Diffusion Coefficients in Crosslinked Polystyrene

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Abstract

We measured the breakthrough curves for rectangular pulses of methane, ethane, and acetylene at low concentrations adsorbed on crosslinked polystyrene at 0, 25, and 30°C. The method of moments was utilized to evaluate the diffusion coefficients of the three gases based on a homogeneous-solid diffusion model.

INTRODUCTION

Moment analysis has made a large contribution to the understanding of chromatography and the adsorption of gases. The differential equations of adsorption can be solved analytically only for the simplest models; for models with linear isotherms, the moments of the time-dependent transmission are algebraic expressions in terms of the kinetic parameters. In theory, by numerical evaluation of the moments under various bed conditions, the kinetic parameters such as the longitudinal dispersion, solid-phase diffusion, and mass-transfer coefficients can be calculated for adsorbates with linear isotherms; however, evaluation of

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the parameters is hampered by inaccuracies in the higher moments (*1-3*) and the large number of parameters. These inaccuracies often restrict the use of moment analysis to models with either fewer mass-transfer mechanisms or lumped parameters, or to flow ranges, particle sizes, or other bed parameters that allow the neglect of several of the kinetic processes. Derivations of the moments were reported for homogeneous-solid diffusion models (*3-6*), where the adsorber is treated as a solid without porosity, and for pore diffusion models (*7-11*) which often require assumptions about the dominant modes of mass transfer and the pore structure. Comprehensive reviews of both models were published by Weber and Chakravorti (*11*), Monsour et al. (*12*), and Famularo et al. (*13*).

Although porous polymers are used extensively for the analytical separation of complex mixtures (*14*), the study of the adsorption kinetics and the pore structure of these adsorbers has not been pursued actively. One reason for this neglect is that the different preparation history of each crosslinked resin may affect the internal structure. Several authors have commented on lot-to-lot variability of retention times (*14, 15*) and on the dependence of the retention times on the molecular weight of the resin (*16*). For these reasons, many authors prefer to prepare their own crosslinked resins. Swelling was also reported for several of these polymers above the glass-transition temperature (*16, 17*). In spite of these limitations, it is of interest to evaluate the diffusion coefficients in these polymers. This paper reports diffusion coefficients extracted by the method of moments from the measured transmission of a rectangular pulse change in the input concentration of methane, ethane, and acetylene through a commercially produced crosslinked polystyrene at temperatures of 0, 25, and 30°C. A model that contains only gaseous-phase and solid-phase diffusion was chosen because the mesoporous nature of the polystyrene is likely to be dominated by diffusion inside the particles.

THE MODEL

The model used in this study, which was described in Huang et al. (*6*), includes a velocity-independent longitudinal dispersion and treats the porous adsorbent as a homogeneous solid. Since mass-transfer resistance is small (*18*), it is neglected. The isotherm relation is assumed to be linear:

$$q(z,R,t) = KC(z,t) \tag{1}$$

where C and q are the gas-phase and the solid-phase concentrations, and K is the dimensionless adsorption capacity. Since an analytical solution to this system is not possible in a closed form, the system of equations is solved normally in the Laplace domain from the moments of the transmission curves. The transmission T is defined as the output concentration divided by the steady input concentration. The nth reduced moment is defined as

$$\mu'_n = \mu_n/\mu_0 = \left[\int_0^\infty T(t)(t - \mu_1)^n dt \right] / \left[\int_0^\infty T(t)dt \right] \qquad (2)$$

which can be evaluated in the Laplace domain since

$$\mu_n = (-1)^n \lim_{p \to 0} \{d^n[\tilde{T}(p)]/dp^n\} \qquad (3)$$

where p is the Laplace variable. For a rectangular input pulse of width τ starting at $t = 0$, the first and second reduced moments of the transmission curve can be evaluated from Eq. (3) as (18):

$$t_p = \mu_1 - \tau/2 = (1 + \alpha K)L/u \qquad (4)$$

$$M_2 = (\mu'_2 - \tau^2/12)u/L = 2D_L(1 + \alpha K)^2/u^2 + 2\alpha KR^2/15D_s \qquad (5)$$

