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GAS–SOLID CHROMATOGRAPHY OF PROPANE ON CROSS-LINKED POLYSTYRENE AT 25°C

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SUMMARY

Breakthrough curves of propane in a chromatographic column packed with cross-linked polystyrene were measured for different concentrations and flow-rates. The adsorption isotherm, as determined from a mass-balance equation, was found to be a Freundlich-type isotherm. A theoretical model for the asymptotic concentration profile is discussed in order to examine the longitudinal diffusion coefficient and the lumped mass-transfer coefficient. Slopes of breakthrough curves at the inflection points were applied to calculate these two parameters for different input concentrations. The imperfection of the model is disclosed in this result because the data deviate from the theoretical prediction at high flow-rates, and the longitudinal diffusion coefficient and the lumped mass-transfer coefficient depend on the input concentration which contradicts the assumption of the model.

INTRODUCTION

In a recent paper[1], we studied the asymptotic concentration profile (ACP) of ethane under an equilibrium assumption for a column packed with activated carbon. The ACP, sometimes called a self-sharpening boundary, occurs for a step-increase in the concentration for an adsorbate that exhibits a convex isotherm and also for a step-decrease in the concentration for an adsorbate with a concave isotherm[2]. Mathematically, the ACP occurs as a result of cancellation between the curvature of the isotherm and the effect of diffusion. Thus, when an observer moves with the average speed of the adsorbate, the observer will see a time-independent profile in his coordinate system. Because of the existence of this moving coordinate system, it is possible to describe the adsorbate concentration by an ordinary differential equation instead of a partial differential equation.

Since the asymptotic concentration profile depends on the balance between the curvature of the isotherm and the diffusion processes in the column, study of the profile provides information about diffusion processes. There are three diffusion pro-

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cesses that are important in gas–solid chromatography (GSC): longitudinal diffusion in the gas-phase, interfacial diffusion resistance, and solid-phase diffusion. Longitudinal diffusion in a packed column is a function of flow-rate; it depends also on the size and geometry of the adsorbent. For a spherical adsorbent, it can be correlated with the Reynolds number and the Schmidt number of the fluid phase[3]. Interfacial diffusion resistance was correlated[4] also as a function of the Reynolds number and the Schmidt number; however, in most GSC, the last effect can be neglected[5]. Solid-phase diffusion depends on pore structure and adsorbent molecular properties. A wide range of values has been reported[6] for the solid-phase diffusion coefficient. When the solid-phase diffusion rate is small, the speed of equilibrium is slow and the ACP is no longer valid.

Solid-phase diffusion incurs mathematical difficulties also, because the concentration depends on the radial coordinate of the adsorbent pellet. In an early study of chromatography theory, Glueckauf and Coates[7] proposed to describe the time-dependent concentration of the adsorbate in the solid phase by a lumped first-order ordinary differential equation. Their suggestion is followed in the literature. In this paper, we use a model that involves Glueckauf and Coates diffusion term and calculate the longitudinal diffusion coefficient and the rate coefficient of Glueckauf and Coates expression from data on the ACP.

THEORY

Consider a mixture of trace components and the carrier gas passing with a constant interstitial flow-rate u through a packed column with a void fraction ε. The relation between the gas-phase concentration C and solid-phase concentration q is given as

