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Transport of Methane, Acetylene, and Acetaldehyde through Activated Carbon

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Abstract

The outlet concentration as a function of time for pulsed and stepped inputs of 100 ppm concentrations of methane, acetylene, and acetaldehyde adsorptives in helium at 1 atm pressure through columns of activated carbon at 25°C were measured and correlated with the solutions to a longitudinal-diffusion model with a linear isotherm. The solutions provided good fits to the experimental data for adsorptives with linear and almost linear isotherms, viz., methane and acetylene, respectively. The nonlinear isotherm of acetaldehyde precludes the determination of the longitudinal diffusion coefficient.

INTRODUCTION

The isothermal transport of an adsorptive gas through a packed adsorber column is affected by the shape of the adsorption isotherm and by several dispersion mechanisms such as longitudinal and intraparticle diffusion, surface kinetics, and mass-transfer resistance. Because the formulation and solution of the equations that describe all of the dispersion processes is a difficult task, simplifying assumptions regarding the number and nature of the dispersion mechanisms have to be introduced.

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In the simple case when the adsorption isotherm is linear and the longitudinal diffusion is the dominant dispersion mechanism, the transmission function $T(t)$, defined as the normalized time-dependent concentration at the column outlet, can be obtained in closed form for various inputs (*1, 2*). The solutions are useful for the analysis of experimental data and for the evaluation of adsorber columns under different conditions.

In this paper we report measurements of the transmission of various input concentration functions of adsorptives with linear and nonlinear isotherms. These transmission data are analyzed with the longitudinal-diffusion model with a linear isotherm; the results for different input concentration functions are compared. The effects of the isotherm nonlinearity and the limits of validity of the longitudinal-diffusion model are discussed.

THEORETICAL BACKROUND

In the longitudinal-diffusion model the transport of an adsorptive gas through a packed column of length L is described by the following partial differential equation (*3*):

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

Here D_L is the diffusion coefficient, u is the interstitial flow velocity, and ε is the interstitial void fraction of the adsorber. The adsorptive concentration $C = C(z,t)$ in the gas phase and the adsorbate concentration $q = q(z,t)$ in the solid phase are related by the adsorption isotherm equation:

$$q = q(C) \tag{2}$$

When the isotherm equation is nonlinear, different concentrations of adsorptive travel through the column at different speeds and, depending on the orientation of the isotherm curvature, sharpening or broadening of the shape of the input concentration profile is observed at the column outlet.

The solution to Eqs. (1) and (2) may be expressed in terms of a dimensionless transmission T:

$$T(t) \equiv C(L,t)/C_0 \tag{3}$$

where C_0 is the initial concentration at the input to the column. When the isotherm is linear, the transmission function for various input-concentration profiles can be obtained by standard methods. Thus, for a step-increase in the input concentration from 0 to C_0 as shown in Fig. 1(a), the transmission is (*4*)

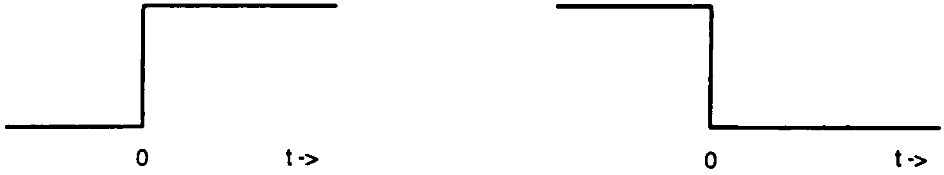
$$T_a(t) = \frac{1}{2}\exp\left(\frac{uL}{D_L}\right)\operatorname{erfc}(s_+) + \frac{1}{2}\operatorname{erfc}(s_-) \tag{4}$$

where

$$s_\pm(t) \equiv \left(\frac{uL}{4D_L}\right)^{1/2}\left[\left(\frac{t_p}{t}\right)^{1/2} \pm \left(\frac{t}{t_p}\right)^{1/2}\right] \tag{5}$$

and

$$t_p \equiv \left[\frac{(1-\varepsilon)K}{\varepsilon} + 1\right]\frac{L}{u} \tag{6}$$



a. step-increase

b. step-decrease

c. positive pulse

d. negative pulse

FIG. 1. Step and pulse input-concentration profiles.

The step-increase in input concentration results in a net uptake (i.e., adsorption) of adsorbate by the column; hence, the subscript *a* on the transmission $T_a(t)$ denotes adsorption.

