Predicting Packed-Bed Breakthrough Behavior from PFG NMR Diffusion Data

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Pulsed field gradient (PFG) NMR measurements have been conducted to measure self-diffusion coefficients of gases within porous media. Analysis of these microscopic data with the use of a previously developed long-range diffusion model has enabled us to accurately predict breakthrough curves for transport through packed-bed adsorption columns, and the length of unused bed (LUB). This methodology enables the evaluation of mass-transfer coefficients without the complications associated with transient sorption experiments, that is, heat effects, and thereby offers a reasonable alternative to conventional breakthrough experimentation for the evaluation of mass-transfer coefficients, and LUB for large-scale unit operations. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 589–595, 2004

Introduction

The dynamics of gas adsorption within a packed-bed adsorbent column are dictated by gas-solid phase equilibria, heat transfer, mass transfer, and their mutual coupling. Any transient sorption experiment involves the generation of heat because of the heat of adsorption, and, consequently, a temporary desorption of gas from the solid surface because of the increase of the sample temperature. The swing in temperature in turn directly affects gas diffusion rates. Separating and quantifying these three aspects of adsorption has been the focus of continued research efforts of adsorption scientists (Ruthven, 1984). Consequently, new experimental techniques that enable the decoupling of heat and mass transfer from equilibrium measurements are continuously being sought after as are theoretical insights which enable large-scale adsorption behavior to be predicted from microscopic measurements (Eic et al., 1988; Sircar et al., 1999; Rynders et al., 1997). Because equilibrium and thermal properties can be easily obtained by performing volumetric or gravimetric isotherm experiments at various temperatures and by micro-calorimetric methods, we focus in this work on defining mass-transfer rates within porous media from lab scale quantities of material, and on applying that information to anticipate large-scale breakthrough behavior.

The diffusion coefficient of gases in microporous adsorbent materials is among the most important parameters describing mass transfer through adsorbent beds because diffusion rates often control cycle times, and influence the design of industrial separation processes. Mass transfer through commercial zeolites, which are typically formed by extruding (or pressing) a crystalline powder with a binder into pellets, is generally governed by the rate of macropore diffusion (Kärger et al., 1992).

Mass-transfer coefficients of gases in a porous media for industrial gas separation unit operations are traditionally assessed by performing large-scale, transient experiments, such as breakthrough tests, which require large amounts of adsorbent and gas. Furthermore, the data analysis of these experiments is complicated because heat, mass, and equilibrium are coupled, transient, and must be considered explicitly. To simplify the analysis, it is a common practice to mitigate heat effects in the experiments by employing the gas of interest under very dilute conditions. Regardless of the degree of dilution, however, some level of local temperature fluctuation is inevitable in transient sorption experiments.

As an alternative to traditional breakthrough experimentation one can apply benchtop laboratory methods, such as pulsed field gradient (PFG) NMR or tracer exchange techniques (Rynders et al., 1997), which enable self-diffusion measurements to be conducted at isothermal conditions, thereby eliminating any complications associated with heat-transfer

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effects. The relatively long mixing times required for tracer exchange measurements, however, limit this technique to the analysis of systems exhibiting relatively slow kinetics, such as intracrystalline-limited diffusion (Rynders et al., 1997; Mohr et al., 1999). Consequently, the PFG NMR technique was considered the superior option for the systems of interest here. In addition, the applicability of PFG NMR has already been successfully demonstrated in quantifying Brownian motion within various molecular systems ranging from polymer solutions and melts (Rittig et al., 1999), gel electrolytes (Bamford et al., 2001), biological (Knauss et al., 1999) and surfactant systems (Söderman et al., 1999), and porous solids (Kärger et al., 1992).

In this work, we have applied PFG NMR to investigate the self-diffusion of nitrogen, methane and carbon monoxide in a series of porous commercial materials including 5A, 13X (NaX), and silica gel adsorbents, in a pressure range from 0.5 atm to 5 atm, and have applied this information to successfully predict breakthrough behavior in large-scale adsorption columns for systems that exhibit constant pattern behavior (Sircar et al., 1983). Because performing PFG NMR measurements directly at typical breakthrough conditions, that is, ~25 atm helium with 0.5–1% of adsorbate, is experimentally challenging, we have resorted to correlating self-diffusion coefficients with an appropriate model, and, thus, extrapolating the self-diffusion behavior to the conditions of interest.

