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GAS-SOLID CHROMATOGRAPHY OF AN ARGON-HELIUM MIXTURE MOMENT ANALYSIS OF A TRANSMISSION CURVE

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SUMMARY

Transmission curves of argon in an adsorber bed packed with activated carbon were measured at 273 and 313 K. Transmission is the ratio of the adsorbate concentration at the outlet of an adsorber bed to that at the inlet. The adsorption isotherm, as determined from a mass-balance equation, was found to be linear. The method of moments was used to extract two kinetic parameters (*viz.*, the longitudinal diffusion coefficient and the solid-phase diffusion coefficient) at these two temperatures. Also, the dimensionless adsorption capacity was determined at both temperatures. The activation energy of diffusion in the solid phase is found to be close to the isosteric heat of adsorption.

INTRODUCTION

Huang *et al.*¹ proposed a moment-analysis method for calculating both the longitudinal and the solid-phase diffusion coefficients from a transmission curve for an adsorbate-adsorbent system with a linear isotherm. Transmission is the ratio of the adsorbate concentration at the outlet of an adsorber bed to that at the inlet. This model used a homogenous solid-diffusion model of the adsorbent with a linear isotherm and neglected interfacial mass-transfer resistance. Huang *et al.* calculated diffusion coefficients for 1% methane in helium adsorbed on Columbia 4LXC 12/28 activated carbon at 298 K. The adsorption isotherm of 1% argon in helium at 293 K is also linear on this adsorbent². The adsorption of argon on this activated carbon was studied by Madey *et al.*³ who used the transmission equation of Madey and Pflumm⁴ to extract a single effective diffusion coefficient. An analytical solution for the time-dependent transmission for adsorption with both gas- and solid-phase diffusion, mass-transfer resistance and chemical reaction was derived by Huang *et al.*⁵.

Even without chemical reaction or mass-transfer resistance, the solution for the time-dependent transmission for this model is not in a form amenable to extracting the two diffusion coefficients; however, the method of moments allows the kinetic parameters to be calculated without the need for an analytical solution. This work uses the moment analysis method to calculate the longitudinal and solid-phase diffusion coefficients for a step increase of nominally 1% argon adsorbed on Columbia activated carbon at 273 and 313 K.

MOMENT ANALYSIS

For a packed column, the gas-phase concentration C and the solid-phase concentration q are related by the following equations⁵⁻⁷

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \frac{1 - \varepsilon}{\varepsilon} \frac{\partial \bar{q}}{\partial t} \quad (1)$$

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

and

$$\bar{q} = \frac{3}{R^2} \int_0^R q r^2 dr \quad (3)$$

Here, it is assumed that any variations in concentration or velocity over a given cross-section of the bed can be neglected. For a step-increase in the concentration of the adsorbate, the initial and boundary conditions are:

$$C(z,0) = 0, \quad q(z,r,0) = 0 \quad (4)$$

$$C(0,t) = C_0, \quad q(0,r,0) = 0 \quad (5)$$

$$C(\infty,t) = 0, \quad q(\infty,r,t) = 0 \quad (6)$$

For a linear isotherm,

$$q(z,R,t) = KC(z,t) \quad (7)$$

The dimensionless adsorption capacity K ($\equiv q_0/C_0$) can be calculated from the mass-balance equation for the adsorbate⁸.

The transmission function $T(t)$ [$\equiv C(L,t)/C_0$] for a step-increase in the input concentration of the adsorbate is an S-shaped curve which rises slowly from zero and reaches a steady value of unity. Let t_p denote the mean residence time (or the propagation time) for the adsorbate to saturate the adsorber bed. In order for the moments of the transmission function to be finite, we define a new function $f(t)$:

$$f(t) = g(t) - T(t) \quad (8)$$

where the step function $g(t)$ is:

$$g(t) = \begin{cases} 0 & \text{for } 0 < t < t_p \\ 1 & \text{for } t \geq t_p \end{cases} \quad (9)$$