For a step-decrease in the input concentration from C_0 to 0 as shown in Fig. 1(b), the transmission function is

$$T_d(t) = 1 - T_a(t) \tag{7}$$

The step-decrease in input concentration results in a net loss (i.e., desorption) of adsorbate by the column; hence, the subscript *d* on the transmission denotes desorption.

A rectangular input-pulse can be considered as a combination of a step-increase followed after a time τ by a step-decrease in the input concentration. Thus, the transmission function for the positive pulse of Fig. 1(c) is:

$$T_p^+(t) = T_a(t) - T_a(t - \tau)h(t - \tau) \tag{8}$$

where $h(t - \tau)$ is the unit step function at time $t = \tau$, and t is measured from the start of the pulse.

The negative-rectangular-input pulse of Fig. 1(d) can be viewed as a step-decrease followed by a step-increase in the input concentration. In practice, the column is first saturated by a continuous flow of the adsorptive gas, the flow of adsorptive is interrupted, and pure carrier gas is introduced at the same flow rate. After a time τ, the flow of the adsorptive gas is restored. The transmission function for the negative rectangular pulse is analogous to Eq. (7):

$$T_p^-(t) = 1 - T_p^+(t) \tag{9}$$

The transmission for a narrow positive-rectangular-input pulse can be approximated by the solution to Eq. (1) with delta function boundary conditions (*5*); that is,

$$T_p^+(t + \tau/2) \approx T_\delta^+(t) \tag{10}$$

with

$$T_\delta^+(t) = \frac{\tau}{2} \left[\frac{uLt_p}{\pi t^3 D_L}\right]^{1/2} \exp\left[-[s_-(t)]^2\right] \tag{11}$$

A narrow negative-pulse may be approximated with Eqs. (9) through (11).

The symmetry expressed by Eqs. (7) and (9) is a consequence of the linearity of the adsorption isotherm and the longitudinal diffusion process. These equations do not hold when nonlinearities are introduced to the mathematical model by the curvature of the adsorption isotherm. It is interesting to examine the perturbation effects of slight nonlinearities in the isotherm on the transmissions of different input concentration functions; conversely, information on the dispersion mechanisms can be deduced from the transmission features of various inputs.

EXPERIMENTAL PROCEDURES

We measured the isothermal transmission of positive (Fig. 1c) and negative (Fig. 1d) rectangular input pulses through columns packed with Columbia 4LXC 12/28 activated carbon. Details of the experimental apparatus are given in Ref. *4*. We used a stainless steel flow system that allowed selection of the gas stream flowing through the column. The desired shape of the input pulse was achieved by appropriate switching between two gas streams (viz., the gas mixture and the pure carrier gas) with equal volumetric flow rates. The desired flow rates were measured and maintained to within ±0.5% with a volume displacement flowmeter and pneumatic flow controller. The concentration at the outlet of the column was measured with an automated data acquisition system which consisted of a (Carle 4301) automated sampling valve, a (Varian 3700) gas chromatograph equipped with a flame ionization detector, and an (Infotronics CRS-280) digital integrator. For all the measurements reported here, the column temperature was maintained at 25.00 ± 0.02°C by means of a dual water-bath system. Measurements were taken for three ad-

TABLE 1

Adsorptive Concentrations in a Helium Carrier Gas and the Characteristics of the Adsorbent Columns

Adsorptive	Concentration C_0 (ppm)	Column length L (cm)	Column diameter d (cm)	Mass of adsorbent M (g)
Methane	105	30.1	1.716	26.14
Acetylene	100	10.0	0.459	0.588
Acetaldehyde	102	10.0	0.466	0.688

sorptives (viz., methane, acetylene, and acetaldehyde) at nominal concentrations of 100 ppm in a helium carrier gas with a nominal total pressure of 1 atm. The gas mixtures were prepared by a specialty gas supplier (viz., the Linde Division of the Union Carbide Corp). The adsorptive concentrations and the characteristics of the columns used in the measurements are listed in Table 1.

EXPERIMENTAL RESULTS

a. Methane Pulses

Shown in Fig. 2 are the experimental transmissions of positive 105-ppm methane pulses with durations of 50, 100, 200, and 500 s. The column length was 30.1 cm and the interstitial flow velocity was 0.682 cm/s. The solid lines represent least-squares fits to the transmission function given by Eq. (8) for a positive input pulse. The delta function solution for the transmission given by Eq. (10) represents the data equally well for pulse durations from 50 to 200 s.

