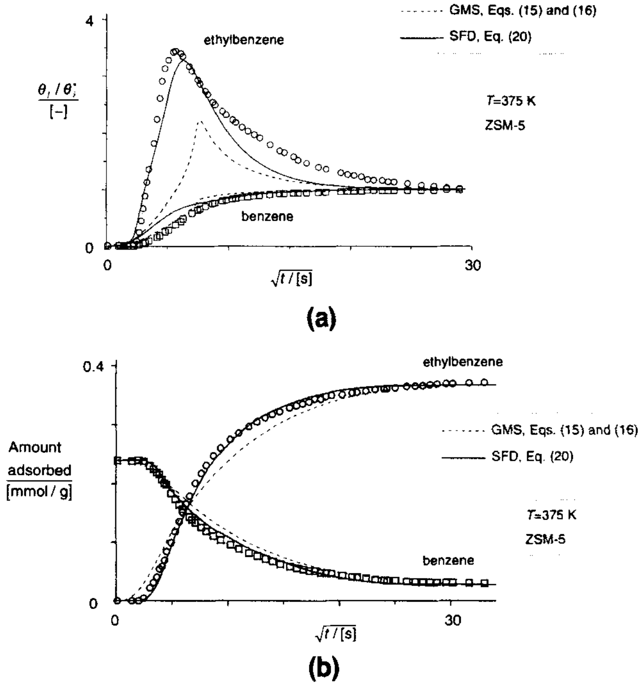

Figure 7. Transient uptake profiles for a mixture of benzene and ethylbenzene in ZSM-5 as function of the square root of time.

Experimental results (Niessen, 1991) and theoretical predictions, using the one-component mass-transfer rates. Input conditions are in Table 6. (a) Codiffusion. (b) Counterdiffusion.

Counterdiffusion

The uptake profiles for the case of counterdiffusion are depicted in Figure 7b. The differences for this situation between the predictions of the SFD and the GMS model are small. We see that the contribution of the counterexchange in binary diffusion causes a much greater difference between the SFD and GMS model than for the situation of counterdiffusion. For the situation of counterdiffusion the difference between the binary uptake profiles predicted by the GMS and the SFD model is much smaller than the difference between the profiles in the situation of binary codiffusion.

This indicates that codiffusion experiments seem the best way to study binary diffusion in molecular sieve materials. A better distinction between the various models for zeolite diffusion can be made from binary codiffusion experiments. In this way, combining one-component uptake with binary codiffusion, the proper diffusion model can be determined.

Conclusions

A concept of the GMS formulation, the Fick diffusivity considered as contributions from kinetic and thermodynamic

Table 6. Input Conditions for the Binary Simulations, Using the One-Component GMS, or Corrected, Diffusivities and the Surface Occupancies at the Beginning and at the End of the Uptake Process*

Two-Comp.	SFD Model $\mathfrak{D}_i(0)$ $m^2 \cdot s^{-1}$	GMS Model $\mathfrak{D}_i(0)$ $m^2 \cdot s^{-1}$	Codiffusion θ_i	Counterdiffusion θ_i
Benzene	3.5×10^{-14}	1.3×10^{-14}	$0.0 \rightarrow 0.1$	$0.8 \rightarrow 0.1$
Ethylbenzene	0.8×10^{-14}	0.3×10^{-14}	$0.0 \rightarrow 0.8$	$0.0 \rightarrow 0.75$
Ratio of diffusivities	4.4	4.3		

*The two models refer to the one-component Fick diffusivities given in Table 4.

effects, has been applied to binary diffusion in zeolites. Binary diffusion coefficients and uptake profiles have been predicted from one-component mass-transfer rates, in terms of the GMS diffusivities, and a model for the counterexchange between the two mixture components. The dependence of the GMS, or corrected, diffusivity, on the amount adsorbed is taken into account.

Unfortunately, the values of the one-component Fick and consequently the GMS diffusivities depend on the model used in the description of the uptake profiles.

Different theoretical models have been derived from the generalized Maxwell–Stefan equations for the description of multicomponent diffusion in molecular sieve materials. Using a criterion for single-file diffusion, in terms of the GMS counterexchange coefficient, a distinction is made between diffusion in pore-type and cage-type zeolitic structures.

Diffusion in zeolites is modeled as an activated process. The random-walk mechanism has been applied to describe kinetic contributions to the diffusion process in molecular sieve materials. The GMS diffusivity can be expressed in terms of the jump frequency of the adsorbed molecules. The dependence of the jump frequency on the occupancy can be related to the dimension of the pore structure and the maximum number of molecules per cage. For pore-type structures only one molecule can be adsorbed at a site, which is located at the channel intersection.

In this way the concentration dependence of the GMS or corrected diffusivity can be explained in terms of physical parameters characterizing the adsorbent and the properties of the adsorbates.

From comparison of computational and theoretical results it can be concluded that one- and two-component diffusion in pore-type structures can be described with a single-file diffusion model.

