An Analysis of Sorption Heat Effects in the Pulse Gas Chromatography Diffusion Experiment

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In recent years it has become increasingly evident that the evaluation of zeolytic diffusivities by the sorption rate method is often complicated by nonisothermalities due to the exothermic heat of sorption (Chihara et al., 1976; Lee and Ruthven, 1979; Ruthven et al., 1980; Ruthven and Lee, 1981; Haul and Stremming, 1984; Bulow et al., 1984). The sample particles in a sorption rate determination are normally immersed in a near-stagnant fluid, and as a consequence the heat transfer between the sample and the surrounding fluid is poor. In contrast, the sample particles in a pulse chromatography experiment are immersed in flowing carrier and it is usually assumed that because of superior heat transfer characteristics, the experiment will behave isothermally. It is the purpose of this communication to examine this common assumption in some detail.

The only previous analysis of thermal effects in the pulse chromatography experiment appears to be that of Cerro and Smith (1969). In their study, a deviation from linear chromatography theory was demonstrated by varying the injection pulse size and concentration and observing variations in the first moment of the response curve. Independent measurements of the adsorption isotherm confirmed that much of the experimentation was within the Henry's law region, hence the nonlinearity was attributed to an adsorption heat effect. Small temperature variations were actually measured in breakthrough chromatography experiments.

The present communication is concerned with a different situation from that studied by Cerro and Smith. Standard practice is to vary injection pulse size to test for system linearity, and only after passing this test (observing no effect of injection pulse size) is the experimentation continued. In order to insure the absence of system nonlinearities it is usually necessary to work with much smaller pulses than employed by Cerro and Smith. The question remains, however, as to whether the demonstration of system linearity is sufficient to insure the absence of thermal effects.

The Model

Consider a pulse chromatography experiment in which the carrier gas prior to sample injection is maintained at some temperature, T_o, and concentration, C_o. Since our interest is with the thermal effect, it will be assumed that the particle-associated mass transfer resistances, both internal and external, are negligible. Allowance is made for axial dispersion of mass within the column. The heat transfer resistance is assumed to be concentrated at the surface of the particles; i.e., the thermal conductivity is sufficiently large to maintain a uniform temperature throughout the particle. It is further assumed that the temperature of the fluid phase surrounding the particle does not deviate from the baseline value, T_o. This is reasonable in view of the fact that Cerro and Smith, while working at much higher pulse concentrations than we envision, were unable to detect a gas phase temperature variation in their pulse chromatography experiments.

On the basis of these assumptions, a diffusing component mass balance across a differential element of column provides:

$$D_z \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} = [\epsilon_z + \epsilon_y(1 - \epsilon_z)] \frac{\partial C}{\partial t} + (1 - \epsilon_y)(1 - \epsilon_z) \frac{\partial q}{\partial t} \quad (1)$$

where $C(z, t)$ and $q(z, t)$ are respectively the gas phase and sorbed phase concentrations. Consistent with the literature on zeolite diffusion we are assuming that a single "sorbed" phase exists within the zeolite crystal. The particle energy balance is written:

$$\frac{3h}{r_y}(T_o - T) + (1 - \epsilon_y)(-\Delta H_s) \frac{\partial q}{\partial t} = \rho_s c_s \frac{\partial T}{\partial t}. \quad (2)$$

In the absence of mass transfer resistances, sorption is instantaneous and we have $q = q^*(T, C)$. Thus, for a small perturbation about the baseline we can write:

$$\frac{\partial q}{\partial t} = \alpha \frac{\partial T}{\partial t} + \beta \frac{\partial C}{\partial t} \tag{3}$$

where α and β are constants calculated from:

$$\alpha = \left(\frac{\partial q}{\partial T}\right)_{C_o}, \quad \beta = \left(\frac{\partial q}{\partial C}\right)_{T_o}. \tag{4}$$

For example, if we are in the Henry's law region and the temperature dependence of the Henry's law constant K_c is in accord with a van't Hoff type relation, one obtains the following expressions for α and β:

$$\alpha = \frac{q_o \Delta H_s}{R T_o^2}, \quad \beta = q_o/C_o = K_{c,o}. \tag{5}$$

This linearization of the sorption isotherm is only valid for small temperature deviations from the carrier baseline. The analysis is applicable only when system linearity has been demonstrated by experiment, as described above.

The algebra is simplified by working with the variables $C' = C - C_o$ and $T' = T - T_o$, which describe deviations from baseline concentration and temperature. Upon eliminating q in Eqs. 1 and 2 we have:

$$D_z \frac{\partial^2 C'}{\partial z^2} - u \frac{\partial C'}{\partial z} = a \frac{\partial C'}{\partial t} + b \frac{\partial T'}{\partial t} \tag{6}$$

and

$$d \frac{\partial T'}{\partial t} + e \frac{\partial C'}{\partial t} = \frac{3h}{r_y} T'. \tag{7}$$

