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Gas–Solid Chromatography of Methane–Helium Mixtures: Transmission of a Step Increase in the Concentration of Methane through an Activated Carbon Adsorber Bed at 25°C

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Abstract

Time-dependent transmission or "breakthrough" curves of methane in helium flowing through an activated carbon adsorber bed were measured for methane concentrations between 34 and 105 ppm, and for mixture flow rates between 0.69 and 6.64 cm/s. The transmission is the ratio of the outlet concentration to the inlet concentration. The experimental transmission curves for a step-function increase in the methane concentration are compared with the predictions from a model which assumes a linear adsorption isotherm and equilibrium between the gas and solid phases. These two basic assumptions are discussed in detail. The data show that the two assumptions hold within the concentration and flow rate regions of this study. Effective diffusion coefficients of methane were calculated from the transmission data and found to increase with increasing flow rates.

INTRODUCTION

The study of the transmission or "breakthrough" curve of a contaminant gas in a carrier gas flowing through a fixed adsorber bed is important in studies of the dynamics of chromatography (*1*, *2*). From a measurement of a transmission curve, one can determine two parameters that characterize the gas–adsorbent system: the effective diffusion coefficient, which is a dynamic property, and the isothermal adsorption capacity, which is a static property (*3*, *4*). The use of the transmission curve offers a convenient way to determine adsorption capacities of gases on a solid adsorbent in the region of low partial pressures (*5*, *6*). The mathematical equations

describing the adsorption and desorption processes can be applied also to other studies such as liquid chromatography (*7*) and ion-exchange chromatography (*8*). In all of these applications, the dispersion process is an important factor that determines the performance of the technique. The fact that the contaminant gas flows around the granules of the adsorbent results in paths of different lengths with a consequent distribution of retention times. Some other effects, such as the Brownian motion of the contaminant in the carrier gas and the mass-transfer resistance between the carrier gas and the solid absorbent, can also contribute to the dispersion process (*9*). For a constant carrier-gas flow, the dispersion phenomenon can be described by a one-dimensional partial differential equation (*10–12*):

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

Here the phenomenological parameter D represents the effective diffusion coefficient along the bed length coordinate z. The concentration $c(z, t)$ of the contaminant in the gas phase is a function of time t and z, u is the interstitial flow velocity of the gas mixture, q is the average concentration of the contaminant gas in the adsorbent which includes the pore volume, and the void volume fraction ε includes only the volume external to the adsorbent particles.

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

$$c(x, 0) = 0 \tag{2a}$$

$$c(0, t) = c_0 \tag{2b}$$

$$c(\infty, t) = 0 \tag{2c}$$

By selecting suitable flow rates and maintaining a low partial pressure for the contaminant gas in the carrier gas, we can achieve a linear equilibrium relation between the concentrations of the contaminant in the gas and solid phases; i.e.,

$$q = K'c = [K(1 - \varepsilon_p) + \varepsilon_p]c \tag{3a}$$

and

$$K = \frac{K' - \varepsilon_p}{1 - \varepsilon_p} \tag{3b}$$

Here K and K' are dimensionless adsorption capacities, and ε_p is the pore volume fraction within the adsorbent granules. The true adsorption capacity K is the volume of gas adsorbed per unit volume of the solid

adsorbent (which does not include the pore volume), whereas the apparent adsorption capacity K' is the gas volume adsorbed per unit volume of adsorbent (which includes the pore volume but not the interstitial volume). Note that the introduction of ε_p separates the true adsorption capacity K from the apparent adsorption capacity K'. The factor $\varepsilon_p c$ in the right-hand member of Eq. (3a) represents the contaminant in the pore volume; the factor $K(1 - \varepsilon_p)c$ is the contaminant adsorbed on the solid.