When the transmission data for each pulse are normalized to the corresponding maximum value, the experimental values are described well by a single theoretical curve generated with either the rectangular or delta-function equation sets, as illustrated in Fig. 3 for input pulse widths from 20 to 200s. The 500-s input pulse duration is significant with respect to the duration of the dispersed output pulse; therefore, it appears wider than the other pulses on the normalized graph. This pulse may be represented accurately by Eqs. (8) and (9) as shown in Fig. 2.

Figure 4 shows the normalized transmission of negative pulses (Fig. 1d) through a column saturated with 105 ppm methane. The column conditions are the same as those used for the positive pulses. The parameters of the fit for both experiments are given in Table 2. The agreement between the values obtained for the positive and negative pulses is a consequence of the linearity of the adsorption isotherm for methane at the concentrations used.

b. Acetylene Pulses

Shown in Fig. 5 are the transmissions of negative pulses of acetylene through a column 10 cm long saturated with 100 ppm acetylene. The three

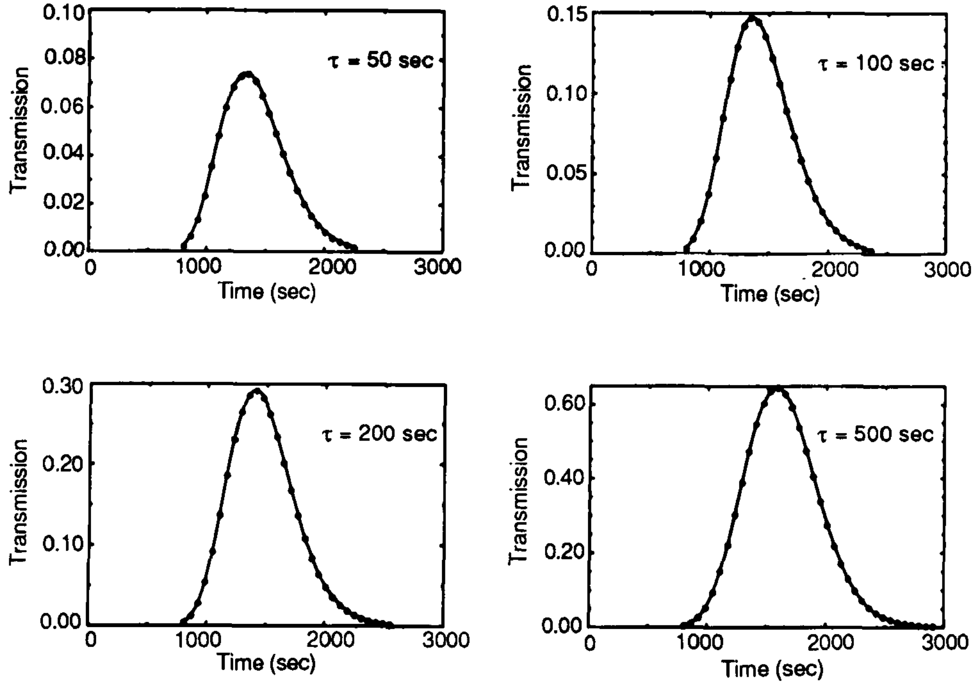


FIG. 2. Experimental and theoretical transmissions for rectangular input pulses with widths of 50, 100, 200, and 500 s for 105-ppm methane in helium flowing with an interstitial flow velocity of 0.682 cm/s through an adsorber column 30.13-cm long packed with Columbia 4LXC 12/28 activated carbon at 25°C as a function of time measured from the start of the input pulse.

panels are for three pulse widths flowing at different interstitial flow rates. The theoretical transmission function, represented by the solid line, provides a good fit to the data. The transmission data for step-increase and step-decrease inputs were analyzed; the values of the longitudinal diffusion coefficient, derived by least-squares fits to the data, are plotted in Fig. 6 as a function of the interstitial flow rate. The diffusion coefficients derived from the transmission of negative pulses are plotted in the same figure for comparison. Transmission data were not taken for positive acetylene pulses. In the Discussion Section we will elaborate on the correlation between the values of the diffusion coefficients and the shape of the isotherm.