Here u is the interstitial flow velocity, R is the radius of the spherical particles, D_L is the effective longitudinal dispersion coefficient, D_s is the solid-phase diffusion coefficient, L is the bed length, and α is defined as $(1 - \varepsilon)/\varepsilon$, where ε is the volume void fraction of the bed. The propagation time t_p is the average residence time of adsorbate in the bed. The first moment allows the calculation of the adsorption capacity without the need to measure the isotherm. The second moment corrected for pulse width, M_2, can be evaluated numerically from the transmission curve. If M_2 is plotted versus $1/u^2$, a straight line results with the slope and intercept yielding numerical values of the longitudinal dispersion and solid-phase diffusion coefficients, respectively. As expected (3, 19), the right-hand side of Eq. (5) is exactly twice that of the first moment for the step input boundary conditions in Huang et al. (6).

It should be mentioned that Eq. (5) is a special case (in the low velocity regime) of the more general solution with a velocity-dependent D_L. If D_L is not constant, but instead is the sum of a constant molecular dispersivity and an eddy diffusion term which is linear in the velocity (i.e., $D_L = D_0 + Eu$), the moment expression which replaces Eq. (5) is

$$M_2 = 2D_0(1 + \alpha K)^2/u^2 + 2E(1 + \alpha K)^2/u + 2KR^2/15D_s \qquad (6)$$

Equation (6) is a parabola in the variable $1/u$. The value of D_s is calculated from the value of M_2 at $1/u = 0$ in both models. A linear $1/u^2$ plot does not rule out the velocity-dependent model. Any linear equation in $1/u^2$ results automatically in a parabola in $1/u$. It is possible for data that fit the velocity-independent model in Eq. (5) to produce a parabola with negative coefficients for one or more of the three terms when fitted to the model in Eq. (6). Because much of the data in this study fell into this category, the results reported in this study were calculated from the model with a constant D_L.

EXPERIMENTAL METHOD

The experimental apparatus to measure dynamic transmission curves was described in a previous paper (20). Two different length adsorber beds, made of 0.5 in. o.d. stainless steel, contain nonpolar adsorbent Chromosorb 106 (Johns-Manville Corp., Denver, Colorado), a copolymer of polystyrene and divinylbenzene. The crosslinked polystyrene beads (20/40 mesh) have a particle density of 0.54 g/cm³, an average radius of 0.30 mm, and a surface area of 780 m²/g. The bed parameters are listed in Table 1. Temperatures were maintained to within ±0.02°C, and flow controllers maintained the volumetric flow rates to within ±0.5%. The gases were custom mixtures in a helium carrier, supplied in standard cylinders (Matheson Corp., East Rutherford, New Jersey).

RESULTS AND CONCLUSIONS

The adsorptions of three light hydrocarbon gases (i.e., methane, ethane, and acetylene) were measured in this study. The linearity of the isotherms can be assessed by observing the exponents in the Freundlich isotherms.

TABLE 1
Parameters of Two Adsorber Beds

Bed	Length, L (cm)	i.d. (cm)	Mass of adsorbent (g)	Void fraction, ε
Long	25.4	1.09	8.43	0.342
Short	10.0	1.08	3.23	0.350

The Freundlich exponent for acetylene at 273 K was 0.974 (*21*), and those for ethane at 273, 298, and 303 K were 0.949, 0.983, and 0.989, respectively (*22*), in the concentration ranges used in this study. A methane isotherm was not obtained on polystyrene because of short propagation times, but methane adsorbed on polystyrene should be more linear than the heavier alkane ethane (*23*). The adsorption capacities (K) were nearly constant as a function of concentration (*22, 24*). These results imply that Eq. (5) should be applicable for these three gases. The effect on the pulse transmission curves of varying the input pulse width was measured for 9830 ppm ethane adsorbed on the long bed at 303 K. The same series of pulse widths was utilized at two flow velocities. The propagation time ($\mu_1 - \tau/2$) was independent of the pulse width at both velocities. From Eq. (4), the quantity ($\mu_1 - \tau/2)u/L$ is ut_p/L, which is also equal to $(1 + \alpha K)$. Values of ut_p/L indicate that the adsorption capacity was velocity-independent and independent of the pulse width. The calculated second moments (M_2) were also independent of the pulse width. The dimensionless adsorption capacities calculated from Eq. (4) for the three gases at the experimental conditions, averaged for the different velocities, are shown in Table 2; relative uncertainties in the average adsorption capacities are typically 3 to 4%.