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

$$\frac{\partial q}{\partial t} = k(q^* - q) \equiv k[f(C) - q] \tag{2}$$

The initial and boundary conditions for an initially desorbed column are

$$C(z,0) = 0;\ q(z,0) = 0 \tag{3}$$

$$C(0,t) = C_0;\ q(0,t) = 0 \tag{4}$$

$$C(\infty,t) = 0;\ q(\infty,t) = 0 \tag{5}$$

The following dimensionless variables are defined

$$\xi \equiv \frac{z}{L} - \frac{\lambda u t}{L} \tag{6}$$

$$m \equiv \frac{1-\varepsilon}{\varepsilon} \tag{7}$$

$$\lambda \equiv \left[1 + m\frac{f(C_0)}{C_0}\right]^{-1} \tag{8}$$

$$Pe \equiv \frac{uL}{D_L} = \text{axial Peclet number} \tag{9}$$

$$St \equiv \frac{kL}{u} = \text{Stanton number} \tag{10}$$

When the ACP is reached, both the gas-phase and the solid-phase concentration are functions of ξ only. But the gas-phase concentration and the solid-phase concentration do not equilibrate for the same ξ; instead, they are governed by the following simultaneous equations

$$\frac{1}{Pe}\frac{d^2C}{d\xi^2} - (1-\lambda)\frac{dC}{d\xi} + \lambda m\frac{dq}{d\xi} = 0 \tag{11}$$

$$-\lambda\frac{dq}{d\xi} = St(q^* - q) \tag{12}$$

Eqns. 11 and 12 are transformations of eqns. 1 and 2 under the ACP assumption. By differentiating eqn. 12 with respect to ξ and combining with eqn. 11, the solid-phase concentration q can be eliminated to give

$$\frac{\lambda}{PeSt}\frac{d^3C}{d\xi^3} - \left\{\frac{1}{Pe} + \frac{\lambda(1-\lambda)}{St}\right\}\frac{d^2C}{d\xi^2} + (1-\lambda)\frac{dC}{d\xi} - \lambda m\frac{dq^*}{d\xi} = 0 \tag{13}$$

An integration of eqn. 13 from $-\infty$ to ξ gives

$$-\frac{\lambda}{PeSt}\frac{d^2C}{d\xi^2} + \left\{\frac{1}{Pe} + \frac{\lambda(1-\lambda)}{St}\right\}\frac{dC}{d\xi} = (1-\lambda)C - \lambda mq^* \tag{14}$$

Here we used the fact that C, q^*, and all derivatives are zero at $\xi = -\infty$. Eqn. 14 was derived by Rhee and Amundson[9] in their theoretical discussion of the asymptotic profile for a Langmuir system. They used a numerical method to calculate concentration profiles based on assumed parameters. Because the adsorption isotherm and the parameters Pe and St are to be measured in our study, an alternative method is applied in the discussion later.

EXPERIMENTAL

The flow system and experimental procedure were described earlier[5]. The chromatographic column is a stainless-steel cylinder, 10 × 1.08 cm I.D., which contains 3.23 g of (20–40 mesh) Chromosorb 106 (Johns-Manville, Denver, CO, U.S.A.). This adsorbent is a cross-linked polystyrene with true density 1.12 g/cm^3 and pore volume 0.98 cm^3/g. The chromatographic column was immersed in a water bath which controlled the temperature at 25°C to within ±0.02°C. The composition of the inlet gas was controlled by two valves which separately adjusted the flow-rates of the pure helium and the calibrated propane–helium mixture. The calibrated propane–helium mixture was prepared by Matheson Gas Products (East Rutherford, NJ, U.S.A.) with a nominal propane concentration of 10,000 ppm. The concentration of propane at the outlet of the chromatographic column was measured at regular time intervals (of 50 sec in most runs) by a Varian 3700 gas chromatograph with a column packed with Chromosorb 102. At a column temperature of 135°C, the elution time of propane is 30 sec. The area of each sample peak is integrated by a Spectra-Physics Minigrator. The resolution of successive peaks is good. The Minigrator did not produce any event marker which would indicate overlapping signals.