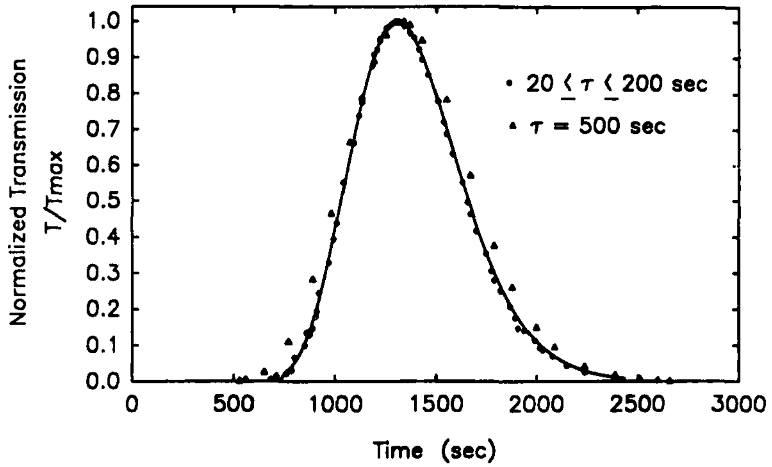


FIG. 3. Normalized experimental and theoretical transmissions for rectangular input pulses with widths 20, 50, 100, 200, and 500 s of 105-ppm methane in helium flowing with an interstitial flow velocity of 0.682 cm/s through an adsorber column 30.13-cm long packed with Columbia 4LXC 12/28 activated carbon at 25°C as a function of time measured from the center of the input pulse.

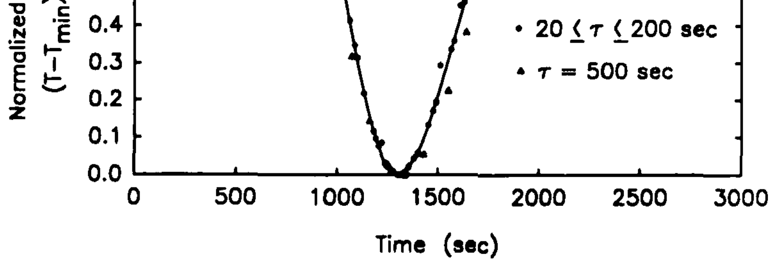


FIG. 4. Normalized experimental and theoretical transmissions for rectangular input pulses of pure helium with widths 20, 50, 100, 200, and 500 s in a gas stream of 105-ppm methane in helium with an interstitial flow velocity of 0.682 cm/s flowing through an adsorber column 30.13-cm long packed with Columbia 4LXC 12/28 activated carbon at 25°C as a function of time measured from the center of the input pulse.

TABLE 2
The Longitudinal Diffusion Coefficient D_L and the Propagation Time t_p Derived from the Least-Squares Fits of the Transmission Equations to the Measured Transmissions of Positive and Negative Rectangular Pulses of 105-ppm Methane in Helium

	Positive pulse		Negative pulse	
Pulse width τ (s)	Propagation time t_p (s)	Diffusion coefficient D_L (cm^2/s)	Propagation time t_p (s)	Diffusion coefficient D_L (cm^2/s)
20	1390	0.440	1386	0.415
50	1388	0.421	1387	0.415
100	1391	0.419	1385	0.417
200	1379	0.419	1383	0.415
500	1389	0.419	1382	0.414

