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Gas-Solid Chromatography: Longitudinal and Intraparticle Diffusion of Acetylene in Activated Carbon

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Abstract

The time-dependent transmission of 100 ppm acetylene in helium at 1 atm through columns of Columbia 4LXC 12/28 activated carbon at 25°C was measured at several flow rates in the range from about 1 to 7 cm^3/s. Transmission is the gas-phase concentration at the column outlet divided by the input concentration. The gas- and adsorbed-phase diffusion coefficients were calculated from a homogeneous-solid diffusion model by means of the method of moments. The gas-phase diffusion coefficient was constant in this range of flow rates. Fitting the experimental transmission curves to a theoretical transmission expression for a model with only gas-phase diffusion indicated that solid-phase diffusion in this carbon cannot be neglected at high flow rates.

INTRODUCTION

A narrow pulse of adsorbate gas injected into a carrier gas stream at the inlet of a packed adsorbent column is dispersed as it flows through the column by isotherm nonlinearity, longitudinal and intraparticle diffu-

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sion, surface kinetics, and mass-transfer resistance. These dispersive phenomena result in an adsorbate pulse at the outlet of the column that is wider in time and lower in concentration than the pulse introduced at the inlet. A step function change of adsorbate concentration introduced to the column is dispersed by the same processes from a sharp boundary between two different concentrations to a more gradual concentration profile of finite slope.

The adsorber can be modeled by pore-diffusion or solid-diffusion models (*1–3*). The pore-diffusion model includes the effects of gaseous diffusion in the pore, adsorption on the pore walls, and diffusion in the solid; numerical solutions of this model require major assumptions about the pore structure and limiting processes in the adsorbent particle (*1*). The homogeneous-solid diffusion model (*2*) treats the porous adsorbent as a solid with a single effective diffusion coefficient that combines the effects of all the solid-phase processes treated by the pore-diffusion model; however, the resulting intraparticle diffusion coefficient is much harder to interpret physically and to correlate with the diffusion data. For linear isotherms, this formulation allows an analytic solution to the differential equations by the method of moments. The purpose of this paper is to report the measurement of diffusion coefficients for acetylene in helium adsorbed on Columbia 4LXC 12/28 activated carbon at 25°C and to compare these results with the values for other light gases on the same carbon.

THEORETICAL BACKGROUND

The equations for a homogeneous-solid diffusion model with a linear isotherm and with negligible mass-transfer resistance (*1*, *4*) are

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_{\text{ave}}}{\partial t} \tag{1}$$

$$\frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{2}$$

$$q_{\text{ave}} = \frac{3}{R^3}\int_0^R qr^2 dr \tag{3}$$

where C and q are the gas- and solid-phase concentrations of the adsorbate, D_L and D_s are the longitudinal and intraparticle diffusion coefficients, u is the interstitial flow velocity, ε is the interstitial void fraction of the adsorber bed, and R is the radius of the adsorbent particles. The dependent variables C and q are related at the gas-solid interface by the adsorption isotherm:

$$q = KC \tag{4}$$

where K is the dimensionless adsorption capacity. These equations were solved by the method of moments to determined the longitudinal and intraparticle diffusion coefficients for step-function (*4*), delta-function (*5*), and finite-width (*6*) pulse inputs in the region of low to moderate flow velocities where D_L is considered to be constant. For sufficiently-low flow rates, molecular diffusion will be the principal contribution to longitudinal diffusion and cause it to dominate as the dispersing mechanism. The other dispersion processes act as resistances between the bulk gas stream and the adsorbent surface. The effects of these resistances vanish as the rate of mass transport becomes small; under these conditions, Eq. (3) simplifies to $q_{\mathrm{ave}} = q$ and Eq. (3) is not needed. The time-dependent solution of Eqs. (1) and (4) for either step or pulse inputs (*7*) may then be utilized to extract the value of D_L by fitting theoretical output curves to the experimental data. The value of D_L determined in this way may be compared to the assumed constant value determined from the moment analysis.

MOMENT ANALYSIS METHOD

The transmission of an adsorbate through a column of length L can be expressed in terms of a dimensionless transmission T:

$$T(t) \equiv \frac{C(L,t)}{C_0} \tag{5}$$

where C_0 is the input concentration. The nth moment with respect to the propagation time t_p for the transmission $T(t)$ is

$$\mu_n = \int_0^\infty (t - t_p)^n T(t)dt \tag{6}$$

The propagation time t_p is determined by numerical integration of experimental transmission curves. For a step increase in the input concentration, the column has a net uptake of adsorbate; for this adsorption case, the propagation time is given by

$$t_p^A = \int_0^\infty [1 - T(t)]dt \tag{7}$$

Similarly, for a step decrease in the input concentration, the column releases adsorbate; for this desorption process, the propagation time is given by