The model of choice to describe self-diffusion behavior in microporous particles was conceived by Kärger et al. (1981), and has been shown to represent self-diffusion in microporous crystalline powders reasonably well by assuming that the long-range self-diffusivity ($\mathscr{D}_{LR}$) is governed predominantly by transport through intercrystalline space. In our previous work, this theory has been evaluated and applied to porous pellets, which are of more practical interest, by appropriately defining the porosity values that characterize the system, and by considering transport in macro- and mesopores (Rittig et al., 2002a, 2003).

Our self-diffusion data were well-represented by the long range diffusion model (LRDM) (Rittig et al., 2002a, 2003). The global approach taken in this work, therefore, has been to examine the self-diffusion of gases within porous media via PFG NMR, correlate the results with the LRDM, and apply this information to predict large-scale breakthrough behavior in packed-bed adsorption units.

For the sake of clarity, throughout this article a script $\mathscr{D}$ will refer to a self-diffusion coefficient (which describes a Brownian motion process) whereas a blocked, that is, nonscript, D will refer to a transport/mutual diffusion coefficient (which describes a process driven by a chemical potential gradient.)

Experimental

Sample preparation

The detailed sample preparation procedure has previously been described, and, therefore, shall be only summarized here (McDaniel, 1996; Rittig, 2002b). Pelletized zeolites, obtained from different manufactures, were activated (to remove adsorbed water) under dynamic vacuum ($<10^{-4}$ torr) with a 1 K/min thermal ramp. The pellets were held for 60 min at 373, 423, 473, and 523 K, and ultimately heated to 673 K and held for at least 12 h. After activation, the samples were transferred without exposure to air, to an argon-purged glove box, wherein a known amount of activated material was placed in a 10 mm quartz NMR tube. The sample tube was sealed with a valve and attached to a classical volumetric expansion unit (ASAP™ 2010 from Micromeritics, Inc. Norcross, GA). After degassing at ambient temperature to $< 10^{-4}$ torr, samples containing 0.5 to 5 atm ^{13}CO (99+%, Isotech), CH_4 (APCI) and/or $^{15}N_2$ (99+%, Isotech) were prepared.

Samples for use in PFG NMR diffusion studies were prepared by the following protocol. The free space volume within the sample tubes was determined by helium expansion experiments. Following evacuation, the calibrated manifold was charged to a particular pressure with the gas of interest. After equilibrating, the gas was expanded into the sample cell, and the sample tube was immersed into liquid nitrogen. Finally, the tube was sealed with an acetylene torch, and the free space lost during sealing of the sample was determined by performing a second helium expansion experiment. The resulting cell volume was determined by the difference. Although the pressure within the NMR sample tube and the surface excess on the zeolite could be calculated from knowledge of a sorption isotherm (measured independently) and an appropriate equation of state for the gas phase, we typically performed gas-phase NMR experiments which provided direct measurements of the pressure and surface excess within our sample tubes (Rittig et al., 2002b).

The macro-mesopore and micropore porosities, as well as the associated pore-size distributions, were determined by complementary mercury intrusion, helium pycnometry, and, in the case of silica gel, nitrogen isotherm measurements at 77 K. The average pore diameter used in our self-diffusion analyses was the hydraulic (or tubular) diameter (Webb et al., 1997).

Breakthrough measurements

Breakthrough tests were performed on a 0.9 in ID by 6 ft stainless steel column. Sample taps and thermocouples were evenly spaced at 1 ft intervals along the length of the column. The top and bottom of the column were sealed with 2.75 in con-flat flanges. Mass-flow controllers (Brooks Model 5851) regulated gas-flow rates to the column, and accumulated flow was recorded with a dry test meter equipped with a Gurley Precision Instruments Series 911S rotary incremental encoder. Valve sequencing was accomplished with an Allen Bradley PLC, and the data recorded with RSView software. Certified gas blends of the test gas molecule in a helium carrier were obtained from Air Products and Chemicals, Inc. and used both as the feed gas, and to span the Gow-Mac Instruments Model 50 gas analyzer before a test.