For binary diffusion in cage-type structures the influence of the counterexchange between sorbed molecules is demonstrated. Also, the concentration dependence of GMS diffusivity, as given by Eq. 29, should be taken into account. For a description of multicomponent diffusion in cage-type zeolitic structures, the GMS formulation, which takes counterexchange into account, is preferred.

Experimental results of the transient uptake of a binary mixture of benzene and ethylbenzene is in good agreement with a single-file diffusion model, which uses the GMS formulation to predict the uptake profiles.

Counterexchange between sorbed molecules can play an important role in the transport process of binary mixtures in zeolitic structures, especially in cage-type structures. A confirmation of this effect can be obtained from measuring binary diffusion in a cage-type zeolite, such as zeolite X.

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Notation

b_i = adsorption equilibrium constant in Langmuir and statistical isotherm of component i, Pa^{-m}
B_{ij} = elements of matrix of GMS diffusion coefficients, $\mathrm{m^2 \cdot s^{-1}}$
c_{tot} = concentration of total mixture, $\mathrm{mol \cdot m^{-2}}$
f_i = fugacity of component i, $\mathrm{N \cdot m^{-2}}$
J_i = surface diffusion flux of component i, $\mathrm{mol \cdot m^{-1} \cdot s^{-1}}$
l = length, m
m = constant in Langmuir–Freundlich isotherm
n_i = amount adsorbed of component i, $\mathrm{mol \cdot g^{-1}}$
$n_{S,i}$ = saturation amount adsorbed of component i, $\mathrm{mol \cdot g^{-1}}$
n_i^* = equilibrium amount adsorbed of component i, $\mathrm{mol \cdot g^{-1}}$
$n_{0,i}$ = parameter in the Langmuir–Freundlich isotherm, $\mathrm{mol \cdot g^{-1}}$
N_i = surface molar flux of component i, $\mathrm{mol \cdot m^{-1} \cdot s^{-1}}$
p = pressure, Pa
p_i = (partial) pressure of component i, Pa
r = particle coordinate ($0 \leq r \leq R$), m
R_g = gas constant, $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
t = time, s
V = volume of a cage, $\mathrm{m^3}$
x = space coordinate, m
β = effective molecular volume, $\mathrm{m^3}$
λ = displacement, distance between two adjacent sites, m
ν_i = jump frequency of component i, $\mathrm{s^{-1}}$
ν^0 = effective jump frequency, $\mathrm{s^{-1}}$
μ_i = surface chemical potential of component i, $\mathrm{J \cdot mol^{-1}}$

Subscripts and Superscripts

A = apparent diffusivity
S = saturation
tot = total
0 = initial condition at $t = 0$
∞ = equilibrium value
$*$ = equilibrium value
0 = standard state

Literature Cited

Aust, E., K. Dahlke, and G. Emig, "Simulation of Transport and Self-Diffusion in Zeolites with the Monte Carlo Method," *J. Catal.*, **115**, 86 (1989).

Barrer, R. M., "Migration in Crystal Lattices," *Trans. Farad. Soc.*, **37**, 590 (1941).

Barrer, R. M., and W. Jost, "A Note on Interstitial Diffusion," *Trans. Faraday Soc.*, **45**, 928 (1949).

Chen, Y. D., and R. T. Yang, "Concentration Dependence of Surface Diffusion and Zeolitic Diffusion," *AIChE J.*, **37**, 1579 (1991).

Chen, Y. D., and R. T. Yang, "Predicting Binary Fick Diffusivities from Pure-component Fickian Diffusivities for Surface Diffusion," *Chem. Eng. Sci.*, **47**, 3895 (1992).

Chen, Y. D., R. T. Yang, and L. M. Sun, "Further Work on Predicting Multicomponent Diffusivities from Pure-component Diffusivities for Surface Diffusion and Diffusion in Zeolites," *Chem. Eng. Sci.*, **48**, 2815 (1993).

Crank, J., *The Mathematics of Diffusion*, Clarendon Press, Oxford (1975).

Dahlke, K. D., and G. Emig, "Diffusion in Zeolites—A Random-walk Approach," *Cata. Today*, **8**, 439 (1991).

Darken, L. S., "Diffusion, Mobility and their Interrelation through Free Energy in Binary Metallic Systems," *Trans. AIME*, **175**, 184 (1948).

Fiedler, K., and D. Gelbin, "Model for Analysing Diffusion in Zeolites," *J. Chem. Soc. Faraday Trans. I*, **10**, 2423 (1978).

Gelbin, D., and K. Fiedler, "On the Concentration Dependence of Diffusion in Zeolites," *AIChE J.*, **26**, 510 (1980).

Goddard, M., and D. M. Ruthven, "Sorption and Diffusion of C8 Aromatic Hydrocarbons in Faujasite Type Zeolites: II. Sorption Kinetics and Intercrystalline Diffusivities," *ZEOLITES*, **6**, 283 (1986).

Habgood, H. W., "The Kinetics of Molecular Sieve Action. Sorption of Nitrogen-Methane Mixtures by Linde Molecular Sieve 4A," *Can. J. Chem.*, **36**, 1384 (1958).

Hill, T. S., *An Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, MA (1962).