The propagation time t_p is related to the transmission function⁹:

$$t_p = \int_0^{\infty} [1 - T(t)] dt \quad (10)$$

The n th- order moment of the function $f(t)$ with respect to the propagation time t_p is¹⁰:

$$\mu_n = \int_0^{\infty} (t - t_p)^n f(t) dt \quad (11)$$

The definition in eqn. 8 is used because, unlike the moments of the transmission function $T(t)$, all of the moments of the function $f(t)$ with respect to the propagation time t_p are finite. The first-order moment of the function $f(t)$ with respect to t_p is:

$$\mu_1 = \int_0^{\infty} (t - t_p) f(t) dt \quad (12)$$

The propagation time t_p is defined such that the zeroth order moment of $f(t)$ vanishes; accordingly, the first-order moment (eqn. 12) reduces to

$$\mu_1 = \int_0^{\infty} tf(t) dt \quad (13)$$

Evaluating the first moment in the Laplace domain, Huang *et al.*¹ obtained the following equation relating the moment μ_1 and the diffusion coefficients D_s and D_L :

$$u\mu_1 = \frac{R^2 L K \alpha}{15 D_s} + \frac{L D_L}{u^2} (1 + \alpha K)^2 \quad (14)$$

with

$$\alpha = \frac{1 - \varepsilon}{\varepsilon} \quad (15)$$

Eqn. 14 is a straight line in the variable $1/u^2$ provided that the diffusion coefficients D_L and D_s are independent of u . 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.

EXPERIMENTAL

The flow system and instrumentation used are described in a previous paper⁸. The stainless-steel adsorber bed (25.5 cm × 2.21 cm I.D.) was packed with 39.0 g of type 4LXC 12/28 activated carbon, which has an intrinsic density of 1.56 g/cm³ and a pore volume of 0.51 cm³/g. For the measurements at 273 K, the bed was immersed in an ice-water bath. A constant-temperature water bath was used at 313 K. The flow-rate of the argon–helium mixture was controlled to an accuracy of ± 0.5%. The interstitial velocity of the gas mixture through the bed ranged from 0.067 to 0.929 cm/s. The pressure in the bed was typically between 770 and 890 mmHg. The pressure drop across the bed was < 10 mmHg. The concentration of argon at the outlet of the adsorber bed was measured at regular time intervals with a Varian 3700 gas chromatograph and a Spectra-Physics Minigrator.

RESULTS AND DISCUSSION

Transmission curves

We measured the transmission of 10000 ppm argon in helium* at 273 K and 313 K flowing at various velocities through a cylindrical bed (25.5 cm × 2.21 cm I.D.) packed with type 4LXC 12/28 activated carbon. Time-dependent transmission curves at 273 K are presented in Fig. 1 for interstitial flow velocities ranging from 0.092 to 0.929 cm/s; those at 313 K are shown in Fig. 2 for interstitial flow velocities ranging from 0.093 to 0.342 cm/s.

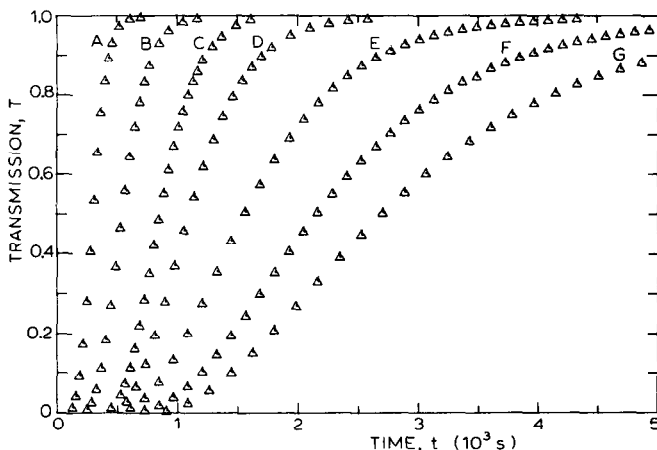


Fig. 1. Transmission of 10000 ppm argon in helium flowing through a (25.5 cm × 2.21 cm I.D.) cylindrical adsorber bed packed with 4LXC 12/28 activated carbon at 273 K. Interstitial flow velocity (cm/s): (A) 0.929; (B) 0.479; (C) 0.321; (D) 0.236; (E) 0.157; (F) 0.115; (G) 0.092.

* Prepared by Union Carbide, Linde Division, from ultra-high-purity argon (99.999%) and ultra-high-purity helium (99.999%).