Adsorbents were loaded into the column and the column was tapped to generate a uniform packing density. Following, the column was purged with helium until a steady base line was achieved on the Gow-Mac gas analyzer. However, when the base line was stable, the Allen Bradley control program was initiated, and the column was pressurized to 25 atm with helium. At a pressure of 25 atm, the gas flow automatically switched to the test gas, and data logging commenced on a 10 s interval recording pressure, bed temperature at 3 locations, cumulative flow, and the adsorbate concentration exiting in the column. Typical flow rates where 41 lb-mole/ft^2-h and to minimize possible heat effects the concentration of carbon monoxide was typically kept at 500 ppm, whereas for methane and nitrogen the concentration was approximately 1%.

PFG NMR Measurements

The NMR data were collected with a Bruker AMX-360 NMR spectrometer equipped with a wide-bore magnet which has been described earlier (Rittig et al., 2002a, 2003; McDaniel, 1996). The instrumental setup contains a Bruker microimaging accessory that includes the gradient pulse amplifiers for generation of the gradients. The NMR probe was equipped with a $^{15}N/^{1}H$ or $^{13}C/^{1}H$ double-tuned radio-frequency coil insert which can accommodate sample tubes up to 10 mm in dia.. The temperature was maintained with a Eurotherm B-VT2000 temperature control unit. All experiments were performed at 25 °C ± 0.5 K.

For diffusion measurements, the stimulated echo sequence ($\pi/2-t_1-\pi/2-t_2-\pi/2-t_1-$fid) has been used because the spin–spin-relaxation times (T_2) are usually much shorter than the spin–lattice-relaxation times (T_1) (Callaghan et al., 1993). In the case of a random walk, the measured spin attenuation Ψ because of the field gradient applied after the first and third $\pi/2$ rf. pulse can be described by (Kärger et al., 1992)

$$\Psi = \frac{A}{A_0} = \exp\left(-\frac{q^2\langle z^2(\Delta)\rangle}{2}\right) \tag{1}$$

where $\langle z^2(\Delta)\rangle$ denotes the mean square displacement of the diffusing molecules, Δ is the diffusion time ($\Delta = t_1 + t_{12}$), and q is the abbreviation for $q = \delta\gamma g$. Here, δ is the duration of the gradient pulse, and g is the strength of the gradient pulses, and γ is the gyromagnetic ratio of the investigated nucleus (for example, ^{1}H, ^{13}C, ^{15}N). The total magnetizations with and without applied gradients are A and A_0, respectively. No additional gradient justification was necessary with the described hardware when two pregradients were applied before the pulse sequence having the same gradient strength and duration.

Background and Theory

A commonly employed description of combined bulk and Knudsen diffusion is given by the dusty gas model (DGM) (Evans et al., 1961; Mason et al., 1983), and is often cited (Krishna, 1993) as the starting point for analyzing gas transport within porous solids. The principle behind the DGM model is relatively straightforward. The pore wall within a solid is envisioned to consist of giant molecules of dust uniformly distributed in space, which are considered as a stationary species in an n+1 component mixture comprised of n gas constituents. By writing a force balance between the chemical potential gradient of any mobile species and the frictional force that the molecule experiences with the other species during motion, and assuming ideal gas behavior, one obtains

$$\left(\frac{-1}{RT}\right)\frac{\partial P_i}{\partial z} = \sum_{i=1}^{n}\left[\frac{y_jN_i - y_iN_j}{D_{B,ij}}\right] + \frac{N_i}{D_{K,i}} \tag{2}$$

where y_i, N_i, and P_i are the mole fraction, molar flux, and partial pressure of component i, respectively. $D_{B,ij}$ and $D_{K,i}$ are the bulk diffusion coefficient for the binary pair i-j and the Knudsen diffusion coefficient of component i, respectively. Finally, R is the gas constant, and T is the absolute temperature.