Karge, H. G., and W. Niessen, "A New Method for the Study of Diffusion and Counterdiffusion in Zeolites," *Catal. Today*, **8**, 451 (1991).

Kärger, J., and M. Bülow, "Theoretical Prediction of Uptake Behaviour in Adsorption Kinetics of Binary Gas Mixtures Using Irreversible Thermodynamics," *Chem. Eng. Sci.*, **30**, 893 (1975).

Kärger, J., and D. M. Ruthven, *Diffusion in Zeolites*, Wiley, New York (1992).

Krishna, R., "Multicomponent Surface Diffusion of Adsorbed Species: A Description Based on the Generalized Maxwell-Stefan Equations," *Chem. Eng. Sci.*, **45**, 1779 (1990).

Kirshna, R., "A Unified Approach to the Modelling of Intraparticle Diffusion in Adsorption Processes," *Gas Sep. Purif.*, **7**, 91 (1993).

Marutovsky, M., and M. Bülow, "Sorption Kinetics of Multicomponent Gaseous and Liquid Mixtures on Porous Adsorbents," *Gas Sep. Purif.*, **1**, 66 (1987).

NAG, Numerical Algorithm Group, Fortran library manual, mark 15 (1991).

Niessen, W., "Untersuchungen zur Diffusion und Gegendiffusion in Zeolithen mit Hilfe der FTIR-Spectroskopie," PhD Thesis, Franz Haber Institut der Max Planck Gesellschaft, Berlin (1991).

Niessen, W., and H. G. Karge, "Investigation of Diffusion and Counter-diffusion of Benzene and Ethylbenzene in ZSM-5 Zeolites by a Novel IR Technique," *Stud. Surf. Sci. Catal.*, **60**, 213 (1991).

Niessen, W., H. G. Karge, and L. Jozefowicz, "Thermodynamic and Kinetic Data of Sorption in Zeolites Determined by FTIR," *Proc. Int. Conf. on Fundamentals of Adsorption*, M. Suzuki, ed. Kodansky, Tokyo, p. 475 (1993).

Niessen, W., and H. G. Karge, "Diffusion of *p*-Xylene in Single and Binary Systems in Zeolites Investigated by FTIR Spectroscopy," *Microporous Mat.*, **1**, 1 (1993).

Palekar, M. G., and R. A. Rajadhyaksha, "Sorption in Zeolites: I. Sorption of Single Component and Binary Sorbate Systems," *Chem. Eng. Sci.*, **40**, 1085 (1985).

Qureshi, W. Q., and J. Wei, "One- and Two-Component Diffusion in Zeolite ZSM-5: I. Theoretical," *J. Catal.*, **126**, 126 (1990a).

Qureshi, W. Q., and J. Wei, "One- and Two-Component Diffusion in Zeolite ZSM-5: II. Experimental," *J. Catal.*, **126**, 147 (1990b).

Reed, D. A., and G. Ehrlich, "Surface Diffusion, Atomic Jump Rates and Thermodynamics," *Surf. Sci.*, **102**, 588 (1981).

Riekert, L., "Rates of Adsorption and Diffusion of Hydrocarbons in Zeolites," *AIChE J.*, **17**, 446 (1971).

Round, G. F., H. W. Habgood, and R. Newton, "A Numerical Analysis of Surface Diffusion in a Binary Adsorbed Film," *Sep. Sci.*, **1**, 219 (1966).

Ruthven, D. M., R. I. Derrah, and K. F. Loughlin, "Diffusion of Light Hydrocarbons in 5A Zeolite," *Can. J. Chem.*, **51**, 3514 (1973).

Ruthven, D. M., "Sorption of Oxygen, Nitrogen, Carbonmonoxide, Methane and their Binary Mixtures of these Gases in 5A Molecular Sieve," *AIChE J.*, **22**, 753 (1976).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York (1984).

Tsikoyiannis, J. G., and J. Wei, "Diffusion and Reaction in High-Occupancy Zeolite Catalysts: I. A Stochastic Theory," *Chem. Eng. Sci.*, **46**, 233 (1991).

Van den Broeke, L. J. P., S. A. Nijhuis, and R. Krishna, "Monte Carlo Simulations of Diffusion in Zeolites and Comparison with the Generalized Maxwell-Stefan Theory," *J. Catal.*, **136**, 463 (1992).

Vignes, A., "Diffusion in Binary Solutions," *Ind. Eng. Chem. Fundam.*, **5**, 189 (1966).

Xiao, J., and J. Wei, "Diffusion Mechanism of Hydrocarbons in Zeolites: I. Theory," *Chem. Eng. Sci.*, **47**, 1123 (1992a).

Xiao, J., and J. Wei, "Diffusion Mechanism of Hydrocarbons in Zeolites: II. Analysis of Experimental Observations," *Chem. Eng. Sci.*, **47**, 1143 (1992b).

Yang, R. T., Y. D. Chen, and Y. T. Yeh, "Predictions of Cross-Term Coefficients in Binary Diffusion: Diffusion in Zeolite," *Chem. Eng. Sci.*, **46**, 3089 (1991).

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