The analytical solution of Eq. (1) with the initial and boundary conditions (2) and the relations (3) were known for several years (*10–12*). In terms of the nomenclature of Madey and Pflumm (*12*), the transmission through a bed with length L is

$$T = \frac{c}{c_0} = \frac{1}{2}\exp(\Delta^{-1})\operatorname{erfc}(s_+) + \frac{1}{2}\operatorname{erfc}(s_-) \tag{4}$$

with

$$\text{Arguments:} \qquad s_\pm \equiv \frac{1}{2\Delta^{1/2}}\left[\left(\frac{t_p}{t}\right)^{1/2} \pm \left(\frac{t}{t_p}\right)^{1/2}\right] \tag{5}$$

$$\text{Dispersion number:} \qquad \Delta \equiv D/uL \tag{6}$$

$$\text{Propagation time:} \qquad t_p \equiv \left[\frac{(1 - \varepsilon)K'}{\varepsilon} + 1\right]\frac{L}{u} \tag{7}$$

The time-dependent transmission function depends explicitly only on two parameters: the dispersion number Δ and the propagation time t_p. These two parameters can be calculated from the transmission data by a numerical method described by Madey and Charles (*13*).

EXPERIMENTAL PROCEDURES

The flow system, shown schematically in Fig. 1, is constructed of stainless-steel tubing and valves with Teflon seats and gaskets. Flow controllers FCA, FCB, and FCC enable independent settings of the gas flow rate from cylinders A, B, and He (helium). Rotameters RA, RB, RC, and RD give an approximate value of the flow rate. The flowmeter FM measures the flow rate with an accuracy of $\pm 0.5\%$. Three-way ball valves B1, B2, B3, and B4 can divert the flow to the electronic dual-channel mass-flow controller (Emerson Electric Co., Brooks Instrument Div. Model 5841-1A1CC) which controls the flow rate to $\pm 1\%$. Three-way ball valves B5, B6, and B7 enable mixing of up to three gas streams. Similar valves B8 and B9 permit two modes: (1) flow through the adsorber bed and (2) flow bypassing the adsorber bed. The latter configuration is applied for calibration and normalization purposes. The pressure drop across

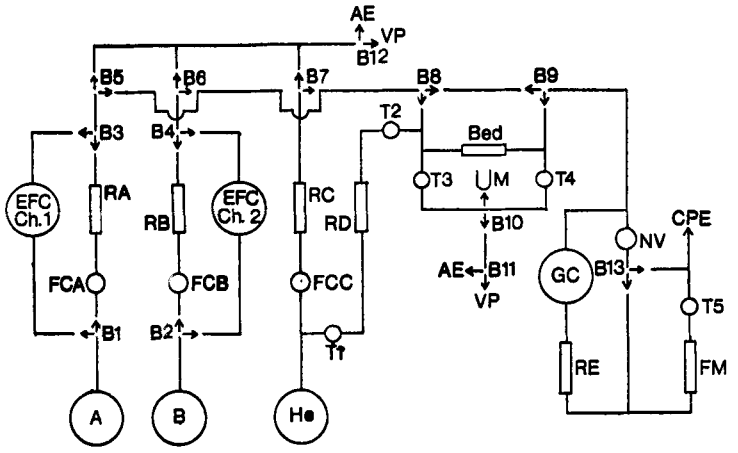

FIG. 1. Schematic diagram of the flow system.

the bed was measured by using the manometer M, and by appropriate manipulation of toggle valves T3 and T4. The automatic data acquisition system, located at the downstream side of the adsorber bed, consists of an automatic sampling valve (Carle Instruments Co. Model No. 4301), a Varian 3700 gas chromatograph with a flame ionization detector, and an Infotronics CRS-280 digital integrator. The data acquisition system measured the outlet concentration of contaminant gas at regular time intervals.

The cylindrical stainless-steel adsorber bed (30.13 cm long and 1.716 cm i.d.) was packed with 26.13 g of "Columbia" type 4LXC 12/28 activated carbon. This carbon has intrinsic density 1.560 g/cc (*14*), surface area 1130 m^2/g (*15*), and pore volume 0.51 cc/g (*15*). Before measuring the mass of the carbon, the adsorber bed was desorbed at 200°C with helium flowing through the adsorber bed at a rate of 200 cc/min for 36 h. Also, after each run, the bed was desorbed for 12 h under the same temperature and helium flow conditions as above. The bed was immersed in a constant-temperature water bath which maintained the temperature within ± 0.02°C at 25°C. Repeated experiments verified the reproducibility of the results.