$$t_p^D = \int_0^\infty T(t)dt \tag{8}$$

Although the propagation time for a step function is finite, all the moments of $T(t)$ are infinite. For a step input, the kinetic information is contained in the slope of the transmission curve; while for a pulse input, this information is in the peak variance (*8*). The usual methods calculate either the slope or the variance, whichever is indicated by the input function; however, the numerical calculation either of a slope or the width of a peak with a long tail can introduce error into the calculation (*9, 10*). The procedure of Huang et al. (*4*) creates a new transmission function $f(t)$ by combining the transmission function $T(t)$ with a unit step function $h(t - t_p)$:

$$h(t - t_p) = \begin{matrix} 0 \\ 1 \end{matrix} \quad \begin{cases} t - t_p < 0 \\ t - t_p \geqslant 0 \end{cases} \tag{9}$$

The function $f(t)$ for adsorption transmission curves is given by

$$f^A(t) = h(t - t_p) - T(t) \tag{10}$$

For desorption transmission curves, the function $f(t)$ is

$$f^D(t) = h(t - t_p) + T(t) - 1 \tag{11}$$

The use of $f(t)$ in place of $T(t)$ in Eq. (6) shifts the kinetic information into the first moment for a step input, which is easier to measure experimentally and is subject to less error (*10, 11*).

By applying the boundary conditions for a step input to the homogeneous-solid diffusion model in the Laplace domain, Huang et al. (*4*) related the first-order moment to D_L and D_s by

$$\frac{u\mu_1}{L} = \frac{R^2K(1-\varepsilon)}{15D_s\varepsilon} + \frac{D_L}{u^2}\left(1 + \frac{1-\varepsilon}{\varepsilon}K\right)^2 \tag{12}$$

A graph of $u\mu_1/L$ vs $1/u^2$ is a straight line according to Eq. (12).

EXPERIMENTAL METHOD

We measured the adsorption and desorption of 100 ppm acetylene in a helium carrier gas flowing through adsorber columns packed with Columbia 4LXC 12/28 activated carbon at 25°C at interstitial flow velocities from about 1 to 7 cm/s. The columns were operated at a nominal total pressure of 1 atm. The flow system was described previously (*12*). This carbon has a mean radius of 0.46 mm (*13*). The dimensions, mass of carbon, and void fraction for each of the columns are listed in Table 1.

The adsorption isotherm for acetylene was found previously to be linear (*14*) for this type of carbon in the range of partial pressures up to 76 mtorr encountered in this work. The dimensionless adsorption capacity K, defined in Eq. (4) and determined from mass balance (*4*), has a value of 500 ± 20.

Transmission curves for the adsorption of 100 ppm acetylene on Columbia activated carbon at 25°C at three flow rates are shown in Fig. 1 for adsorption and in Fig. 2 for desorption. Based on the assumption that D_L is independent of the velocity u, a plot of $u\mu_1/L$ as a function of $1/u^2$ is a straight line. This plot is presented in Fig. 3 for 25 experimental runs. The overall correlation coefficient obtained from a least-squares fit of the data to a straight line was better than 0.99; the slope and intercept yield values

TABLE 1
Parameters of Columbia 4LXC 12/28 Activated Carbon Adsorber Columns

Bed	Length (cm)	Diameter (cm)	Mass of carbon (g)	Interstitial void fraction
1	10.0	0.46	0.588	0.591
2	10.0	0.78	1.664	0.601
3	10.0	1.09	3.397	0.585
4	20.0	0.46	1.148	0.598
5	30.1	1.72	26.14	0.569
6	40.0	0.49	2.637	0.591

