Adsorption 11: 427–432, 2005

Knudsen Diffusion and Viscous Flow Dusty-Gas Coefficients for Pelletised Zeolites from Kinetic Uptake Experiments

RICHARD S. TODD AND PAUL A. WEBLEY*
Department of Chemical Engineering, Monash University, Clayton, Victoria, Australia
paul.webley@eng.monash.edu.au

ROGER D. WHITLEY AND MATTHEW J. LABUDA
Air Products and Chemicals Inc., 7201 Hamilton Boulevard, Allentown, Pennsylvania, USA

Abstract. A simple volumetric uptake apparatus was used to determine uptake data of N_2 on a sample of LiLSX zeolite for two different particle sizes, two temperatures, and a variety of different dosing pressure levels. Using a mass and energy conservation model for the dosing and sample volumes and the Dusty Gas Model + viscous flow for the mass transfer description at the pellet level, the Knudsen and viscous flow structural parameters were derived. Our analysis gave structural coefficients $C_K = 0.0827 \pm 0.018$ and $C_v = 0.0608 \pm 0.026$ which gave good agreement across all of the experimental runs conducted for both particle sizes and all pressure ranges. From these, tortuosity coefficients for Knudsen and viscous flow were derived and gave $\tau_K = \varepsilon_{P,\text{macro}}/C_K = 3.7 \pm 0.8$ and $\tau_v = \varepsilon_{P,\text{macro}}/C_v = 5.1 \pm 2.2$ respectively. These are in good agreement with reported values. The apparatus and procedure is not very sensitive to the viscous flow coefficient but is sensitive to the Knudsen coefficient. All other parameters of the model were measured or determined by calibration experiments. This study suggests that the apparatus may be useful for determination of some of the fundamental structural coefficients employed in the Dusty Gas Model.

Keywords: kinetics, gas, diffusion, uptake, mass, transfer

Introduction

A large variety of experimental methods have been proposed in the literature to quantify the transport of gas through an adsorbing zeolite crystal and/or pellet and this is still an active area of research today (Kärger, 2003). Common methods include the Wicke-Kallenbach cell (Haugaard and Livbjerg, 1998), gravimetric (Wloch, 2003), volumetric (Qinglin et al. 2003), chromatographic (Chun and Lee, 2000) and pulsed field gradient nuclear magnetic resonance (Gladden, 1994). A majority of these techniques have been used to study micropore diffusion within zeolite crystals with much less emphasis placed on macropore diffusion in pelletised materials. There is an even smaller body of work that has experimentally investigated the Dusty Gas Model (DGM) for a sorbent pellet that exhibits macropore diffusion control. The use of the DGM has been mainly confined to the mathematical description of transport in porous materials (e.g., Reyes and Jensen, 1985; Burganos and Sotirchos, 1989).

When viscous flow is incorporated into the Dusty Gas Model (denoted here VF + DGM) as a parallel transport path, three structural parameters are required to complete the full description of diffusion (in the absence of surface diffusion): C_V, C_K, C_M. These three structural parameters modify the viscous flow coefficient, the Knudsen diffusion coefficient, and the molecular diffusion coefficient respectively, and are related to the complex pore network structure of the material (Hartmann and Mersmann, 1996). It is customary to express these three coefficients as (ε_p/τ_j) where ε_p

---

*To whom correspondence should be addressed.

is the pore void fraction to which the diffusion mechanism refers and τ_j the tortuosity for mechanism j. Since the transport mechanisms do not necessarily occupy the same portion of pore network, it is unlikely that a single value of ε_p and τ_j will suffice to reduce all three transport coefficients. The ability to estimate all three structural parameters from one experiment is very difficult given that the experimentally measured process response will invariably reflect all three transport mechanisms. The degrees of freedom available to manipulate each coefficient limits the amount of information contained within one particular experiment. For this reason, we have obtained each structural coefficient of the VF + DGM from two sets of experiments which serve to isolate particular transport mechanisms. The first set of experiments and analysis, reported in this paper, isolate the mechanisms of Knudsen diffusion and viscous flow by using a pure component gas within a volumetric device. Using these values, a separate study examined the determination of the molecular diffusion structural diffusion parameter using chromatographic experiments (Todd and Webley, 2004).