The gas mixture was prepared by a specialty gas supplier. The 105 ppm concentration of methane is known to within 1%. Lower inlet concentrations of methane can be obtained by adding pure helium to the methane–helium mixture. Since the concentration of methane is small, one can assume that the mass flow rate is uniform through the bed. The total pressure in the adsorber bed ranged between 740 and 780 mmHg and the pressure drop ranged between 10 and 20 mmHg. The pressure drop is

small, and throughout this study we assume the gas flow rate is constant in the bed.

RESULTS AND DISCUSSION

Listed in Table 1 are the measured transmissions of 105 ppm methane in helium at four different flow rates. Although the actual sampling intervals are 30 s, the two lower flow rates in Table 1 include only a portion of the data for convenience in tabulating. Dispersion numbers and propagation times were calculated by minimizing the sum of the squares of the errors between the experimental and the predicted transmissions (*13*). Values of the propagation times and the dispersion numbers are listed in Table 2 for 105 ppm methane in helium and some lower-concentration mixtures.

Propagation times can be calculated directly by integrating the transmission data. For any type of gas–solid equilibrium isotherm, the solid-phase concentration q_0, corresponding to the gas-phase concentration c_0, can always be calculated from the mass-balance equation

$$q_0(1 - \varepsilon)L + c_0\varepsilon L = uc_0\varepsilon \int_0^\infty [1 - T(t)]\, dt \tag{8}$$

Here the right-hand side represents the methane retained in the adsorber

TABLE 1

Transmissions of 105 ppm Methane-Helium Mixture at Different Flow Rates through Columbia 4LXC 12/28 Activated Carbon at 25°C

u = 0.687 cm/s		u = 1.38 cm/s		u = 2.70 cm/s		u = 6.64 cm/s	
Time t (s)	Transmission T	Time t (s)	Transmission T	Time t (s)	Transmission T	Time t (s)	Transmission T
870	0.0084	510	0.0171	300	0.0722	120	0.0157
990	0.0520	570	0.0979	330	0.2832	150	0.6462
1110	0.1508	630	0.2776	360	0.5884	180	0.9837
1230	0.3052	690	0.5140	390	0.8263	210	0.9952
1350	0.4845	750	0.7279	420	0.9414	240	0.9963
1470	0.6513	810	0.8695	450	0.9796		
1590	0.7825	870	0.9438	480	0.9899		
1710	0.8734	930	0.9764	510	0.9922		
1830	0.9293	990	0.9878	540	0.9933		
1950	0.9610	1050	0.9915				
2070	0.9784						
2190	0.9863						
2310	0.9908						

TABLE 2

Propagation Times, Dispersion Numbers, and Adsorption Capacities of Methane in the Columbia 4LXC 12/28 Activated Carbon Adsorber Bed at 25°C

Methane concentration x_0 (ppm)	Interstitial flow velocity u (cm/s)	Propagation time t_p (s)	Dispersion number $\Delta \times 10^2$	Dimensionless adsorption capacity[a] K
105	0.687	1390	2.02	71.7
105	1.38	694.6	1.08	71.7
105	2.70	353.9	0.618	71.7
105	6.64	145.6	0.416	72.6
85	0.690	1386	1.99	71.8
34	0.690	1385	1.89	71.8

[a]Values of K are based on $\varepsilon_p = 0.443$ and $\varepsilon = 0.568$, which come from Refs. *14* and *15*.

bed. The first term on the left-hand side is the methane retained on the granules of the adsorbent; the second term is the methane in the interstitial regions.

