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A Theory for Two-Component Diffusion in Zeolites

In recent years, models have been developed to describe diffusion of point-like molecules in zeolites (*1–9*), with a particular emphasis on zeolite catalyst ZSM-5. In the present model, an attempted jump of a molecule to an occupied site results in the molecule remaining at its original site. This model has received the most attention in the literature relating to zeolites (*1, 6–9*). The same model is sometimes referred to as a "minimally interacting lattice gas" in the physics literature, where self-diffusion has been extensively studied, e.g. (*10–12*).

We use the simulation method employing Poisson-distributed event times described previously (*8*), with two distinguishable diffusing species designated A and B. It is assumed that components A and B have *identical* diffusive and adsorptive properties. All of the simulation results reported here were obtained by averaging 400 simulations conducted on an initially empty 100 × 20 lattice. The lateral edges abutted impermeable sites and the top and bottom edges were exposed to gases of constant composition and pressure.

The apparent diffusion coefficient D_A^+, of component A, for example, is defined by:

$$J_A = -D_A^+ \nabla\theta_A, \tag{1}$$

where J_A is the measured flux of component A between two adjacent rows and $\nabla\theta_A$ is the measured gradient of A concentration between the same two adjacent rows.

Co-diffusion simulations were conducted, in which, the top edge of the lattice was exposed to gaseous A and B at constant composition and pressure, and the bottom edge was exposed to a vacuum. The co-diffusion simulation results at steady state can be summarized by

$$D_A^+ = D_B^+ = D_0, \tag{2}$$

where D_0 is the single component diffusion coefficient, and

$$\nabla\theta_B = \frac{\theta_B}{\theta_A}\nabla\theta_A. \tag{3}$$

Counter-diffusion simulations were also conducted, in which, the lattice was exposed to pure A at the top of the lattice and pure B at the bottom of the lattice at the same pressure. The combined occupancy $\theta_T = \theta_A + \theta_B$ was constant throughout the lattice at steady state.

Figure 1 shows the steady state concentration profile and apparent diffusivity of A, for a pressure such that $\theta_T = 0.9$ at steady state. There is an edge effect which increases the apparent diffusivities near the edges, particularly for higher occupancy simulations. At steady state, the (bulk) diffusivity between internal rows (rows 4 to 17) is approximately constant. The counter-diffusion results, in the bulk, at steady state can be summarized by

$$D_A^+ = D_B^+ = D_0(1 - \theta_T)f(\theta_T), \tag{4}$$

and

$$\nabla\theta_A = -\nabla\theta_B. \tag{5}$$

$f(\theta_T)$ is the (bulk) correlation factor (*10–12*) for self-diffusion, which accounts for correlations in the movement of adjacent molecules. According to Tahir-Kheli and Elliot (TKE) (*11*),

$$f(\theta_T) = (1 + \langle\cos\phi\rangle)\Big/\left(1 + \frac{2 - 3\theta_T}{2 - \theta_T}\langle\cos\phi\rangle\right) \tag{6}$$

where for a square lattice, $\langle\cos\phi\rangle = -0.36338023$. A more accurate approximation has subsequently been provided by Tahir-Kheli and El-Meshad (TKEM) (*12*).

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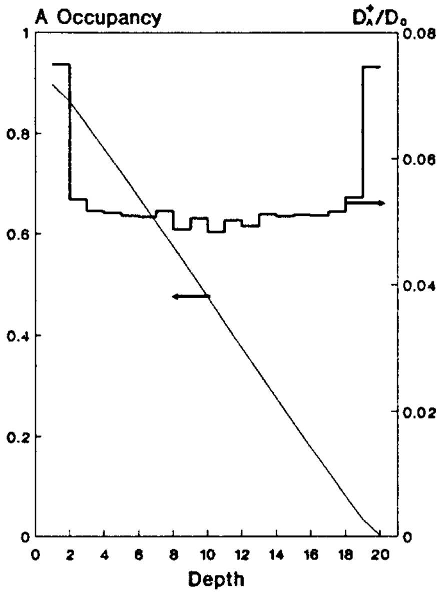

FIG. 1. Steady state pure counter-diffusion at a steady state combined concentration of $\theta_T = 0.9$. (———) steady state concentration profile for component A, (▬▬▬) apparent diffusivity of component A.

The bulk correlation factors are plotted together with the TKE and TKEM theories in Fig. 2. The difference between the simulation and both theories is within the statistical uncertainty of the simulation results. Also shown in Fig. 2 are the values for the edge correlation factor (for diffusion between the two rows nearest the edge of the lattice).

The diffusion equation is

$$\begin{pmatrix} J_A \\ J_B \end{pmatrix} = -\begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix}\begin{pmatrix} \nabla\theta_A \\ \nabla\theta_B \end{pmatrix}. \quad (7)$$

Equating the fluxes in Eq. (7) with the fluxes obtained from the co- and counter-diffusion simulations, Eqs. (1)–(5), and solving for the diffusion matrix **D** gives:

$$\mathbf{D} = D_0\begin{pmatrix} (1 - \theta_B g) & \theta_A g \\ \theta_B g & (1 - \theta_A g) \end{pmatrix}, \quad (8)$$

where

$$g(\theta_T) = f(\theta_T) + \frac{1 - f(\theta_T)}{\theta_T}.$$

The factor $g(\theta_T)$ is approximately equal to $1.571 - 0.571\theta_T$.