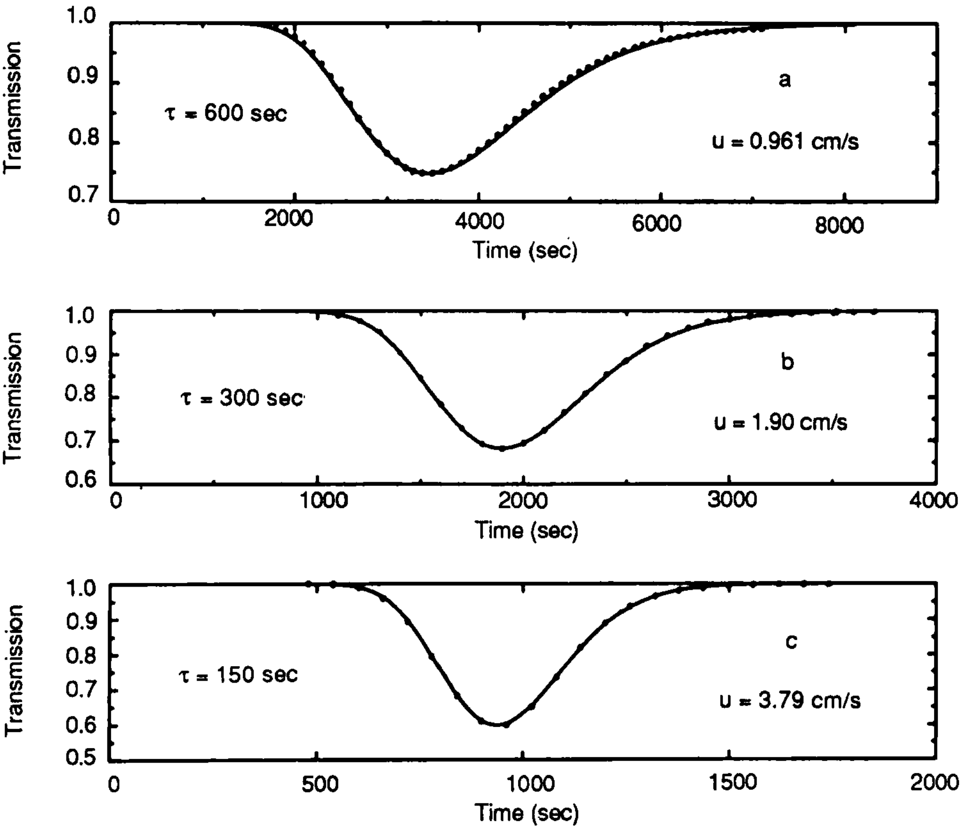


FIG. 5. Experimental and theoretical transmissions for rectangular input pulses of pure helium with widths 150, 300, and 600 s in a gas stream of 100-ppm acetylene in helium with an interstitial flow velocity of 0.961, 1.90, and 3.79 cm/s, respectively, flowing through an adsorber column 10.0-cm long packed with Columbia 4LXC 12/28 activated carbon at 25°C as a function of time measured from the start of the input pulse.

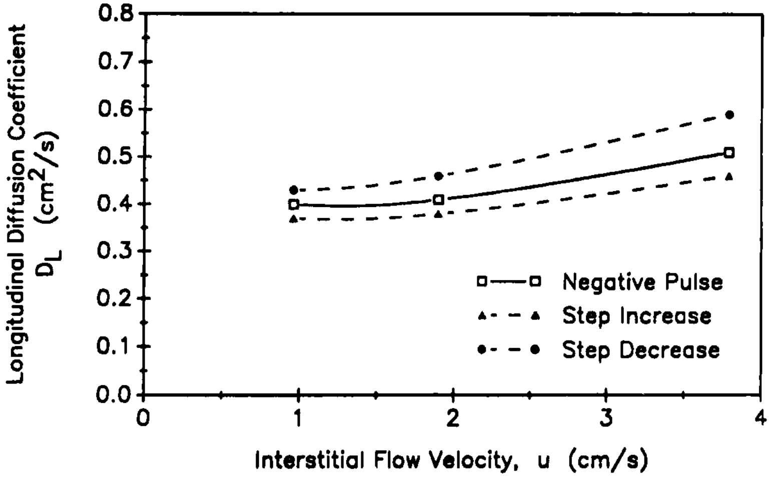


Fig. 6. The longitutudinal-diffusion coefficient determined with the longitudinal-diffusion model with a linear isotherm as a function of the interstitial flow velocity for negative rectangular pulse inputs, and positive and negative step function inputs, of 100-ppm acetylene in a helium carrier at a nominal total pressure of 1 atm flowing through Columbia 4LXC 12/28 activated carbon at 25°C.

c. Acetaldehyde Pulse

Shown in Fig. 7 is the transmission of a negative pulse of acetaldehyde through a column saturated with 102-ppm acetaldehyde. The least-squares fit of Eq. (9), which is represented by the solid line in the figure, deviates from the experimental data.

DISCUSSION

The measurements for methane were taken at concentrations in a linear region of the adsorption isotherm (*6*). The corresponding adsorption isotherm for acetylene is an almost-linear Type I isotherm (*6, 7*). The slope of the acetylene isotherm varies by ±1.7% from the mean slope over the range of concentrations from 0 to 100 ppm. Thus, Eqs. (4) through (11) are expected to hold for methane and, to a lesser extent, for acetylene; in fact, the agreement between the experimental and theoretical transmission functions is very good for both adsorptives.