RESULTS AND DISCUSSION

Determination of the isotherm

The time-dependent concentration of propane at the column exit was measured for several concentrations and for several flow-rates at 25°C. The first series of runs was conducted to measure the adsorption isotherm. The equilibrium solid-phase concentration q_0, corresponding to the gas-phase concentration C_0, was calculated from the mass-balance equation[5]:

$$q_0(1 - \varepsilon)L + C_0\varepsilon L = uC_0\varepsilon \int^{\infty}\left(1 - \frac{C}{C_0}\right)\mathrm{d}t \equiv uC_0\varepsilon t_p \tag{15}$$

The propagation time t_p was calculated from transmission data by numerical integration. The propagation time represents the average retention time of the sample. Mathematically, it is the zeroth-order moment of the breakthrough curve relative to the time origin. Eqn. 15 gives a relation between the solid-phase concentration and the gas-phase concentration without any assumption on diffusion processes.

Fig. 1 shows the relation between the solid-phase concentration and the gas-phase concentration. These results follow the Freundlich isotherm very well; therefore, in this study we have

$$f(C) \equiv q^* = AC^n \tag{16}$$

A linear least-squares calculation based on the logarithms of the gas- and solid-phase concentrations gives $n = 0.783$ and $A = 5.60$ when both q^* and C are expressed as mole/cm^3. The fact that propane follows the Freundlich isotherm indicates that the surface-energy distribution of polystyrene is more homogeneous than that of carbon[10]. It has been pointed out by Tompkins[11] that the Freundlich isotherm can be derived from the Langmuir isotherm with an assumption of an exponential distribution of surface energy. According to the equation of Tompkins, the exponent n of eqn. 16 varies inversely with the absolute temperature. A detailed discussion on

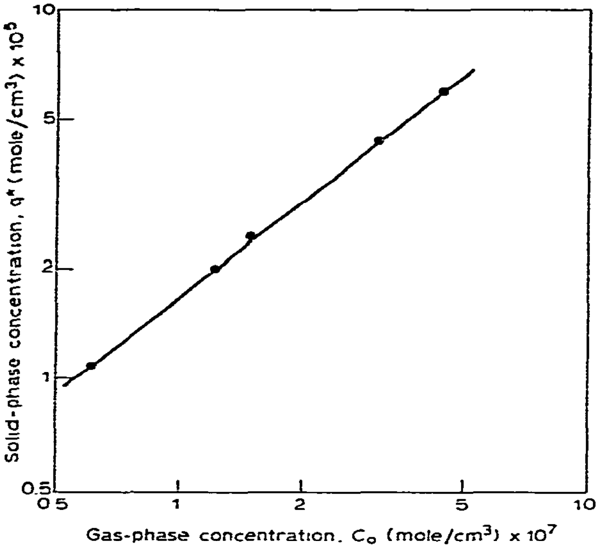

Fig. 1. Adsorption isotherm of propane on cross-linked polystyrene at 25 C.

physicochemical properties of adsorption on polystyrene will be the subject of a forthcoming article.

Determination of diffusion coefficients

A simple method is suggested here to evaluate D_L and k. Since the breakthrough curve is an S-type curve, an inflection point exists where the second derivative of the breakthrough curve *versus* time or coordinate is zero. From eqn. 16, we have

$$\left\{\frac{1}{Pe} + \frac{\lambda(1-\lambda)}{St}\right\}\left(\frac{\mathrm{d}C}{\mathrm{d}\xi}\right)_i = (1-\lambda)C_i - \lambda m q^* \tag{17}$$

or

$$\frac{D_L}{\lambda u^2} + \frac{(1-\lambda)}{k} = -\left[(1-\lambda)T_i - \lambda m\frac{f(C_i)}{C_0}\right]\left(\frac{\mathrm{d}t}{\mathrm{d}T}\right)_i \tag{18}$$

where

$$T = \frac{C}{C_0} \tag{19}$$

The subscript i in eqns. 17 and 18 denotes the condition at the inflection point. Eqn. 18 indicates that a plot of the right-hand-side *versus* $1/\lambda u^2$ will be a straight line. Both D_L and k can be calculated from the slope and the intercept of this line.