Substituting the transmission Eq. (4) and performing the integration, we find [the definitions of K and c_0 in this paper are not the same as in previous papers (*3–6*)]

$$q_0 = \frac{c_0 \varepsilon}{(1 - \varepsilon)} \left(\frac{u t_p}{L} - 1 \right) \tag{9}$$

Since $q_0 = K' c_0$, Eq. (9) becomes

$$u t_p = \frac{K'(1 - \varepsilon)L}{\varepsilon} + L \tag{10}$$

which is equivalent to Eq. (7). Although the procedure from Eq. (8) to Eq. (10) is not applicable when Eq. (4) is not valid, Eq. (8) may always be used for calculating the values of K, K', and q_0.

Equation (10) gives the relation between two dynamic properties (viz., u and t_p) and other physical properties of the system (viz., K', ε, and L). The adsorption capacities K' and K are similar to the partition coefficient in gas–liquid absorption studies in the sense that each is a ratio of two volume quantities (*16*); however, the values of K' and K depend on the surface area of the solid. Although a porous carbon with twice the specific area will have twice the K value, the value of K' will not be twice as large because it depends on the pore volume fraction ε_p. For a given absorber bed, Eq. (10) indicates that there is a reciprocal relation between flow rate and the propagation time. This relation can be applied to check the data at different flow rates.

Calculated K values for different flow rates and different methane concentrations are listed in Table 2. These values indicate that Eq. (10) holds except at the highest flow rate where only a few measurements were made. The constancy of K values for different methane concentrations shows also that the linear isotherm, Eq. (3), is valid for the concentration range of this study. Also, we performed a numerical integration on the transmission data of 105 ppm methane for the lowest flow rate. The numerical integration gives a propagation time of 1391 s, which agrees with the value in Table 1 and justifies the use of the simultaneous optimization of both Δ and t_p by the method of Madey and Charles (*13*).

A more quantitative criterion on the equilibrium assumption, Eq. (3), can be made by using a different relation (*10*) between c and q:

$$\frac{dq}{dt} = k_c a(c - q/K') \tag{11}$$

This equation specifies that the time rate of change of solid-phase concentration is proportional to the product of a mass-transfer coefficient k_c, the specific exterior surface area a of solid particles, and the "driving force" which is represented by the difference between the gas-phase concentration c in the bulk flow and the concentration q/K' near the solid surface. The correlation of the mass-transfer coefficient k_c is given by Petrovic and Thodos (*17*) as

$$k_c = 0.357u\,\mathrm{Re}^{-0.359}\,\mathrm{Sc}^{-0.667} \tag{12}$$

where Re and Sc are the dimensionless Reynolds and Schmidt numbers, respectively. (The correlation was given for the equimolal counterdiffusion mass-transfer coefficient k_c'; however, because the mole fraction of methane is small, we neglect the difference between k_c' and the mass-transfer coefficient k_c through the stationary gas phase.) The value of a for nearly-spherical particles can be estimated from (*18*)

$$a = \frac{6(1 - \varepsilon)}{d_p} \tag{13}$$

where d_p is the mean particle diameter.

Equation (11) then can be written in a dimensionless form:

$$\frac{1}{\alpha}\frac{d(q/q_0)}{d(t/t_p)} = \frac{c}{c_0} - \frac{q}{K'c_0} \tag{14}$$

Here

$$\alpha = k_c a t_p/K' = 2.14(1 - \varepsilon)\left[\frac{1 - \varepsilon}{\varepsilon} + \frac{1}{K'}\right] L d_p^{-1}\,\mathrm{Re}^{-0.359}\,\mathrm{Sc}^{-0.667} \tag{15}$$

The dimensionless quantity α is a factor that represents the relative speed between the interphase mass transfer rate and the longitudinal moving rate of the adsorbed component. Note that Eq. (14) is a first-order differential equation; any change of gas-phase concentration will change the solid-phase concentration at a speed proportional to α. At a time equal to the propagation time t_p, the difference in the solid-phase concentration from the equilibrium value is given by the factor $\exp(-\alpha)$. In order to reach equilibrium quickly, α must be large, which corresponds to small mass-transfer resistance. In the limiting case when $\alpha \to \infty$, q will be equal to $K'c_0$ and the equilibrium assumption is attained. Because α is a function of the Reynolds number, it decreases with increasing superficial flow velocity. The values of α, listed in Table 3, are far greater than unity. Thus, even allowing for some uncertainties in the use of Eqs. (12) and (13), we find that the equilibrium assumption is valid for this study.