The application of this equation is hindered as are most diffusion models, by the actual distance a molecule travels, while traversing a distance in the z-coordinate. The molecular transport path in a porous medium is tortuous and generally the extra distance a molecule travels, while diffusing in the z-direction cannot be accounted for *a priori*. To explicitly express this concept, one can apply a linear driving force approximation with the common assumption that the average diffusion distance a molecules travels into a spherical particle is to the surface of a hypothetical spherical particle whose volume is half of the real particle volume. Implementing these assumptions leads to

$$\frac{\beta\Delta P_i}{RT} = \sum_{i=1}^{n}\left[\frac{\bar{y}_jN_i - \bar{y}_iN_j}{D_{B,ij}}\right] + \frac{N_i}{D_{K,i}} \tag{3}$$

with the parameter β defined as

$$\beta \approx \frac{10}{\tau d_P} \tag{4}$$

Here d_p is the pellet diameter, and τ is a tortuosity factor, which accounts for the extra distance a molecule must traverse, while diffusing in the z-direction because of the winding nature of the pore structure. Because we have introduced the linear driving force approximation, we therefore consider the average concentrations within the pellet denoted by overbars in Eq. 3.

To solve the process model equations that describe column breakthrough behavior, we have applied a proprietary software package previously discussed (Hartzog et al., 1995) called Simulator for Packed Bead Adsorption Cycles (SIMPAC). The governing partial differential equations are discretized in space with biased upwind differencing with flux corrections, and the resulting system of time-dependent, explicit, first-order ordinary differential equations are solved with the LSODES sparse solver from ODEPACK (Hindmarsh, 1983), with the backward difference option for stiff systems.

The parameter β, defined in Eq. 4, is commonly employed as a regression parameter to provide the best fit to experimental breakthrough data of an adsorbate passing through a bed of adsorbent. This parameter, which is specific to the adsorbent and independent of adsorbate, can therefore be employed to predict breakthough behavior at other experimental conditions, and for other adsorbates. Clearly, this is an efficient means of representing transport in porous media.

Although the parameter β is employed as the regression parameter, it could be calculated directly from Eq. 4, if the tortuosity factor could be approximated accurately. Recently, we have demonstrated that tortuosity factors can indeed be obtained reliably by the analysis of experimental self-diffusion data with a newly developed long-range diffusion model which is applicable to describe self-diffusion behavior in porous media (Rittig et al., 2002a, 2003). In previous work, we have applied pulsed field gradient (PFG) nuclear magnetic resonance (NMR) to measure self-diffusion coefficients in pure and multicomponent gases within a variety of adsorbents, and have modeled these data with a long-range diffusion model, the concept of which was initially proposed by Kärger and coworkers (Kärger et al., 1981; McDaniel et al., 1996). The tortuosity factors extracted from our previous studies (Rittig et al., 2002a, 2003) were shown to be: (1) reasonable in magnitude, (2) independent of adsorbate, (3) independent of temperature and pressure, and (4) applicable in both pure and multicomponent systems. In addition, we have demonstrated that unanticipated self-diffusion behavior could be predicted with confidence once a few (2–3) pure component data points for a single adsorbate/adsorbent system have been measured.

Although there has recently been both theoretical (Malek et al., 2001) and experimental (Geier et al., 2002) evidence that suggests two different tortuosity factors should be used to describe transport in the Knudsen and bulk regimes, all of the data measured in this investigation are far removed from the Knudsen limit. Consequently, there was no need to resort to the use of two tortuosity factors to describe our data.

Tortuosity factors can be ascertained simply by comparing the experimental self-diffusion data, for example, PFG NMR data, to predictions from the long-range diffusion model (LRDM). Because the LRDM assumes transport within straight cylindrical channels, it follows that

$$\tau = \frac{\mathscr{D}_{LR}^{MODEL}}{\mathscr{D}_{LR}^{EXP}} \tag{5}$$

where EXP and MODEL refer to the experimental and predicted values of the long-range diffusion coefficient.

The value for the long-range self-diffusion coefficient $\mathscr{D}_{\mathrm{LR}}$ for a diffusant within a pelletized sample can be approximated (Rittig et al., 2002a, 2003) by

$$\mathscr{D}_{\mathrm{LR}} \cong p_{\mathrm{inter}} \mathscr{D}_{\mathrm{inter}} \tag{6}$$

where p_{inter} is the fraction of molecules within the macro-mesopore space, and $\mathscr{D}_{\mathrm{inter}}$ is their self-diffusivity which is described by the kinetic gas theory (Rittig et al., 2002a, 2003). The value for p_{inter} can be calculated directly from the adsorption isotherm, as well as the characteristic dimensions of the particle (Rittig et al., 2002a, 2003). By expressing p_{inter} in terms of measurable quantities, the long-range self-diffusion coefficient can be rewritten as

$$\mathscr{D}_{\mathrm{LR}} = \frac{\mathscr{D}_{\mathrm{inter}}}{1 + \dfrac{RT\rho_{\mathrm{p}} n^{\mathrm{m}}}{p\varepsilon_{\mathrm{ma}}}} \tag{7}$$

where ϵ_{ma} is the macro-mesopore porosity (cm^3 macro-mesopores/cm^3 solid + all pores), ρ_{p} is the pellet density (g/cm^3 solid + all pores), and n^{m} is the sorbate loading, that is, surface excess (mmoles/g).