The second series of runs was made for three input concentrations. The input concentration, flow-rate, transmission at the inflection point, and slope of the

TABLE I

THE INPUT CONCENTRATION, THE TRANSMISSION AND THE SLOPE AT THE INFLECTION POINT AND THE INTERSTITIAL FLOW-RATE OF PROPANE

Run	*Input propane concentration* $C_0 \times 10^7$ *(mole/cm³)*	*Transmission at inflection point* T_i	*Slope at inflection point* $\left(\frac{dT}{dt}\right) \times 10^3$ *(sec⁻¹)*	*Interstitial flow-rate* *m(cm/sec)*
1	1.51	0.466	1.277	2.54
2	1.46	0.437	1.094	1.72
3	1.42	0.439	0.847	1.33
4	1.43	0.438	0.715	1.16
5	3.01	0.491	1.820	2.53
6	2.91	0.463	1.292	1.70
7	2.89	0.449	1.042	1.31
8	2.86	0.433	0.878	1.13
9	4.38	0.516	1.970	2.51
10	4.28	0.472	1.431	1.73
11	4.30	0.447	1.145	1.31
12	4.21	0.425	1.020	1.14

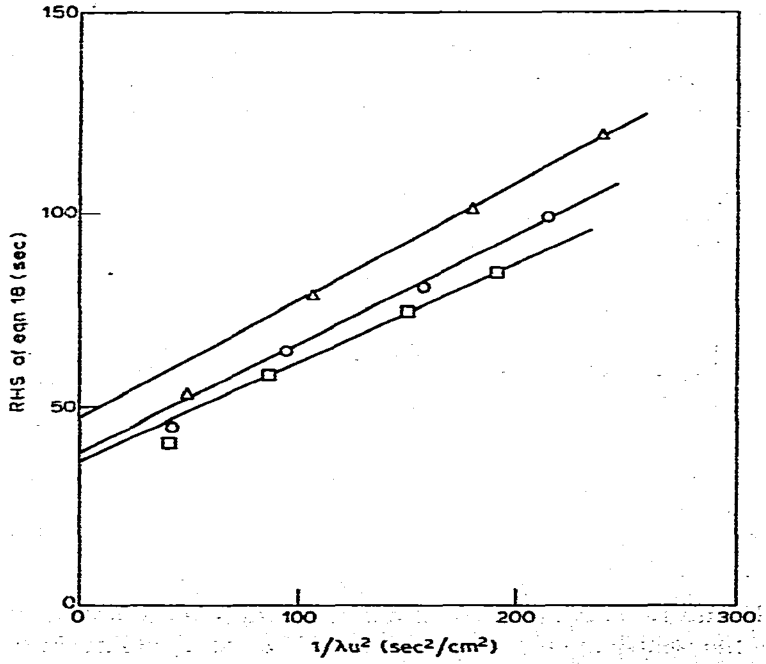

Fig. 2. Plot of the right-hand-side of eqn. 18 *versus* $1/\lambda u^2$ for various input concentrations. The symbols △, ○, and □ represent average input concentrations of $1.46 \cdot 10^{-7}$, $2.92 \cdot 10^{-7}$, and $4.37 \cdot 10^{-7}$ moles/cm³, respectively.

breakthrough curve at the inflection point are given in Table I. The inflection point is determined by interpolating the second-order finite difference of the transmission *versus* time. The right-hand-side of eqn. 18 is plotted in Fig. 2. It can be seen that there is a systematic deviation in the data at the highest flow-rate. This discrepancy can be attributed to the inadequacy of the model as discussed later. Three straight lines were obtained from low flow-rate data, indicating that both k and D_L are functions of the input concentration. The value of these parameters are listed in Table II.