After establishing the linear equilibrium assumption, we compared the time-dependent transmission data with Eq. (4). We plot the experimental data in Fig. 2, which gives the dimensionless transmission c/c_0 versus the dimensionless time t/t_p for the four flow rates listed in Table 1. These data agree with the predicted curves which were calculated using the dispersion numbers in Table 2. It is clearly seen that the transmission curves become more diffuse as the flow rate decreases. Note that a diffuse curve does not necessarily relate to a high effective diffusion coefficient; in fact, the value of the effective diffusion coefficient increases when the flow rate increases, but the dispersion number decreases. The reason that a high-velocity flow results in a steeper transmission curve is clear when the propagation time is taken into consideration. For a high-velocity

TABLE 3

Effective Diffusion Coefficients, Reynolds Numbers, and Values of α in the 4LXC 12/28 Activated Carbon Adsorber Bed at 25°C

Methane concentration x_0 (ppm)	Interstitial flow velocity u (cm/s)	Effective diffusion coefficient D (cm^2/s)	Reynolds[a] numbers $\times 10^2$	Relative[b] speed factor α
105	0.687	0.313	9.6	266
105	1.375	0.334	19.3	272
105	2.70	0.376	37.8	214
105	6.64	0.623	93.0	155
85	0.690	0.310	9.6	266
34	0.690	0.294	9.6	266

[a]Reynolds numbers were calculated using $d_p = 0.14$ cm and $\mu = 2.0 \times 10^{-4}$ g/cm/s.
[b]Values of α are based on Sc = 1.59. Both the viscosity μ and the mutual diffusion coefficient D_{12} are calculated according to a standard method (*21*).

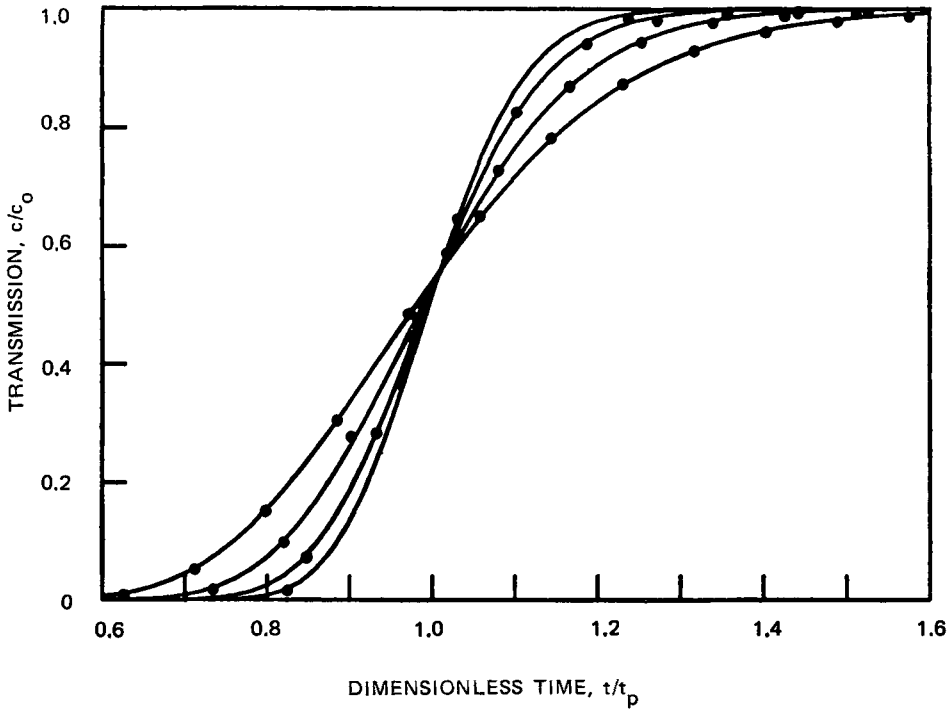

FIG. 2. Transmission versus dimensionless time for four flow rates. Points are experimental results listed in Table 1. Solid curves are predicted results based on Eq. (4). The flow rates, which increase with the steepness of the curves, are 0.687, 1.375, 2.70, and 6.64 cm/s, respectively.