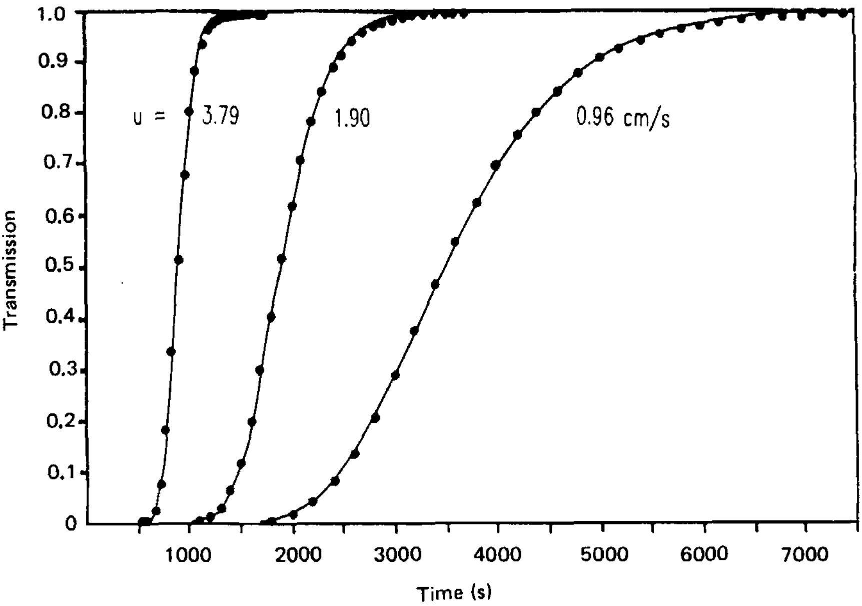

FIG. 1. Transmission of a step increase in the input concentration of 100 ppm acetylene in helium through activated carbon adsorber bed 1 at 25°C at interstitial flow velocities of 3.79, 1.90, and 0.961 cm/s.

of D_L and D_s of 0.38 ± 0.03 and $(3.5 \pm 0.8) \times 10^{-5}$ cm^2/s, respectively. The fact that this plot is a straight line indicates that D_L is constant within this range of flow rate.

We may assess the relative importance of D_L and D_s at various flow velocities by introducing the parameter β which compares the relative importance of the term containing D_L in the moment equation (12) with the term containing D_s (*4*, *11*, *15*).

$$\beta = \frac{15D_LD_s}{R^2u^2K}\left(\frac{\varepsilon}{1-\varepsilon}\right)\left(1 + \frac{1-\varepsilon}{\varepsilon}K\right)^2 \qquad (13)$$

Here $\beta > 1$ indicates D_L is dominant, and $\beta < 1$ indicates D_s dominates. The values of β are greater than 1 for the three interstitial flow velocities listed in Table 2; note that $\beta = 1$ for $u = 5.80$ cm/s.

The importance of solid-phase diffusion at high flow rates can be assessed also by utilizing a simpler model. For the case of a linear isotherm with longitudinal diffusion only, D_s in Eq. (2) is infinite, and

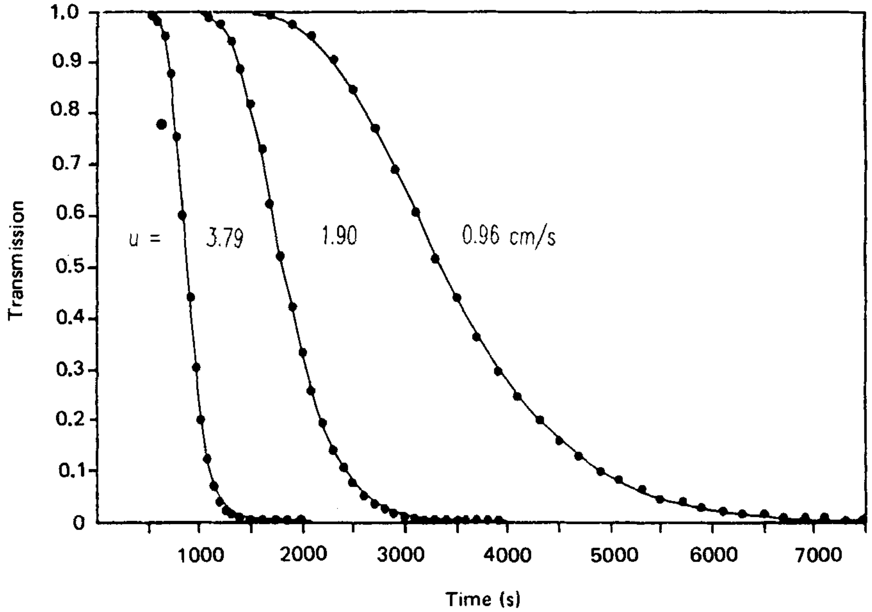

FIG. 2. Transmission of a step decrease in the input concentration of 100 ppm acetylene in helium through activated carbon adsorber bed 1 at 25°C at interstitial flow velocities of 3.79, 1.90, and 0.961 cm/s.