Plots of M_2 vs $1/u^2$ are shown in Figs. 1, 2, and 3 for methane, ethane, and acetylene, respectively. At each concentration and at each tempera-

TABLE 2

Dimensionless Adsorption Capacities Calculated from the First Moments of a Rectangular Pulse of Methane, Acetylene, and Ethane Adsorbed on Crosslinked Polystyrene

Gas	Concentration (ppm)	Temperature (K)	Bed[b]	Adsorption capacity,[a] K
Methane	9,810	303	L	3.34
		273	S	6.72
Acetylene	10,100	303	L	15.4
		298	S	20.6
		273	S	43.8
	101	273	S	46.2
Ethane	9,830	303	L	22.1
		303	L	21.2
		303	S	23.4
		298	S	29.3
	495	273	S	65.3

[a]Relative uncertainties are typically 3 to 4%.
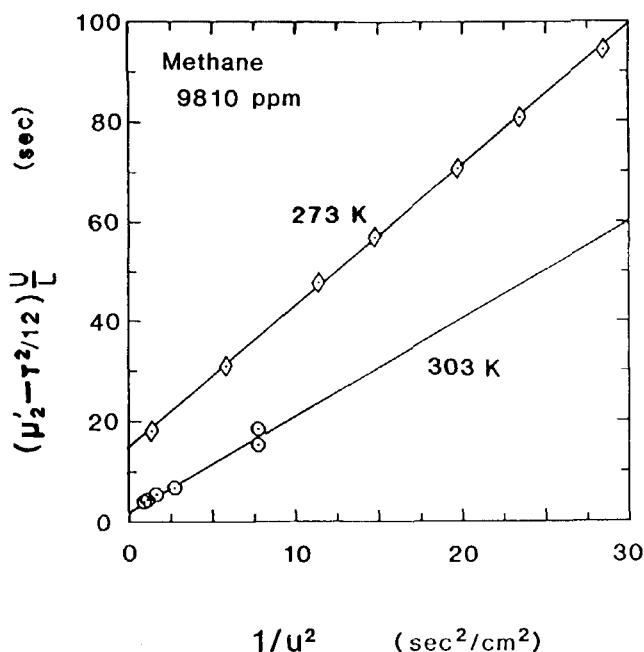[b]$L = 25.4$ cm, short bed length $S = 10.04$ cm.

FIG. 1. The second moment expression M_2 as a function of $1/u^2$ for rectangular pulses of methane adsorbed on crosslinked polystyrene.

ture, the plots are linear and the lines for the two different length beds coincide. The linearity of the plots also indicates that the velocity-independent model of D_L describes the data adequately in this range of flow rates; however, both D_s and D_L depend on concentration. The lack of a tailing off of the moments at high flow rates indicates that mass-transfer resistance is not important, or has a constant effect, justifying its neglect in the theory.