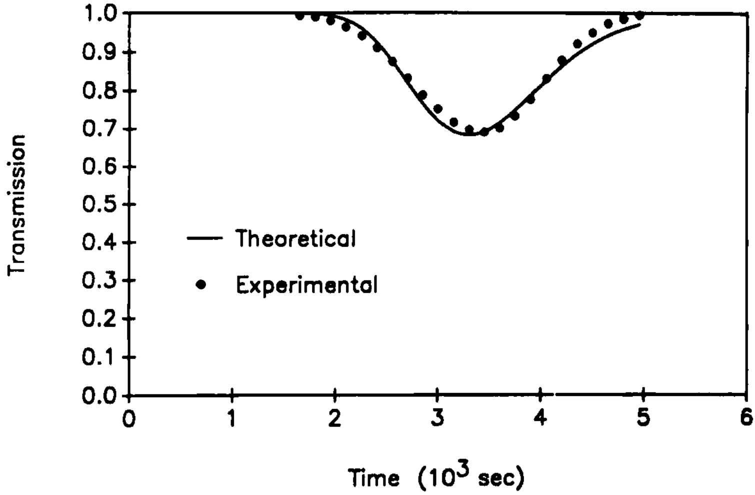


FIG. 7. Least-squares fit of the longitudinal-diffusion model with a linear isotherm to the negative acetaldehyde pulse.

For methane, the values of the retention time, t_p, and the longitudinal diffusion coefficient, D_L, are reproduced well for positive and negative pulses of various widths. The values agree also with the predictions of the longitudinal-diffusion model for step-increase and step-decrease input concentrations (*7*). At the low superficial flow velocities used here for methane, longitudinal diffusion is the dominant dispersion mechanism, and the transport is described adequately by Eq. (1) (*8*).

The slight nonlinearity of the acetylene adsorption isotherm does not seem to affect the ability of Eqs. (4) through (11) to fit the experimental data. The effect of the isotherm nonlinearity is noticeable when the values of D_L for different input functions of acetylene are compare in Fig. 6. The D_L values for a step-increase in input concentration are lower than those for a step-decrease in input concentration, and the negative pulse gives intermediate values of D_L. The shape of the acetylene adsorption isotherm accounts for these results for D_L. For Type I isotherms, the higher concentrations travel faster through the column than the lower concentrations; consequently, the transmission curves are broader (with a correspondingly higher D_L) for the step-decrease inputs than for the step-increase inputs at the same column conditions.

The value of D_L determined for a pulse is affected by the shape of the Type I nonlinear isotherm and the range of concentrations encountered by the pulse during the transport. Because a negative pulse consists of a step-decrease in input concentration followed by a step-increase, the curvature of the isotherm broadens the leading edge and steepens the trailing edge of the transmitted pulse. The resulting output pulse is shaped more symmetrically and is less skewed toward higher times than a pulse that encounters a linear isotherm; however, the Type I isotherm affects the width of the output pulse less than the shape because the pulse edges are displaced in the same direction. The value of D_L in the longitudinal-diffusion model primarily determines the width of the pulse and affects the skew only to a lesser extent. Also, the negative pulse encounters progressively less of the range of nonlinearity as it travels through the column; the transmission pulse of Fig. 5a, for example, shows that only the upper quarter of the concentration range from zero to saturation is affecting the transport of the pulse at the column outlet. Altough the negative pulse encounters the entire range of adsorptive concentrations (and hence all of the isotherm nonlinearity) at the inlet to the column, much of the dispersional effect of the isotherm is avoided for the remainder of the column as the dispersion effects widen the pulse and it becomes less deep.

Both of the negative pulse effects tend to reduce the dependence of D_L on isotherm nonlinearity compared to values of D_L determined from step-increase or step-decrease input concentration changes. For acetylene, which has an almost linear isotherm, the value of D_L determined for the negative rectangular pulse at the lowest flow velocity is midway between the oppositely perturbed values of the step-increase and step-decrease input concentration changes as shown in Fig. 6.

The adsorption capacity for acetaldehyde is about two orders of magnitude higher than that for acetylene (*9*). Also, the Type I isotherm for acetaldehyde is more nonlinear than that for acetylene with a slope that varies by ±28% from the mean slope over the range of concentrations from 0 to 100 ppm. As a result of the nonlinearity of the acetaldehyde isotherm, the transmission curve of Fig. 7 differs considerably from the transmission curves of methane and acetylene; more particularly, the experimental transmission of a negative input pulse of acetaldehyde is symmetric. The longitudinal-diffusion models fails to reproduce this symmetry. We conclude that the dispersion of acetaldehyde in this carbon is dominated by isotherm nonlinearity.

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