Experimental Apparatus and Data Analysis

Experimental data were obtained using a volumetric device that is referred to in this study as the Kinetics Test Unit (KTU). The KTU measures the dynamic change in pressure that occurs when an evacuated sample volume, initially maintained at constant temperature, is suddenly exposed to gas flowing from a dosing volume at higher initial pressure. While this apparatus is not necessarily the best to use for measurement of fast kinetics, it is simple, gives rapid results and can readily be used as a specification tool for adsorbent manufacturers. The dosing and sample volumes are separated by a rapid actuating ball valve. Figure 1 is a schematic diagram of the KTU unit demonstrating the sequence of operations during an experimental run.

Since the pressure dynamic is rapid, usually lasting less than one second, a fast response MKS Baratron pressure transducer (model 627B) is used. This pressure transducer, with a response time of 0.02 s and accuracy of ±0.004 bar over the pressure range 0–1.33 bar.a is mounted on the dosing volume side of the KTU for convenience.

The pressure transducer is logged on a PC at a scan rate of 0.02 s through a PCI-DAS 1200 data acquisition card. The temperature within the sample volume can also be measured at a scan rate of 0.1 s using a T-type junction exposed thermocouple. It is important to note that the junction is exposed to the gas within the sample volume—it is not in intimate contact with the solid adsorbent material. While the dosage volume is not in the water bath, its temperature is equal to that of the temperature controlled laboratory and is measured before each experiment to within 0.5°C.

Prior to measurement of kinetics, the solid adsorbent material is thoroughly degassed in an off-line degassing unit at 400°C under high vacuum overnight and transferred to the KTU sample volume in a dry box. Before measurement the sample and dosage volumes are evacuated to 1.3×10^{-4} bar with a two-stage high vacuum pump. The dosing volume is then charged with 99.99 mol%N_2 to a higher initial pressure. The connecting ball valve between the two initially isolated volumes is then pneumatically opened and the pressure response of the dosing volume measured along with temperature at the center of the sample volume. Since there is no

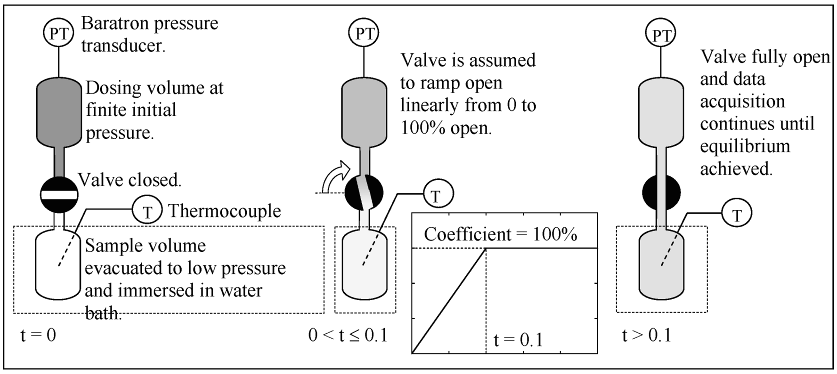

Figure 1. Schematic arrangement of one KTU run from start, $t = 0$, to end, $t \gg 0.1$.

Table 1. Physical properties of zeolite pellets.