The long-range-diffusion coefficient alluded to in Eqs. 6 and 7 is an effective self-diffusion coefficient which represents transport through the intercrystalline space of the material. This coefficient describes the rate of Brownian motion of a molecular random walk throughout the pellet space. The actual sorption process during a breakthrough experiment, however, is a mutual-diffusion process in which the transport rate is governed by the chemical potential gradient. By considering this process from the standpoint of an isothermal Fickian analysis of macropore limited diffusion with simultaneous adsorption, the appropriate differential equation describing this scenario may be written as

$$\frac{\partial c}{\partial t} = \frac{D_P}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r} \right) - \frac{\rho_p}{\varepsilon_{ma}} \frac{\partial n^{\mathrm{m}}}{\partial t} \tag{8}$$

where D_p is the pore diffusivity which can be estimated from a variety of empirical correlations depending on the diffusion regime.

Through the assumption of ideal gas behavior, Eq. 8 can be rearranged into a more commonly recognizable expression for simple diffusion into a sphere, namely

$$\frac{\partial c}{\partial t} = \frac{D_{\mathrm{LR}}}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r} \right) \tag{9}$$

where

$$D_{\mathrm{LR}} = \frac{D_{\mathrm{p}}}{1 + \dfrac{RT\rho_{\mathrm{p}} n^{\mathrm{m}}}{p\varepsilon_{\mathrm{ma}}}} \tag{10}$$

The adsorption aspect of the simultaneous diffusion/adsorption problem being considered has thus been grouped within a newly defined effective mutual-diffusion coefficient D_{LR}. The mutual-diffusion coefficient (D_{LR}) is the transport counterpart to the long-range self-diffusion coefficient ($\mathscr{D}_{\mathrm{LR}}$) discussed previously in Eqs. 6 and 7. The similarity between Eqs. 7 and 10 is apparent.

The long-range self- and transient diffusivities are generally related through the Darken correction (Kärger et al., 1992)

$$D_{\mathrm{LR}} = \mathscr{D}_{\mathrm{LR}} \frac{d \ln p}{d \ln n^{m}} \tag{11}$$

By simple rearrangement of Eq. 11, and reference to Eqs. 7 and 10, one observes that the derivative term in Eq. 11 expresses the ratio of the pore mutual (transport) diffusion coefficient (D_p in Eqs. 8 and 10), and the pore self-diffusion coefficient ($\mathscr{D}_{\mathrm{inter}}$ in Eq. 7). For the case of a Langmuirian isotherm, Eq. 11 takes the form

$$D_{\mathrm{LR}} = \mathscr{D}_{\mathrm{LR}}(1 + bp) \tag{12}$$

where b is the gas-solid interaction parameter. The value of D_{LR}, therefore, can increase or decrease as pressure is changed depending on the pressure dependence of $\mathscr{D}_{\mathrm{LR}}$

It should be noted that if one wishes to employ the simple linear driving force model (Glueckauf et al., 1955) to describe mass transfer into spherical particles, rather than the DGM model, the rate constant would be defined as

$$k = \frac{15 D_{\mathrm{LR}}}{r^2} \tag{13}$$

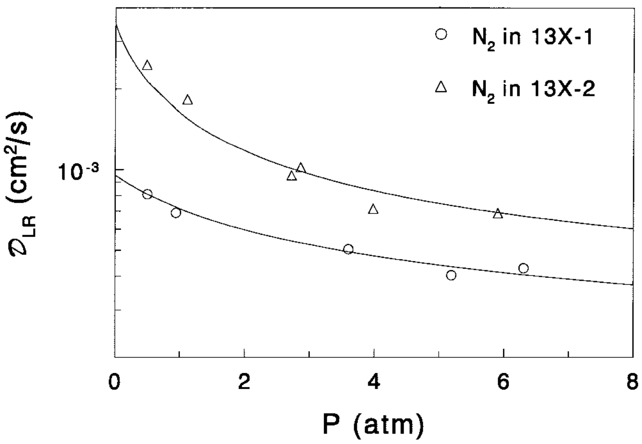

Figure 1. Long-range self-diffusion coefficients of nitrogen in different 13X zeolites measured by ^{15}N PFG NMR.

