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Gas–Solid Chromatography of Methane–Helium Mixtures: Moment Analysis of Breakthrough Curves

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Abstract

A moment analysis method is suggested for calculating parameters of a breakthrough curve generated from a step change of concentration of an adsorbate. The longitudinal diffusion coefficient and the solid-phase diffusion coefficient are determined from the calculated moment. A criterion is given for assessing the relative importance of the longitudinal diffusion coefficient and the solid-phase diffusion coefficient. This criterion also serves as a guide for choosing experimental parameters to determine the solid-phase diffusion coefficients.

INTRODUCTION

Characterization of the diffusion process in a packed column can be made either through the response to a step increase of the input concentration of the adsorbate or through the response to an adsorbate input concentration of pulsed character. Three processes account for the diffusion in a column: longitudinal diffusion in the gas phase, diffusion in the solid phase, and mass-transfer resistance in the gas–solid interface. The last process is generally small (*1*). Determination of the longitudinal and solid-phase diffusion coefficients is usually accomplished by means of a moment analysis on the output peak of a narrow input pulse (*2*). The disadvantage of using a narrow input pulse is that a high adsorbate concentration is needed at the column input. When a syringe is used to inject the sample into a chromatographic column, it is sometimes difficult to estimate the concentration at the column input. A high concentration of the sample can lead to a nonlinear adsorption isotherm. Gas–solid chromatography is especially susceptible to this nonlinearity.

Use of a step change of concentration avoids the problem of a large change in concentration. From our previous study (*1*) it is possible to measure the output concentration of methane in a 34 ppm methane–helium mixture. In this low partial-pressure region the adsorption isotherm is linear. In this paper we propose a moment-analysis method to calculate both longitudinal and solid-phase diffusion coefficients from a breakthrough curve for a system with a linear isotherm.

MOMENT ANALYSIS

For a packed column with a linear isotherm, the gas-phase concentration c and the solid-phase concentration q are related by the following equations (*3–5*):

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

$$\frac{\partial q}{\partial t} = D_s \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial q}{\partial r}\right) \tag{2}$$

and

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

For a step increase in the concentration of the adsorbate, the initial and boundary conditions are

$$C(x, 0) = 0, \qquad q(x, r, 0) = 0 \tag{4}$$

$$C(0, t) = C_0, \qquad q(0, r, 0) = 0 \tag{5}$$

$$C(\infty, t) = 0, \qquad q(\infty, r, t) = 0 \tag{6}$$

$$q(x, R, t) = K'C(x, t) \tag{7}$$

Equations (1), (2), and (3) contain three variables: C, q, and q_{ave}. By taking the Laplace transform, we can eliminate the latter two variables and obtain the transform of the output concentration (*2, 6*):

$$\frac{C}{C_0} = \mathscr{L}^{-1}\frac{1}{s}\exp\left(\frac{uz}{2D_L}\right.$$

$$\left. - z\sqrt{\frac{u^2}{4D_L^2} + \frac{s}{D_L} + \frac{3K'D_s}{R^2}\left[R\sqrt{\frac{s}{D_s}}\coth R\sqrt{\frac{s}{D_s}} - 1\right]}\right) \tag{8}$$

When $D_s \to \infty$, Eq. (8) can be inverted to a simple form (*1*). For a finite value of D_s, we consider this expression:

$$f(t) \equiv \frac{C}{C_0} - u(t_p) \equiv \mathscr{L}^{-1}\{F(s)\} \tag{9}$$

where

$$u(t_p)\begin{cases} = 0, & t < t_p \\ = 1, & t > t_p \end{cases} \tag{10}$$

$$t_p = \left[\frac{(1-\varepsilon)}{\varepsilon}K' + 1\right]\frac{L}{u} \tag{11}$$

Note that $u(t_p)$ is introduced in Eq. (9) so that $f(t)$ is zero at $t = 0$ and $t = \infty$, and the area bounded by $f(t)$ is finite. Now let us consider the first-order moment versus t_p:

$$\mu_1 = \int_0^\infty (t - t_p)f(t)\,dt = \sum_i (t_i - t_p)f(t_i)\,\Delta t \tag{12}$$

The moment μ_1 can be calculated numerically from the output signal. The moment μ_1 and the diffusion coefficients D_s and D_L are related:

$$
\begin{aligned}
u\mu_1 &= u\int_0^\infty tf(t)\,dt - ut_p\int_0^\infty f(t)\,dt \\
&= -u \lim_{s \to 0} \frac{\partial}{\partial s} F(s) - 0 \\
&= \frac{R^2LK'}{15D_s}\left(\frac{1-\varepsilon}{\varepsilon}\right) + \frac{LD_L}{u^2}\left(1 + \frac{1-\varepsilon}{\varepsilon}K'\right)^2 \qquad (13)
\end{aligned}
$$

Equation (13) is a straight line. If the product $u\mu_1$ is plotted versus $1/u^2$, the solid-phase diffusion coefficient and the longitudinal diffusion coefficient can be determined from the intercept and the slope, respectively.