Parameter	Magnitude	Units
Pellet diam, $d_{P,\text{eqv}}$	1.5 ± 0.2; 2.0 ± 0.2	m × 10^3
$\hat\rho_{\text{sample}}$	602 ± 11	kg m^{-3}
$\hat\rho_{\text{pellet}}$	926 ± 77	kg m^{-3}
$\hat\rho_{\text{skeletal}}$	2416 ± 10	kg m^{-3}
ε_P	0.62 ± 0.04	(m^3 total intrapellet gas void) (m^3 pellet)$^{-1}$
$\varepsilon_{\text{macro}}$	0.31 ± 0.04	(m^3 macro pore intrapellet gas void) (m^3 pellet)$^{-1}$
ε_{B}	0.35 ± 0.06	(m^3 interpellet gas void) (m^3 total)$^{-1}$
pore diam, δ	2.5 ± 0.4	m × 10^7
$\hat{c}_s$	960	J kg^{-1} K^{-1}

pressure transducer connected to the sample volume, it is necessary to conduct blank runs to calibrate the valve response dynamic (Brandani, 1998). We recognize that this is a limitation of the device and we are currently correcting this flaw. To calibrate the value of the valve coefficient and still match the correct pressure end-point, crushed zeolite with a nominal pellet diameter of $1.0 \pm 0.1 \times 10^{-5}$ m (referred to as "dust") was used. This condition imposes instantaneous local equilibrium on the adsorption in the sample volume. In addition to dust runs, blank KTU runs were also performed to verify valve response dynamics and to obtain gas to wall heat transfer coefficients (discussed later).

LiLSX pellets were used as the zeolite in this study and their physical properties and nitrogen isotherms are shown in Table 1 and Fig. 2 respectively. It is known from past studies that pelletized samples of X-type zeolites exhibit macropore diffusion control at ambient temperatures (Ruthven and Xu, 1993). The crystals are approximately 1 μm in diameter and because their length scale is much smaller than the pellet (1–2 mm) do not provide the major resistance to mass transfer. If the micropore volume is taken to be that inside the zeolite crystals and the macropore volume that outside the zeolite crystals but still inside the pellets, then an estimate for the macropore void fraction can be made. Using a crystal void fraction of 0.5 (Breck, 1974) for zeolite X and a 12% binder fraction gives a macropore volume fraction of 0.31.

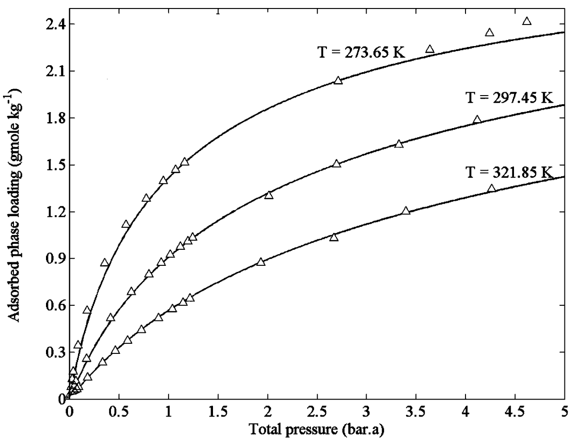

Figure 2. Equilibrium Isotherms for N_2 on LiLSX zeolite.

System Model

KTU runs are performed with a pure gas—this removes any influence of external film mass transfer on overall diffusion rates and allows the full form of the VF + DGM intrapellet flux equation to be reduced to the following expression.

$$N = -\frac{1}{RT}\left[D_K^e + \left(\frac{p^P}{10^{-5}\mu}\right)B^e\right]\frac{\partial p^P}{\partial r} \tag{1}$$

where N is the flux, p^P the pellet pressure and μ the viscosity. Structural coefficients C_K and C_v for Knudsen diffusion and viscous flow are written as:

$$D_K^e = C_K D_K; \quad B^e = C_v \frac{\delta^2}{32} \tag{2}$$

where δ is taken to be the macropore diameter as determined by mercury porosimetry.

The dosing volume that communicates with the sample volume is modelled assuming non-isothermal CSTR behaviour. Flow between the volumes must be accurately represented and any flow resistance (valves, piping, etc.) must be calibrated with data obtained from an independent set of experiments.