The diffusion coefficients calculated from the plots of Eq. (5) are listed in Table 3. The values of the longitudinal dispersion coefficient D_L are typical of gases in the literature (3, 25, 26). The diffusion coefficient in pure polystyrne depends on the molecular weight of the polymer (27); however, the Chromosorb is a crosslinked resin as well as porous. A homogeneous-solid diffusion model makes correlation with literature data difficult, because the only literature data (25, 27, 28) are measured in bulk polystyrene. The values of D_s in porous polystyrene have the same order of magnitude of the diffusion coefficients of gases in a liquid, as tubulated by Szepesy (25). This result agrees with the conclusions of a
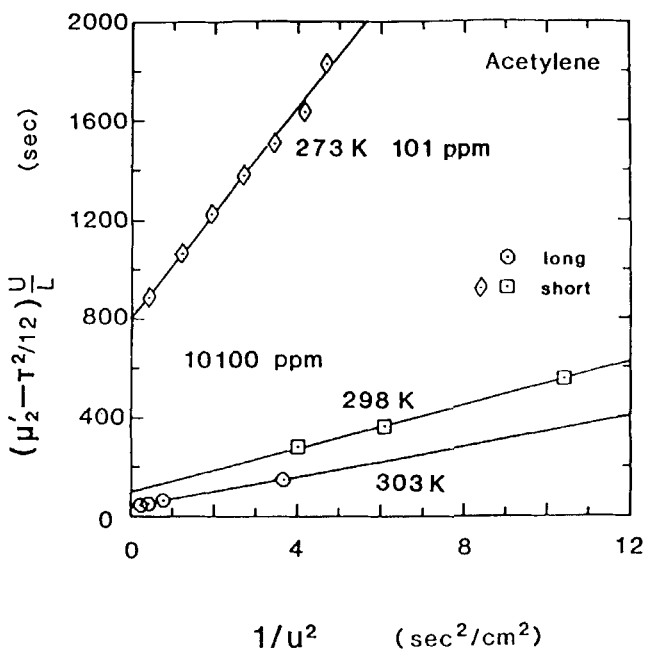
FIG. 2. The second moment expression M_2 as a function of $1/u^2$ for rectangular pulses of ethane adsorbed on crosslinked polystyrene.

TABLE 3

Gas- and Solid-Phase Diffusion Coefficients Calculated by the Method of Moments for Rectangular Pulses of Methane, Acetylene, and Ethane Adsorbed on Crosslinked Polystyrene

Gas	Concentration (ppm)	Temperature (K)	Bed[b]	Diffusion coefficients[a]	
				Solid phase, D_s (10^{-5} cm^2/s)	Gas phase, D_L (cm^2/s)
Methane	9,810	303	L	10.2	0.38
		273	S	3.4	0.18
Acetylene	10,100	303	L	3.1	0.41
		298	S	1.5	0.33
		273	S	0.15	0.36
	101	273	S	0.44	0.32
Ethane	9,830	303	L	1.4	0.39
		303	L	1.7	0.39
		303	S	1.9	0.32
		298	S	0.78	0.26

[a]Relative uncertainties are typically 6% for D_L and 8 to 10% for D_s.
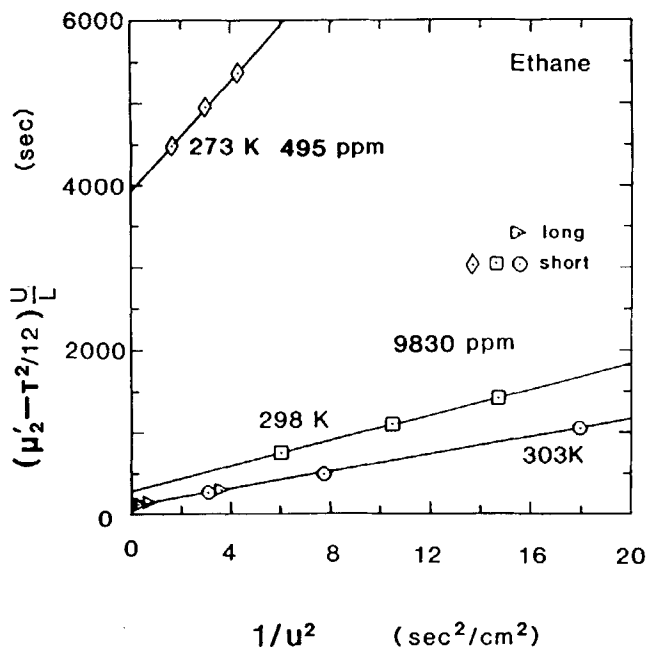[b]$L = 25.4$ cm, $S = 10.04$ cm.