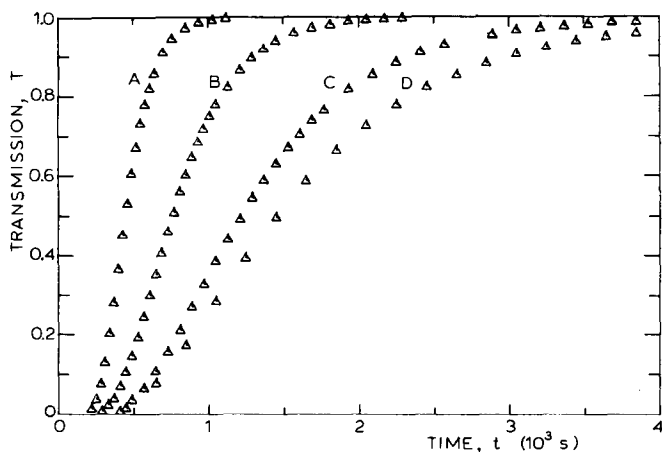


Fig. 2. Transmission of 10 000 ppm argon in helium flowing through a (25.5 cm \times 2.21 cm I.D.) cylindrical adsorber bed packed with 4LXC 12/28 activated carbon at 313 K. Interstitial flow velocity (cm/s): (A) 0.341; (B) 0.190; (C) 0.116; (D) 0.093.

Isotherm

In order to determine the argon isotherm at 273 K, the transmission of argon was measured for four concentrations (*viz.*, 10 000, 6925, 4907 and 2985 ppm) of argon in helium. Argon mixtures at the three latter concentrations were prepared by diluting the mixture of 10 000 ppm argon in helium with pure helium. Each of the four transmission curves were measured at essentially the same interstitial velocity of 0.236 cm/s. The transmission curve for 10 000 ppm argon at this interstitial velocity is included in Fig. 1. The other three transmission curves at the lower concentrations are essentially identical when adjusted for small differences in the flow-rate.

The equilibrium solid-phase concentration of q_0 , corresponding to the gas-

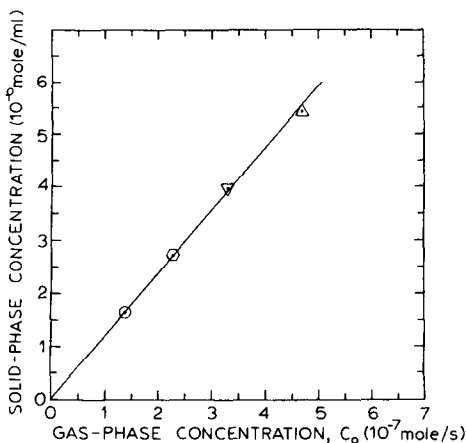


Fig. 3. Adsorption isotherm of argon on activated carbon at 273 K. (Δ) 10 000 ppm; (∇) 6925 ppm; (\odot) 4907 ppm; (\odot) 2985 ppm.

phase concentration C_0 , was calculated from the mass balance equation⁸:

$$q_0(1 - \varepsilon)L + C_0\varepsilon L = uC_0\varepsilon \int_0^{\infty} \left(1 - \frac{C}{C_0}\right) dt \equiv uC_0\varepsilon t_p \quad (16)$$

The propagation time t_p was calculated from a transmission curve by evaluating the integral in eqn. 10 numerically. Fig. 3 shows the relation between the solid-phase concentration and the gas-phase concentration. The isotherm is linear in this concentration region.

Diffusion coefficients

For each transmission curve, the first moment μ_1 was obtained by carrying out the integration indicated in eqn. 12. The calculated values of μ_1 are listed in Table I for the two bed temperatures of 273 and 313 K, respectively.

Fig. 4 is a plot of the product of $u\mu_1$ versus the inverse of the square of the interstitial velocity u . The solid-phase diffusion coefficient and the longitudinal diffusion coefficient were determined from the intercept and slope of the straight lines in Fig. 4, which are represented by the second and first terms of eqn. 14. The values

TABLE I

THE FIRST-ORDER MOMENT AND THE DIMENSIONLESS ADSORPTION CAPACITY FOR 10000 ppm ARGON IN HELIUM FLOWING THROUGH A CYLINDRICAL (25.5 cm × 2.21 cm I.D.) BED PACKED WITH 4 LXC 12/28 ACTIVATED CARBON

Interstitial flow velocity u (cm/s)	First-order moment μ_1 (10^4 s ²)	Adsorption capacity K
<i>Bed temperature = 273 K</i>		
0.928	0.5	12.3
0.479	1.6	11.5
0.321	3.2	12.1
0.236	8.2	11.6
0.193	15.2	11.7
0.157	27.0	11.2
0.115	62.6	11.6
0.092	117.7	11.8
Average 11.7 ± 0.4		
<i>Bed temperature = 313 K</i>		
0.342	1.3	6.3
0.341	1.3	6.5
0.189	6.0	6.1
0.187	6.5	6.1
0.116	25.2	6.2
0.115	25.3	6.3
0.093	48.3	6.1
0.094	47.6	6.3
Average 6.2 ± 0.1		