Conservation of energy and mass of the sample volume containing sorbent is written:

$$\left(V_S - \frac{m_P}{\hat\rho_P}\right)\left(\frac{1}{RT_S}\frac{dp^S}{dt} - \frac{p^S}{RT_S^2}\frac{dT_S}{dt}\right) = (\rho A v)_{\text{dosing,sample}} + \left(\frac{m_P/\hat\rho_P}{4\pi R_P^3/3}\right)4\pi R_P^2 N_{R_P} \tag{3}$$

$$\left(V_S - \frac{m_P}{\hat{\rho}_P}\right)\left[\frac{p^S}{RT_S}\left(c^S - \frac{H^S}{T_S}\right)\frac{dT_S}{dt} + \left(\frac{H^S}{RT_S} - 10^5\right)\frac{dp^S}{dt}\right] = (\rho A v H)_{\text{dosing,sample}} + \left(\frac{m_P}{\hat{\rho}_P}\frac{3}{4\pi R_P^3}\right)4\pi R_P^2[(H_N)_{R_P} + h_{P,S}(T_P - T_S)] - [h_{S,W}A_{S,W}(T_S - T_W)] \quad (4)$$

where H is enthalpy, and T temperature. Note that two heat transfer coefficients (between gas and wall and solid and gas) are present. The equivalent conservation equation for the intrapellet region is also written and coupled to the DGM + VF model (Todd, 2003). In addition to these equations, conservation of mass and energy equations are written for the dosage volume. Details of these can be found in Todd (2003) and are omitted here for brevity.

The conservation and flux equations are fully defined once all of the physical parameters are known. There are three equipment specific parameters that need to be found before the model can be used to extract adsorbent kinetic properties: wall heat transfer coefficients for both sample and dosage volumes and a numerical flow coefficient. The flow coefficient for the valve is determined by blank and "dust" runs in which mass transfer was either very rapid or absent. The heat transfer coefficient from the gas to the wall in both sample and dosage volumes was determined by blank experiments with rapid pressurisation and depressurizations ("reverse" KTU runs).

Results and Discussion

The set of modeling equations outlined above was solved numerically within our adsorption simulator, MINSA (Todd et al., 2003). Sufficient radial discretisation (30 nodes) within the pellet was used to ensure acceptable accuracy. A total of 12 KTU runs with adsorbent were conducted with pellet sizes of 1.5 and 2.0 mm, initial dosage pressures of 0.27, 0.53, and 1.0 bar and water bath temperatures of 273 and 303 K. The matching of experimental data to the model was accomplished by minimizing the global sum of square of errors between each pressure point and the model prediction with appropriate scaling to avoid biases at high pressures. The only adjustable parameters were the two structural coefficients, C_K and C_V. A sensitivity analysis was also conducted to determine the impact of each structural coefficient and the gas-to-solid heat transfer coefficient on the model predictions.

Figure 3(a) and (b) show typical trends observed for dosing volume pressure over the stated range in pellet diameter and operating conditions. Excellent agreement is seen with the two adjustable coefficients, C_K and C_V.

It is important to note that the dust runs (infinite mass transfer coefficient) reflect valve dynamics only whereas the pellet runs, which are clearly "slower" than the dust runs, also incorporate mass transfer (and/or heat transfer) dynamics. It is only with the model presented and careful calibration experiments that these effects can be deconvoluted. Our analysis