RESULTS AND DISCUSSION

The normalized output concentrations for four runs with different flow rates are listed in Table 1 of Ref. *1*. From these data the calculated value of μ_1 is tabulated in Table 1 and plotted in Fig. 1 versus the inverse of the square of the flow rate u. The result is a straight line. The slight deviation of the point at the highest flow rate is not surprising because there are only five points in the transmission data. The agreement can be improved when the number of data points increases as, for example, in the run with the second highest flow rate. From this straight line the longitudinal diffusion coefficient D_L and the solid-phase diffusion coefficient D_s are calculated to be 0.40 and

TABLE 1

Flow Rate, First-Order Moment, and Dimensionless Criterion for 105 ppm Methane in a Column at 25°C Packed with Columbia 4LXC 12/28 Activated Carbon

Interstitial flow rate u (cm/s)	First-order moment $\mu_1(s^2)$	Dimensionless criterion β
0.687	40,150	22.4
1.38	5,261	5.56
2.70	870	1.45
6.64	95.4	0.24

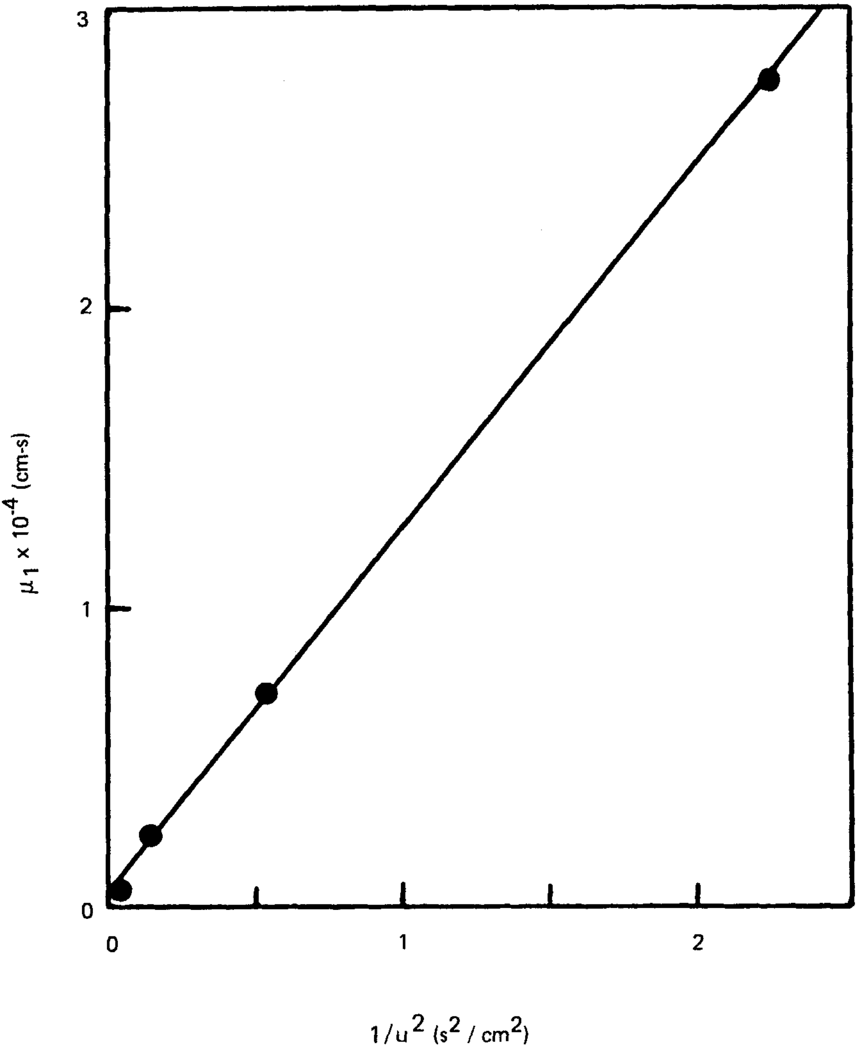

FIG. 1. The product of interstitial flow rate and the first-order moment versus the inverse of the square of the interstitial flow rate.

5.3×10^{-4} cm/s^2, respectively. The value of D_L has the same order of magnitude as values reported in the literature (*7*). Since the flow rate is in the laminar region, molecular diffusion makes the largest contribution to D_L. A wide range of D_s is reported for different adsorbents (*8*). Based on the fact that the diffusion coefficient of a gas in a liquid is on the order of 10^{-5} cm/s^2, the diffusion coefficient of methane in Columbia-type activated carbon is quite large.