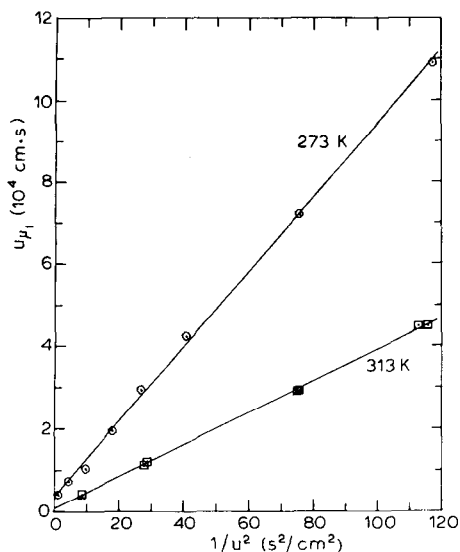


Fig. 4. The product of the interstitial flow velocity and the first-order moment of the time-dependent transmission of 10000 ppm argon in helium flowing through a (25.5 cm \times 2.21 cm I.D.) cylindrical adsorber bed packed with 4LXC 12/28 activated carbon at two bed temperatures of 273 and 313 K versus the reciprocal of the square of the interstitial flow velocity.

of the coefficients D_L and D_s are 0.30 and $9.8 \cdot 10^{-6}$ cm²/s at 273 K and 0.38 and $2.1 \cdot 10^{-5}$ cm²/s at 313 K. There appear to be no references in the literature for the diffusion coefficients of argon in activated carbon. The longitudinal diffusion coefficient has the order of magnitude typical of that for the self-diffusion of gases¹¹. Solid-phase diffusion coefficients for various gases on different adsorbents vary over several orders of magnitude¹²; however, the coefficients obtained here are of the order of the diffusion coefficients of a gas in a liquid^{1,11}.

Adsorption capacity

The dimensionless adsorption capacity K ($\equiv q_0/C_0$) for argon on activated carbon at 273 and 313 K were calculated for each transmission curve from mass-balance eqn. 16. As listed in Table I, the average values are 11.7 ± 0.4 at 273 K and 6.2 ± 0.1 at 313 K. The value of the adsorption capacity at 273 K was determined also from the slope of the linear isotherm in Fig. 3; the resulting value is also 11.7 ± 0.4 . From these values of the adsorption capacity the isosteric heat of adsorption¹³ is calculated as 3.28 kcal/mol, which agrees with the activation energy for solid-phase diffusion (3.21 kcal/mol) calculated from the solid-phase diffusion constants using an Arrhenius relation.

CONCLUSION

The transmission of argon through Columbia 4LXC 12/28 activated carbon was measured at 273 and 313 K for interstitial flow velocities ranging from 0.067 to 0.929 cm/s. From the experimental results at 273 K for four different input concen-

trations, the isotherm was extracted and found to be linear for argon concentration up to 10 000 ppm. The dimensionless adsorption capacity was calculated to be 11.7 at 273 K and 6.2 at 313 K. The first-order moment of a transmission curve for a step-function increase in the input concentration was used to extract the diffusion coefficients. The longitudinal diffusion coefficient D_L and the solid-phase diffusion coefficient D_s were found to be 0.30 and $0.98 \cdot 10^{-5} \text{ cm}^2/\text{s}$ at 273 K and 0.38 and $2.1 \cdot 10^{-5} \text{ cm}^2/\text{s}$ at 313 K.

SYMBOLS

C	gas phase concentration of adsorbate
C_0	inlet concentration of adsorbate
D_L	longitudinal diffusion coefficient
D_s	solid-phase diffusion coefficient
K	adsorption capacity
L	length of adsorbent bed
q	solid-phase concentration
\bar{q}	average solid-phase concentration
q_0	solid-phase concentration at equilibrium
r	radial coordinate of adsorbent particle
R	radius of particle
t	time
t_p	propagation time
T	transmission, $C(L,t)/C_0$
u	interstitial flow velocity
z	longitudinal coordinate

Greek Letters

α	$(1-\varepsilon)/\varepsilon$
ε	void fraction of packed bed
μ_1	first-order moment

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