FIG. 3. The second moment expression M_2 as a function of $1/u^2$ for rectangular pulses of acetylene adsorbed on crosslinked polystyrene.

study by Testin and Stuart (29). The value of D_s calculated is not the true coeffiicent in the solid because most of the diffusion took place in the pore volume. The calculated D_s represents the combined effects of solid diffusion, Knudson diffusion in the pores (dominant over molecular diffusion), adsorption in the pores, and mass-transfer resistance in the adsorbed film; accordingly, the effective diffusion coefficient should be larger than the value in the bulk nonporous solid.

Acknowledgment

REFERENCES

1. M. Suzuki and J. M. Smith, *Adv. Chromatogr., 13,* 213 (1975).

2. L. K. Hsu and H. W. Haynes Jr., *AIChE J., 27,* 81 (1981).

3. H. de Lasa, J. Hazlett, and O. M. Fuller, *Chem. Eng. Sci., 41,* 1233 (1986).
4. E. Grushka, *J. Phys. Chem., 76,* 2586 (1972).
5. M. Kocirik, *J. Chromatogr., 30,* 459 (1967).
6. J. C. Huang, D. Rothstein, B. G. Wu, and R. Madey, *Sep. Sci. Technol., 17,* 1417 (1982).
7. H. Vink, *J. Chromatogr., 20,* 305 (1965).
8. O. Grubner, A. Zikanova, and M. Ralek, *Ibid., 28,* 209 (1967).
9. D. W. Underhill, *Nucl. Appl. Technol., 8,* 255 (1970).
10. P. Schneider and J. M. Smith, *AIChE J., 14,* 762 (1968).
11. T. W. Weber and R. K. Chakravorti, *Ibid., 20,* 228 (1974).
12. A. Mansour, D. U. von Rosenberg, and N. D. Sylvester, *Ibid., 28,* 765 (1982).
13. J. Famularo, J. A. Mueller, and S. Pannu, *J. Water Pollut. Control Fed., 52,* 2019 (1980).
14. O. L. Hollis, *J. Chromatogr. Sci., 11,* 335 (1973).
15. J. R. Linday Smith, A. H. Tameesh, and D. J. Waddington, *J. Chromatogr., 151,* 27 (1978).
16. W. G. Lloyd and T. Alfrey Jr., *J. Polym. Sci., 62,* 301 (1962).
17. H. L. Gearhart and M. F. Burke, *J. Chromatogr. Sci., 11,* 411 (1973).
18. J. C. Huang, D. P. Rothstein, and R. Madey, *J. Chromatogr., 261,* 1 (1983).
19. P. A. Ramachandran and J. M. Smith, *Ind. Eng. Chem., Fundam., 17,* 148 (1978).
20. J. C. Huang, R. Forsythe, and R. Madey, *Sep. Sci. Technol., 16,* 475 (1981).
21. D. P. Rothstein, Unpublished Data.
22. D. P. Rothstein, J. C. Huang, B. G. Wu, T. V. Lee, and R. Madey, *J. Colloid Interface Sci., 106,* 399 (1985).
23. S. Brunauer, *The Adsorption of Gases and Vapors,* Vol. I, Princeton University Press, Princeton, New Jersey, 1945, pp. 55-57.
24. D. P. Rothstein, PhD Thesis, Kent State University, 1986.
25. L. Szepesy, *Gas Chromatography,* Butterworths, London, 1971, pp. 35-37.
26. K. Chihara, M. Suzuki, and K. Kawazoe, *AIChE J., 24,* 237 (1978).
27. V. T. Stannett, in *Diffusion in Polymers* (J. Crank and G. S. Parks, eds.), Academic, New York, 1968, pp. 41-73.
28. G. S. Park, in *Diffusion in Polymers* (J. Crank and G. S. Park, eds.), Academic, New York, 1968, pp. 141-163.
29. R. F. Testin and E. B. Stuart, *Chem. Eng. Prog., Symp. Ser., 63,* 10 (1967).