The physical meaning of μ_1 is that it represents the spreading of the breakthrough curve. By assuming $D_s \to \infty$, it is possible to describe the breakthrough curve by a simple expression (*1*); it is, therefore, interesting to explore the condition that the influence of the solid-phase diffusion coefficient is negligible. A criterion is obtained by considering the two terms in Eq. (13). The first term represents the effect of the solid-phase diffusion coefficient. When $D_s \to \infty$, this term approaches zero and makes no contribution. The second term represents the effect of the longitudinal diffusion coefficient. The ratio of the two terms is taken as the criterion:

$$\beta \equiv \frac{15 D_L D_s}{R^2 u^2 K'} \left(\frac{\varepsilon}{1-\varepsilon} \right) \left(1 + \frac{1-\varepsilon}{\varepsilon} K' \right)^2 \tag{14a}$$

$$\simeq \frac{15 D_L D_s}{R^2 u^2} \left(1 + \frac{1-\varepsilon}{\varepsilon} K' \right) \tag{14b}$$

$$= \frac{15 D_s D_L t_p}{R^2 u L} \tag{14c}$$

When β is greater than unity, the longitudinal diffusion coefficient dominates; and when β is less than unity, the solid-phase diffusion coefficient dominates. From Eq. (14b) it can be seen that the flow rate u is the major parameter that controls the value of β. Values of β are listed in Table 1; when u increases from 0.69 to 6.6 cm/s, the value of β decreases from 22 to 0.24. The effect of D_s is negligible at low flow rates and dominates at high flow rates. It is interesting to point out that one can measure D_L at low flow rates by simply assuming D_s is infinite. The error in the lowest flow rate is less than $\frac{1}{22}$. Our system is particularly useful for measuring the breakthrough curve at low flow rates because more data points are recorded at low flow rates.

For the purpose of measuring D_L of a packed bed, it is possible also to use an adsorbent with large D_s and large K' (see Eq. 14b) in order to increase β. Activated carbon is, in fact, a good candidate. Because the longitudinal diffusion is a process in the gas phase, the value of D_L is unlikely to be affected by the nature of the solid phase. Correlations of D_L with fluid properties are available (*7, 9*). The value of D_s depends both on the properties of the adsorbate and the adsorbent and must be measured on an individual basis; however, our criterion β serves another purpose also: When we want to measure the intercept and the slope from a linear plot, it is best to vary the independent variable so that both the intercept term and the slope term have the same order of magnitude. (The reason is that when one term outweights another, a slight experimental error can have a large influence on the small term; for example, in Fig. 1 an error in the moment measurement could cause a negative intercept because the intercept is the small term.) A mathematically-equivalent statement for choosing variables is that it is best to determine D_s and D_L at the condition around $\beta = 1$. The value of D_L is easily known. Suppose we can accept the region where $0.1 < \beta < 10$ to determine D_s; in this case the statement can be turned into the following condition for D_s only:

$$\frac{R^2u^2}{150\,D_L\left(1+\dfrac{1-\varepsilon}{\varepsilon}K'\right)} < D_s < \frac{R^2u^2}{1.5D_L\left(1+\dfrac{1-\varepsilon}{\varepsilon}K'\right)} \tag{15}$$

The application of Eq. (15) is clear: When K' (which can be varied by changing temperature) and ε are known and the region for the value of D_s is decided, then values of the other parameters (viz., R, u, and D_L) can be chosen to measure the precise value of D_s for the adsorbent based on Eq. (13).

CONCLUSION

We derived an expression for the first-order moment of a breakthrough curve. The moment contains both the longitudinal and the solid-phase diffusion coefficients which can be determined experimentally. We applied this technique to data in a previous article and found that the longitudinal diffusion coefficient dominates at low flow rates. A criterion is suggested to distinguish the relative importance of the two diffusion coefficients. This criterion has further application in choosing the experimental conditions for measuring the solid-phase diffusion coefficient.

SYMBOLS

C	gas phase concentration of adsorbate
D_L	longitudinal diffusion coefficient
D_s	solid-phase diffusion coefficient
K'	average adsorption capacity of adsorbent
L	column length
q	solid-phase concentration
q_{ave}	average solid-phase concentration
R	radius of adsorbent particles
r	radial coordinate of adsorbent particles
s	parameter of the Laplace transform
t	time
t_p	propagation time defined in Eq. (11)
u	interstitial flow rate
$u(t_p)$	step function defined in Eq. (11)
z	longitudinal coordinate

Greek

β	dimensionless criterion defined in Eq. (14a)
ε	void fraction of a packed bed
μ_1	first-order moment of a breakthrough curve

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REFERENCES

1. J. C. Huang, R. Forsythe, and R. Madey, *Sep. Sci. Technol.*, *16*, 475 (1981).
2. M. Suzuki and J. M. Smith, *Adv. Chromatogr.*, *15*, 213 (1975).
3. J. B. Rosen, *J. Chem. Phys.*, *20*, 387 (1952).
4. L. Lapidus and N. R. Amundson, *J. Phys. Chem.*, *56*, 984 (1952).
5. P. F. Deisler, Jr., and R. H. Wilhelm, *Ind. Eng. Chem.*, *45*, 1219 (1953).
6. J. C. Huang, D. Rothstein, and R. Madey, *AIChE J.*, In Press.
7. L. K. P. Hsu and H. W. Haynes, Jr., *Ibid.*, *27*, 81 (1981).
8. K. Chihara, M. Suzuki, and K. Kawazoe, *Ibid.*, *24*, 237 (1978).
9. T. K. Sherwood, R. L. Pigford, and C. R. Wilke, *Mass Transfer*, McGraw-Hill, New York, 1975, Chap. 4.

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