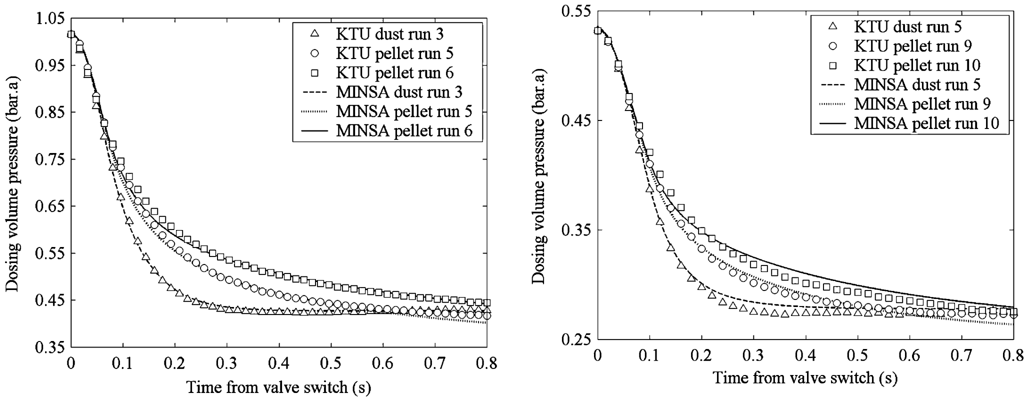

Figure 3. (a) and (b). Typical KTU data and model correlation for pellet and dust runs. Dust Run 3: $P_o = 1.0$ bar, Dust Run 5: $P_o = 0.53$ bar, Pellet Run 5: $d_p = 1.5$ mm, $P_o = 1.0$ bar Pellet Run 6: $d_p = 2.0$ mm, $P_o = 1.0$ bar, Pellet Run 9: $d_p = 1.5$ mm, $P_o = 0.53$ bar, Pellet Run 10: $d_p = 2.0$ mm, $P_o = 0.53$ bar.

gives structural coefficients $C_K = 0.0827 \pm 0.018$ and $C_v = 0.0608 \pm 0.026$ which gave good agreement across all of the KTU runs conducted for both particle sizes and all pressure ranges. From these, if we use $\varepsilon_{P,\mathrm{macro}} = 0.31$, the following estimates of tortuosity using the C values above are obtained: $\tau_K = \varepsilon_{P,\mathrm{macro}}/C_K = 0.31/0.0827 = 3.7 \pm 0.8$ and $\tau_v = \varepsilon_{P,\mathrm{macro}}/C_v = 0.31/0.0608 = 5.1 \pm 2.2$.

The value for τ_K is close to the ideal value of 3.0 obtained for a random interconnected network of uniform diameter cylindrical pores with no dead ends while the value for τ_v is slightly high. The high value for τ_v is attributed to the relatively insensitive nature of fitting C_v when matching numerical data to experimental data. Even so, an estimate of 5.1 for a tortuosity coefficient on viscous flow is still reasonable and well within the usual order of magnitude estimates commonly encountered (Satterfield and Sherwood, 1963). Sensitivity analysis conducted revealed that the effect of the viscous flow structural coefficient was far smaller than the Knudsen flow structural coefficient on the global sum of squared errors. This is reflected in the much larger standard error obtained for this parameter. This suggests that the KTU is not a sensitive apparatus for determination of the viscous flow parameter in the operating range investigated. In effect, all of the data can be represented by a single fitting parameter, the Knudsen flow structural coefficient.

Our simulation imposed the assumption $T_S = T_P$ on all pellet runs by letting $h_{P,S} \to \infty$. Sircar and Kumar (1984) indicate experimental uptake profiles are initially limited by mass transfer resistance where conditions close to adiabatic arise, which is then followed by a region where external film heat transfer resistance dominates as the pellets cool to bath temperature. To quantify the impact of each parameter, first order sensitivity coefficients of the dosing volume pressure as a function of C_K, C_V and $h_{P,S}$ were determined. In all cases, the Knudsen sensitivity coefficient is at least one order of magnitude greater than viscous flow and several orders of magnitude greater than pellet-to-bed heat transfer sensitivity coefficients such that Knudsen tortuosity can be regarded as the limiting mechanism in terms of measured process response. Assuming the pellets are adiabatic gives essentially the same results as an infinite heat transfer coefficient since the thermal mass of the solid is far greater than that of the gas contained within the sample volume. Following the initial period in which mass transfer dominates, a period is entered in which slow thermal dissipation to the surrounding water bath occurs. While external film heat transfer resistance at the pellet surface can be assumed negligible during the mass transfer regime, a Biot and Fourier heat transfer analysis for the sorbent pellets also reveals intrapellet temperature profiles are also negligible (Todd, 2003).