$q_{\text{ave}} = q$. The well-known solution (*16*, *17*) for this system has the following form for a step increase in the input concentration:

$$2T^A = \exp\left(\frac{uL}{D_L}\right) \operatorname{erfc}(s_+) + \operatorname{erfc}(s_-) \tag{14}$$

where the arguments of the complementary error functions are

$$s_\pm \equiv \frac{1}{2}\left(\frac{uL}{D_L}\right)^{1/2}\left[\left(\frac{t_p}{t}\right)^{1/2} \pm \left(\frac{t}{t_p}\right)^{1/2}\right] \tag{15}$$

The solution for a step-decrease in the input concentration is given by

$$T^D = 1 - T^A \tag{16}$$

Fitting the experimental data represented in Figs. 1 and 2 to the function form of Eq. (14) produces values of the diffusion coefficient

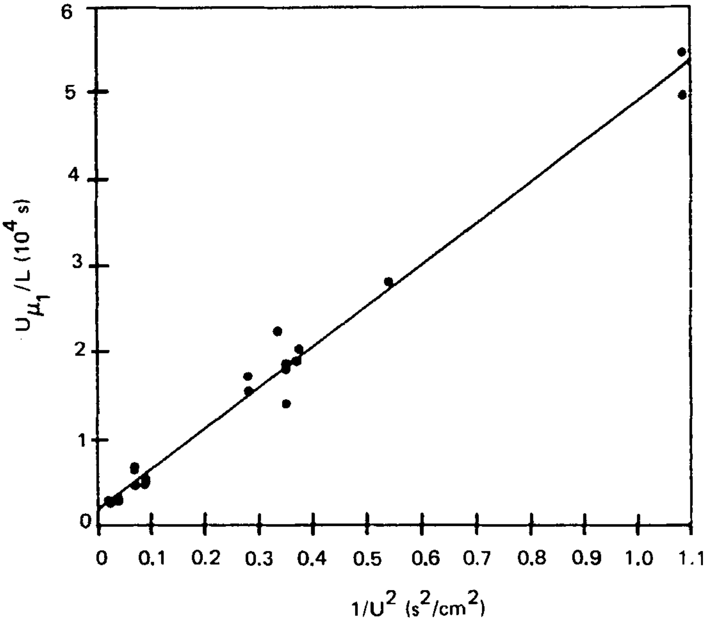

FIG. 3. First-order moment correlation for the adsorption and desorption of 100 ppm acetylene in helium on Columbia 4LXC 12/28 activated carbon at 25°C.

TABLE 2

The Dimensionless Parameter β at Three Interstitial Flow Velocities for the Adsorption of 100 ppm Acetylene on Columbia 4LXC 12/28 Activated Carbon at 25°C

u (cm/s)	β	D_L[a] (cm^2/s)
0.96	37	0.39 ± 0.03
1.90	9.0	0.42 ± 0.03
3.79	2.0	0.53 ± 0.07

[a] Values extracted from the fit of the experimental transmission curves to Eq. (14).

TABLE 3

Longitudinal and Intraparticle Diffusion Coefficients for 1% Argon, 100 ppm Acetylene, and 105 ppm Methane in Helium at 25°C on Columbia 4LXC 12/28 Activated Carbon with a Mean Particle Diameter of 0.92 mm

	Molecular weight	D_L (cm^2/s)	D_s (10^{-5} cm^2/s)
Argon	40	0.35[a]	1.7[a]
Acetylene	26	0.38	4
Methane	16	0.40	10

[a] Interpolated from data at 273 and 313 K (*18*).

D_L for this theoretical model which are included in Table 2. As illustrated by the solid curves in Figs. 1 and 2, the fits to the acetylene data are very good for the measured flow rates. The resulting values of D_L are the same, within experimental error, for adsorption and desorption. At the two lowest flow rates the value of D_L derived from fitting the transmission function is the same, within uncertainties, as the value derived from the moments over the entire flow range. This result shows that the variation in the single-coefficient model is due to the neglect of solid-phase diffusion and that the solution represented by Eq. (14) is useful at low flow rates where $\beta \gtrsim 9$.

The values of D_L and D_s for 100 ppm acetylene in helium on Columbia 4LXC 12/28 activated carbon may be compared also to the values for 105 ppm methane (*4*) and 1.0% argon (*18*) in the same carrier and on the same carbon. Table 3 shows the diffusion coefficients determined by the moment analysis method for the three adsorbates. The values of D_L and D_s vary inversely as the molecular weight of the adsorbate gas, as might be expected on the basis of molecular diffusion.

CONCLUSION

The moment analysis method was successful in correlating the transmission data for step inputs of 100 ppm acetylene in helium adsorbed on activated carbon for flow velocities from about 1 to 7 cm/s. The value of the longitudinal diffusion coefficient, $D_L = 0.38 \pm 0.03$ cm^2/s, was determined more precisely by this method than the value of the intraparticle diffusion coefficient, $D_s = (3.5 \pm 0.8) \times 10^{-5}$ cm^2/s, because the dispersion of the step-function input is dominated by D_L for most of the range of flows investigated. A parameter β characterizes the relative importance of D_L and D_s. In the measurements reported here, β varied from 0.75 to 37. For $\beta \gtrsim 9$, the transmission can be described usefully by an equation with a single diffusion coefficient.

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