The incremental change in the vector occupancy of an internal row n, during a short time δt, according to a finite difference approximation (FDA) to the diffusion equation, is given by

$$\frac{\delta \boldsymbol{\theta}_n}{\delta t} = \left(\frac{\mathbf{D}_{n-1} + \mathbf{D}_n}{2}\right)(\boldsymbol{\theta}_{n-1} - \boldsymbol{\theta}_n) - \left(\frac{\mathbf{D}_n + \mathbf{D}_{n+1}}{2}\right)(\boldsymbol{\theta}_n - \boldsymbol{\theta}_{n+1}), \quad (9)$$

where the first term is the flux from row $n - 1$ to row n and the second term is the flux from row n to row $n + 1$.

The incremental change in an edge row (for example row 1) is given by

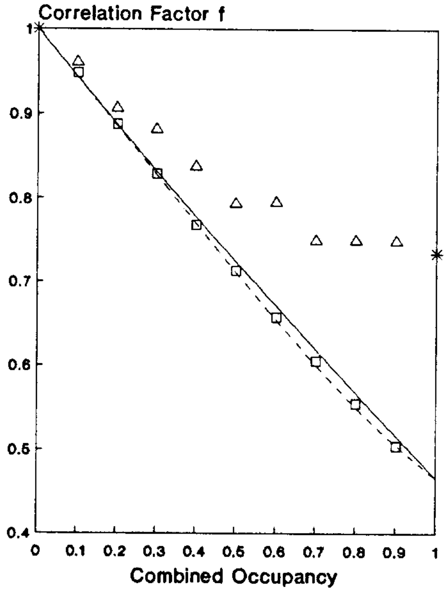

FIG. 2. Correlation factors for pure counter-diffusion determined from theory and Monte Carlo simulations. (□) bulk correlation factor from Monte Carlo simulations, (———) correlation factor according to Ref. (*11*), (– – – –) correlation factor according to Ref. (*12*), (△) edge correlation factor from Monte Carlo simulations, (*) estimated limits of the edge correlation factor, where f_{edge} $(\theta_T = 0) = 1$ and f_{edge} $(\theta_T = 1) = (f(\theta_T) + 1)/2$ (as there is no correlation resulting from a molecule jumping from an edge site to one deeper in the lattice as $\theta_T \to 1$).

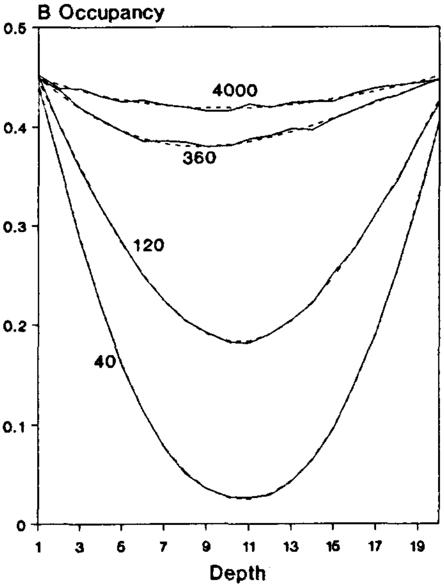

FIG. 3. Concentration depth profiles of component B for "mixed-diffusion" boundary conditions (see text). Parameter = time (τ). (———) Monte Carlo simulation, (———) proposed diffusion theory.

$$\frac{\delta\boldsymbol{\theta}_1}{\delta t} = \begin{pmatrix} p_A(1-\theta_{T,1}) - D_0\theta_{A,1} \\ p_B(1-\theta_{T,1}) - D_0\theta_{B,1} \end{pmatrix} - \left(\frac{\mathbf{D}_1+\mathbf{D}_2}{2}\right)(\boldsymbol{\theta}_1 - \boldsymbol{\theta}_2), \quad (10)$$

where the first term is the flux from the gaseous phase to row 1 (according to the usual two component Langmuir isotherm) and the second term is the flux from row 1 to row 2.

There were no significant differences between the simulation results and FDA values for pure co- and counter-diffusion boundary conditions in the bulk, so a "mixed-diffusion" simulation was conducted, in which component A was driven by a large concentration gradient, whereas there was no (significant) overall concentration gradient of component B. The concentration profiles for B are shown in Fig. 3. Once again, the FDA correctly predicts the transient and steady-state behavior in the bulk. The nonlinearity in the steady state single component profiles is correctly predicted by the present theory, whereas the previous theory (*7*, *9*) predicts linear steady state profiles for the same boundary conditions. At steady state, component B is "diffusively entrained" by the greater flux of component A, due to the driving force for diffusion including the concentration gradient of A.

We have proposed a theory for two component diffusion in zeolites where the single component diffusivities are *equal*. All entries in the diffusion matrix have nonlinear terms which, in general, produce nonlinear steady state profiles and diffusive entrainment of one of the components. The present theory exhibits qualitative and quantitative differences from previous numerical approximations, which can become significant at high occupancies. These differences also appear in the corresponding Monte Carlo results and hence are inherent in the physical model. Although it appears that the theory can only be solved numerically, it has the significant advantage of having no adjustable parameters (except for the single component diffusivity).

Further research is required to generalize this approach to multicomponent systems in which the single component diffusivities are different.

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