Conclusions

A volumetric uptake apparatus has been used to determine Dusty Gas kinetic structural parameters C_K and C_V using a detailed non-isothermal model. The structural parameters can be converted to Knudsen and viscous tortuosities in good agreement with published values. The KTU is a very convenient and rapid apparatus for measuring pellet mass transfer properties and when coupled with a detailed model can be useful for determining the Knudsen flow coefficient. It is not sensitive to the viscous flow coefficient in the operating range investigated and cannot be used to determine the molecular diffusion structural coefficient.

References

Brandani, S., "Analysis of the Piezometric Method for the Study of Diffusion in Microporous Solids: Isothermal Case," *Adsorption*, **4**, 17–24 (1998)

Breck, D.W., *Zeolite Molecular Sieves*, John Wiley and Sons, New York, 1974.

Burganos, V.N. and S.V. Sotirchos "Knudsen Diffusion in Parallel, Multidimensional or Randomly Oriented Capillary Structures," *Chem. Eng. Sci.*, **44**, 2451–2462 (1989).

Chun, C. and C.-H. Lee, "Comparison of Adsorption Dynamics of a Ternary Hydrogen Mixture in Equilibrium and Kinetic Separation Beds," in *Proc. 2nd. Pacific Basin Conf. Adsorption Sci. and Tech.*, pp. 371–375, Brisbane, Queensland, Australia, 14–18 May, (2000).

Gladden, L.F., "Review Article Number 46. Nuclear Magnetic Resonance in Chemical Engineering: Principles and Applications, *Chem. Eng. Sci.*, **49**, 3339–3408 (1994).

Hartmann, R. and A. Mersmann, "Simulation of Single Pellet Adsorption Kinetics with Experimentally Determined Dusty Gas and Surface Diffusion Coefficients," *Fundamentals of Adsorption* 5, M.D. LeVan (Ed.), Kluwer Academic Publishers, Bostom Massachusetts, pp. 361–368, 1996.

Haugaard, J. and H. Livbjerg, "Models of Pore Diffusion in Porous Catalysts," *Chem. Eng. Sci.*, **53**, 2941–2948 (1998).

Kärger J, "Measurement of Diffusion in Zeolites—A Never Ending Challenge?," *Adsorption*, **9**, 29–35 (2003).

Qinglin, H., S.M. Sundaram and S. Farooq, "Revisiting Transport of Gases in the Micropores of Carbon Molecular Sieves," *Langmuir*, **19**, 393–405 (2003).

Reyes, S. and K.F. Jensen, "Estimation of Effective Transport Coefficients in Porous Solids Based on Percolation Concepts," *Chem. Eng. Sci.*, **40**, 1723–1734 (1985).

Ruthven, D.M. and Z. Xu, "Diffusion of Oxygen and Nitrogen in 5A Zeolite Crystals and Commercial 5A Pellets," *Chem. Eng. Sci.*, **48**, 3307–3312 (1993).

Satterfield, C.N. and T.K. Sherwood, *The Role of Diffusion in Catalysis*, Addison-Wesley Publishing, Massachusetts, 1963.

Sircar, S. and R. Kumar, "Non-Isothermal Surface Barrier Model for Gas Sorption Kinetics on Porous Adsorbents," *J. Chem. Soc., Faraday Trans. 1*, 80, 2489–2507 (1984).

Todd, R.S. "A Theoretical and Experimental Study of a Rapid Pressure Swing Adsorption System for Air Separation," Ph.D. Dissertation, Monash University, Australia, 2003.

Todd R.S., G. Buzzi Ferraris, D. Manca, and P.A. Webley, "Improved ODE Integrator and Mass Transfer Approach for Simulating a Cyclic Adsorption Process," *Comput. and Chem. Eng.*, **27**, 883–899 (2003).

Todd, R.S. and P.A. Webley, "Macropore Diffusion Dusty-Gas Coefficient for Pelletised Zeolites from Breakthrough Experiments in the O_2/N_2 System," Submitted (2004).

Wloch, J., "Effect of Surface Etching of ZSM-5 Zeolite Crystals on the Rate of n-hexane Sorption," *Microporous and Mesoporous Materials*, **62**, 81–86 (2003).