flow, the propagation time is so small that the concentration distribution of the trace component changes only slightly from the step input function; therefore, in discussing the shape of transmission curves, the dispersion number is a better parameter than the effective diffusion coefficient.

The increase of the effective diffusion coefficient with increasing flow rate was recognized from the Taylor dispersion formula (*19*) which gives the value of D of the trace component flowing through an empty tube. The modification of the Taylor dispersion formula to a packed tube was made by Van Deemter et al. (*9*). His equation has the general form

$$H = \frac{L}{N} = A + \frac{B}{u} + Cu \tag{16}$$

where H is the height equivalent to the theoretical plate (H.E.T.P.) and N is the number of theoretical plates. Constants A, B, and C in Eq. (12)

represent the contribution of dispersion from different sources (*9*, *16*). The constant A is the eddy diffusion coefficient resulting from different paths in the packed bed, B is the Brownian motion of the trace gas in the carrier gas, and C is the contribution of the mass-transfer resistance.

It has been pointed out by Lee and Madey (*20*) that the plate theory of Glueckauf (*11*) is similar to the differential equation method, and that the following equation relates the number N of theoretical plates and the dispersion number Δ:

$$\Delta = 1/2N \tag{17}$$

It is obvious from Eq. (17) that the flow rate dependence of the dispersion number has the same functional form as Eq. (16). The fact that the dispersion number decreases with flow rate in this study confirms the assumption that the mass-transfer resistance is not important since otherwise the dispersion number would increase.

CONCLUSION

We measured the transmission of low concentrations of methane in a helium carrier-gas flow. Data were compared with the Madey-Pflumm equation and shown to be in good agreement. The linear equilibrium assumption was tested both by comparing the adsorption capacities and by examining the mass-transfer resistance. The conclusion from the present investigations is that the equation and the underlying assumption are adequate for the concentration and the flow rate regions of this study.

SYMBOLS

a	specific exterior area of carbon granules
A, B, C	constants in Van Deemter equation
c	gas phase concentration of the contaminant
D	effective diffusion coefficient
D_{12}	mutual diffusion coefficient of the contaminant gas and the carrier gas
d_p	averaged diameter of carbon granules
H	height equivalent to the theoretical plate
K	true adsorption capacity. The volume of gas adsorbed per unit volume of the solid absorbent (which does not include the pore volume)
K'	apparent adsorption capacity. The volume of gas adsorbed per unit volume of the adsorbent (which includes the pore volume but not the interstitial volume)

k_c mass-transfer coefficient through the nondiffusing gas phase
k_c' equimolal counterdiffusion mass-transfer coefficient
L length of the bed
N number of the theoretical plate
q the average concentration of the contaminant gas in the adsorbent which includes the pore volume. The unit of q is mole per unit volume of adsorbent granules
Re Reynolds number ($\equiv ud_p\rho/\mu$)
$s_\pm$ argument defined in Eq. (5)
t time
t_p propagation time
T transmission ($\equiv c/c_0$)
u interstitial flow velocity
Sc Schmidt number [$\equiv(\mu/\rho)D_{12}$]
x_0 mole fraction of the contaminant gas
z coordinate of bed length
α dimensionless relative speed factor defined in Eq. (15)
ε void volume fraction external to the adsorbent granules
ε_p pore volume fraction within the granules of the adsorbent
Δ dispersion number
μ viscosity of the gas mixture
ρ density of the gas mixture

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