TABLE II

THE LONGITUDINAL DIFFUSION COEFFICIENT, THE LUMPED MASS-TRANSFER COEFFICIENT, AND THE ESTIMATED SOLID-PHASE DIFFUSION COEFFICIENT CALCULATED AT DIFFERENT PROPANE INLET CONCENTRATIONS

Average input concentration $C_0 \times 10^7$ *(mole/cm^3)*	*Longitudinal diffusion coefficient* D_L *(cm^2/sec)*	*Lumped mass-transfer coefficient* $k \times 10^2$ *(sec^{-1})*	*Estimated solid-phase coefficient* $D_s \times 10^5$ *(cm^2/sec)*
1.46	0.300	2.12	4.3
2.92	0.278	2.60	5.3
4.37	0.255	2.73	5.5

Glueckauf and Coates[7] pointed out that the solid-phase diffusion coefficient can be related to the rate coefficient of eqn. 2 by the following relation

$$k = \eta \frac{D_s}{R^2} \tag{20}$$

where η is a constant on the order of unity, and R is the radius of the adsorbent granules. For polystyrene beads with a 20–40 mesh, R is *ca.* 0.45 mm. Values of D_s are estimated by assuming $\eta = 1$ in Table II. We can see that D_L is *ca.* 0.28 and D_s is on the order of $5 \cdot 10^{-4}$ cm^2/sec. The value of D_s is in the middle of values reported for various porous solids.

Because of the concentration dependence of D_L and k, it is interesting to reexamine the approximation in eqn. 2. The coefficients D_L and k are generally assumed to be independent of concentration. This assumption is not only for convenience, but also is essential for the differentiation to be carried out in eqn. 13. If either D_L or k depends on concentration, they will depend also on ξ because the concentration is a function of ξ. Our result is not a surprise. It can be explained in terms of the following three reasons: (1) the solid-phase diffusion coefficient of propane is a function of concentration, which in turn makes k a function of concentration; (2) the ACP is not reached under the conditions of this study; or (3) the solid-phase diffusion coefficient is constant, but eqn. 2 is not a good approximation.

The argument 1 is not a strong reason because the diffusion process in a polystyrene bead, which is attributed to diffusion in the pore space, is constant at low partial pressure. For a system with linear isotherm, the solid-phase diffusion coefficient can be determined precisely through moment analysis[12]. Our study[13] using 1 % ethane in a helium carrier gas indicates that the solid-phase concentration is essentially constant up to 1 %. The argument 2 is not easy to verify in this study; however, an order-of-magnitude analysis can rule out this possibility. From eqn. 2, we note that $1/k$ is effectively a time constant that represents the time for solid particles to reach equilibrium. The dimensionless product $t_p k$ gives the ratio of the elution time to the time required to reach equilibrium. The value of t_p in this study ranges from 1200 to 2700 sec, which is large enough to reach equilibrium. It is likely that the concentration dependence of the parameters originate from the approximation in eqn. 2. Further work should be undertaken to look for an approximation method for the solid-phase concentration in systems with non-linear isotherms.

CONCLUSION

We attempted to measure the longitudinal diffusion coefficient and the rate coefficient of Glueckauf and Coates from the breakthrough curves of propane. Theoretical argument indicates that the measurement of the inflection point of the ACP at different flow-rates can give the two coefficients. The experimental results at different input concentrations show different rate coefficients and different longitudinal coefficients. We concluded that the lumped first-order expression is not adequate when the adsorption is non-linear and that a new approximation method is needed.

SYMBOLS

A	constant
C	gas-phase concentration
C_0	$C(0,t)$
D_L	longitudinal diffusion coefficient
D_s	solid-phase diffusion coefficient
$f(C)$	solid-phase concentration equilibrated with C
i	condition at the inflection point
k	lumped mass-transfer coefficient
L	length of adsorber bed
q	solid-phase concentration
q^*	solid-phase concentration equilibrated with C
R	radius of adsorbent granules
t	time
t_p	propagation time
u	flow-rate
z	distance from column entrance
ε	void fraction
ξ, m, λ, Pe, St, T	see eqns. 6, 7, 8, 9, 10, and 19, respectively
η	constant

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