The solid lines represent correlations of the self-diffusion data with the LRDM with the tortuosity factor as the only adjustable parameter.

where r is the pellet radius and D_{LR} is the same diffusion coefficient presented in Eqs. 10–12.

The approach we have taken to examine our ability to predict large-scale breakthrough behavior can be summarized as follows: (1) measure self-diffusion data for a pure gas in an adsorbent at a single temperature and several pressures with PFG NMR; (2) correlate these data with the LRDM (Eq. 7) with the tortuosity as the only adjustable parameter; (3) calculate a value of β from Eq. 4, and run a breakthrough simulation with SIMPAC; and (4) compare the breakthrough simulation results with experimental data.

Diffusion Results

We have previously (Rittig et al., 2002a, 2003) reported self-diffusion coefficients of the carbon monoxide, methane, and nitrogen as functions of pressure for two 5A adsorbents and a single 13X adsorbent. In this work we have extended our investigations to observe other commercially available 5A and 13X zeolites, as well as silica gel adsorbents. Because the mean displacement traversed during the PFG NMR is orders of magnitudes greater than an average zeolite crystal size, the LRDM is applicable in correlating these self-diffusion data. The pressure dependence for all the systems examined is represented well by the LRDM.

In Figures 1 and 2 we compare the self-diffusion coefficients of nitrogen and carbon monoxide in different 13X and 5A zeolites. Included in these figures are the correlations based on the LRDM which represent the data quite well. Although the magnitude of the self-diffusion coefficients is comparable for the same gas on different materials, it is evident that a material cannot be classified simply as a 13X or a 5A material because observable differences in the self-diffusion coefficients are discernable. Clearly, the internal pore structure can influence the mass-transfer rates and, in turn, profoundly effect performance in a cyclic gas separation unit operation. The slight differences in the pore structure also lead to different expected pressure dependences of $\mathcal{D}_{LR}$ at low absolute pressures (see Figure 2). A detailed discussion of the factors affecting the pressure dependence of $\mathcal{D}_{LR}$ has previously been provided (Rittig et al., 2002a, 2003).

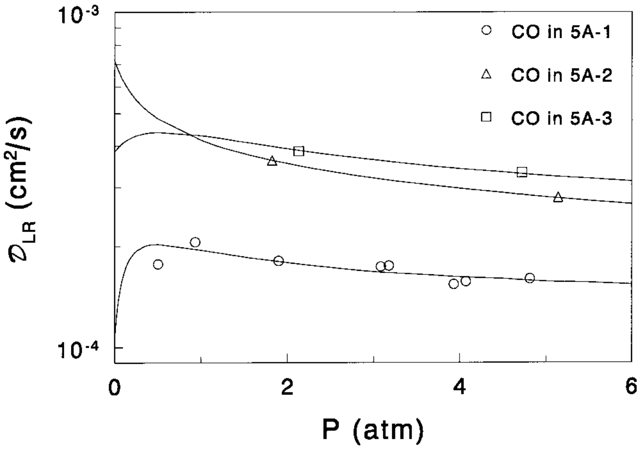

Figure 2. Long-range self-diffusion coefficients of carbon monoxide in different 5A zeolites measured by ^{13}C PFG NMR.

The solid lines represent correlations of the self-diffusion data with the LRDM, with the tortuosity factor as the only adjustable parameter.

In earlier work we have demonstrated (Rittig et al., 2002a, 2003) the utility of the LRDM by correlating self-diffusion coefficients of pure gases measured at a given temperature and variable pressures (similar to the data shown in Figures 1 and 2). From these correlations, we were then able to accurately predict self-diffusion coefficients in binary and ternary gas-mixtures, and at conditions when temperature, surface excess, and pressure were changed simultaneously. Our focus in this article is not, therefore, to revisit the utility of the LRDM, but to demonstrate its applicability (with the use of several experimental self-diffusion data) to predict mass transfer in large-scale unit operations, namely in breakthrough experimentation.

In Figure 3 we present two experimental breakthrough

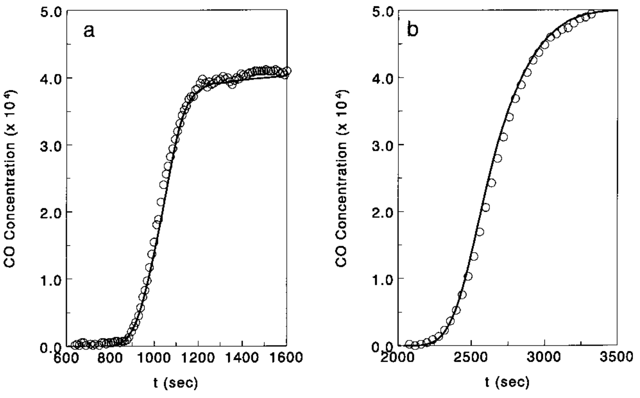

Figure 3. Comparison of experimental breakthrough data (circles) with predictions (solid lines) based on LRDM correlations of PFG NMR diffusion data for 500 ppm CO at 25 atm and at a flow rate of 41 lb-mole/ft^2-h over a (a) 13X and (b) 5A adsorbent.

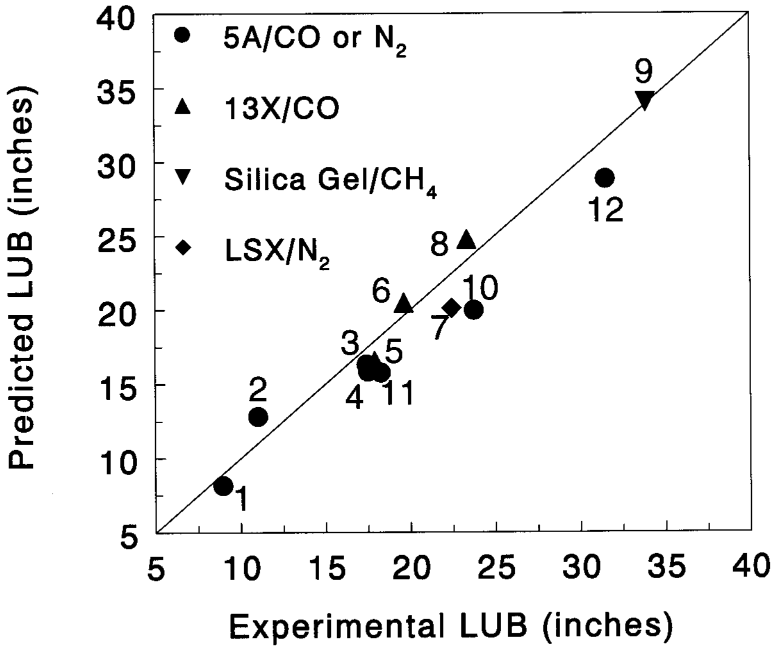

Figure 4. Parity plot of experimental and predicted LUB values.

curves for 500 ppm CO in 25 atm of helium along with simulation results based on predicted β values obtained from LRDM correlations of PFG-NMR data for pure gas transport within a 13X and a 5A adsorbent. The predictions are in excellent agreement with the experimental data. The predicted LDF constants (k in Eq. 13) for these experiments are less than 0.1 s^{-1} indicating that mass-transfer limitations should be anticipated in cyclic processes at these experimental conditions (Hartzog et al., 1995). It is interesting to note that the Darken correction is approximately 6% at these experimental conditions, even though the breakthrough experiments were performed at very low adsorbate concentrations. This reveals the strongly interacting nature of CO with the zeolites even at these dilute operating conditions.

Similar experiments have been performed for a variety of materials and breakthrough conditions. The different material properties and experimental conditions lead into a variation of LUB from 5 to 35 in. Rather than provide a series of experimental breakthrough curves and accompanying predictions, we have opted to summarize our results in a more quantitative manner by comparing the predicted and experimental length of unused bed (LUB), which for a constant pattern and a symmetric shape, is defined as

$$LUB = L \cdot \left(1 - \frac{t_b}{t_m}\right) \tag{14}$$

The parameters referenced in Eq. 14 are: L, the total length of the adsorbent bed t_b, the time when breakthrough first occurs, and t_m, the time when the concentration reaches the half of its ultimate value. The values for t_b and t_m have been determined experimentally from breakthrough tests, and have been extracted from the simulation results. With the experimental length of the column L, the experimental and predicted LUB values can, thus, be compared directly, and the deviations between them quantified. Our experimental results and predictions are depicted in Figure 4 in the form of a parity plot. The 45° line is also included in Figure 4 to highlight the excellence of the LUB predictions based on the LRDM correlations of PFG NMR data. The numbers indicated within the figure represent different adsorbents. It is evident that for different classes of porous materials, with different gases at varying conditions of pressure and concentration, the predicted LUB values match the experimental values accurately. The average relative error in Figure 4 is approximately 8%.

Summary

Pulsed field gradient (PFG) NMR measurements have been conducted to measure self-diffusion coefficients of gases within porous media. Analysis of these microscopic data with the use of a long-range diffusion model (LRDM) has enabled us to accurately predict the length of unused bed (LUB), and breakthrough curves for the transport of gases through a packed-bed adsorption column with the use of milligram quantities of the sample. This methodology enables the evaluation of mass-transfer coefficients without the complications associated with transient sorption experiments, that is, heat effects, and thereby offers a reasonable alternative to conventional breakthrough experimentation for the evaluation of mass-transfer coefficients and LUB.

Acknowledgments

The authors are pleased to dedicate this article to Professor Jörg Kärger in honor of his 60th birthday. F. Rittig gratefully acknowledges the financial support of the Alexander von Humboldt-Foundation for this project. We also thank Dr. Shivaji Sircar, and Dr. Charles G. Coe (APCI), Prof. Jörg Kärger (Leipzig University), and Prof. Douglas Ruthven (University of Maine), for insightful discussions.

Notation

A = total magnetization with applied gradients
A_0 = total magnetization without applied gradients
b = gas-solid interaction parameter, atm^{-1}
c = gas concentration, mole/cm^3 macro-mesopore
d_p = pellet diameter, cm
$D_{B,ij}$ = bulk diffusion coefficient for gas pair ij, cm^2/s
$\mathcal{D}_{inter}$ = self-diffusion coefficient within the macro-mesopore space, cm^2/s
$D_{K,i}$ = Knudsen diffusion coefficient for component i ,cm^2/s
D_{LR} = effective mutual diffusion coefficient, cm^2/s
$\mathcal{D}_{LR}$ = long-range self diffusion coefficient, cm^2/s
D_p = pore diffusivity, cm^2/s
g = strength of the gradient pulses
k = linear driving force constant, s^{-1}
L = total length of the bed, in.
LUB = length of the unused bed, in.
n^m = surface excess, mmoles/g
N_i = molar flux of species i , moles/ft^2-s
p = total pressure, atm
p_{inter} = fraction of molecules within the macro-mesopore space
q = $\delta\gamma g$
r = particle radius, cm
R = Universal Gas Constant, for example,. 0.0821 L-atm/mol-K
t_b = time when the first breakthrough occurs, s
t_m = midpoint time, s
t_1 = time between 2nd and 3rd rf-pulse, ms
t_2 = time between first two $\pi/2$ and $\pi/2$ and the FID, ms
T = absolute temperature, T
y_i = gas phase mole fraction of species i
$\langle z^2(\Delta)\rangle$ = mean square displacement of the diffusing molecules, cm^2

Greek letters

β = distance parameter for DGM model, cm^{-1}
γ = duration of the gradient pulse, ms
δ = gyromagnetic ratio of the investigated nucleus, for exmaple,^1H, ^{13}C, ^{15}N
Δ = diffusion time (=$t_1 + t_2$), ms
ϵ_{ma} = macro-mesopore porosity (cm^3 macro-mesopores/cm^3 solid + all pores)
$\pi/2$ = radio frequency pulse length, ms
ρ_p = pellet density (g/cm^3 solid + all pores)
τ = tortuosity factor
Ψ = normalized spin attenuation, =A/A_o

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Manuscript received Apr. 23, 2003 and revision received July 3, 2003.