As shown by Van der Laan (1958), the choice of boundary conditions generally depends upon the extent of mixing at the column entrance and exit. However, for long columns, these end effects are unimportant and one can use the simplified boundary conditions that were employed in earlier work (e.g., Hsu and Haynes, 1981). Thus:

$$C'(0, t) = n\,\delta(t) \tag{8}$$

$$C'(\infty, t) = \text{finite} \tag{9}$$

$$C'(z, 0) = 0 \tag{10}$$

$$T'(z, 0) = 0. \tag{11}$$

The factor n, which appears in Eq. 8, may be interpreted as a normalization factor equal to the area of the response curve. However, it can also be calculated from:

$$n = w/v \tag{12}$$

where w is the amount of diffusant injected and v is the volumetric flow rate. The quantities a, b, d, and e, which appear in Eqs. 6 and 7, are given by:

$$a = \epsilon_z + \epsilon_y(1 - \epsilon_z) + (1 - \epsilon_y)(1 - \epsilon_z)\beta \tag{13}$$

$$b = (1 - \epsilon_y)(1 - \epsilon_z)\alpha \tag{14}$$

$$d = (1 - \epsilon_y)(-\Delta H_s)\alpha - \rho_s c_s \tag{15}$$

$$e = (1 - \epsilon_y)(-\Delta H_s)\beta. \tag{16}$$

Equations 6 and 7 can be transformed into the Laplace domain and the resulting differential equation can be solved to obtain:

$$\tilde{C}' = n \exp\left[\frac{uL}{2D_z}\left(1 - \sqrt{1 - 4fD_z/u^2}\right)\frac{z}{L}\right] \tag{17}$$

and

$$\tilde{T}' = \left(\frac{es}{3h/r_y - ds}\right)\tilde{C}'. \tag{18}$$

These equations give the Laplace domain concentrations and temperatures at any point in the column. The residence time distribution or E-curve is obtained by setting $z = L$ and $n = 1$ in Eq. 17. Thus:

$$\tilde{E} = \exp\left[\frac{uL}{2D_z}\left(1 - \sqrt{1 + 4fD_z/u^2}\right)\right]. \tag{19}$$

The quantity f in these expressions is given by:

$$f = as + \frac{bes^2}{3h/r_y - ds}. \tag{20}$$

Moments of the *E*-curve

The first and second moments of the time domain E-curve are obtained in the usual manner by evaluating the first and second derivatives of $\tilde{E}(s)$ in the limit as $s \longrightarrow 0$. For the first moment about the origin, this operation provides:

$$\mu = \frac{L}{u}[\epsilon_z + \epsilon_y(1 - \epsilon_z) + (1 - \epsilon_y)(1 - \epsilon_z)\beta] \tag{21}$$

and for the second moment or variance about the mean we have:

$$\sigma^2 = \frac{2LD_z}{u^3}[\epsilon_z + \epsilon_y(1 - \epsilon_z) + (1 - \epsilon_y)(1 - \epsilon_z)\beta]^2 + \frac{2L(1 - \epsilon_z)(1 - \epsilon_y)^2(-\alpha\beta)(-\Delta H_s)r_y}{3uh}. \tag{22}$$

Equation 21 and the first term of Eq. 22 are identical to results already derived by Haynes and Sarma (1973) when β is in accord with the Henry's law expression, Eq. 5. The second term is new and represents the contribution of external heat transfer resistance to the broadening of the chromatographic response peak. By evaluating this term and comparing with the observed variance, one can obtain a quantitative measure of the importance of the thermal effect.

Most pulse chromatography experiments utilize a pure nonadsorbed carrier gas (e.g., helium). In this circumstance we have $C_o = q_o = 0$ and from Eq. 5 it is apparent that $\alpha = 0$. Thus the heat transfer contribution to σ^2 in Eq. 22 is also zero and the moments equations are identical to the isothermal case. This analysis indicates that the demonstration of system linearity (by varying input pulse size or concentration) is sufficient to insure that no heat effect is present provided that the column is operating at infinite dilution (pure carrier). Such is not the case with a mixed carrier gas.

Time Domain Solution

It is a simple matter to obtain an analytical solution in the time domain when $\alpha = 0$ by analogy to the result already reported by Hsiang and Haynes (1977). Thus:

$$C' = n\left(\frac{z}{L}\right)\sqrt{\frac{\mu^3}{2\pi\sigma^2 t^3}}\exp\left\{-\frac{\mu}{2\sigma^2 t}\left[t-\mu\left(\frac{z}{L}\right)\right]^2\right\}. \quad (23)$$

Where μ is given by Eq. 21 and σ^2 is given by Eq. 22 with the last term omitted ($\alpha = 0$).

The generation of an analytical solution for $\alpha \neq 0$ appears to be a more formidable problem. Accordingly, we have developed numerical solutions using a method similar to that employed by Hsu and Haynes (1981). This involves transforming Eq. 17 into the frequency domain, performing the complex algebra to separate C' into its real and imaginary parts:

$$\tilde{C}'(j\omega) = Re(\omega) + jIm(\omega) \quad (24)$$

and obtaining the inverse Fourier transform by means of the equation:

$$C' = \frac{2}{\pi}\int_o^\infty Re(\omega)\cos\omega t d\omega. \quad (25)$$

The integral is readily evaluated using Filon's integration formula (Tranter, 1974). The temperature is obtained by identical operations on Eq. 18.

We recently reported a pulse gas chromatographic study on the system *n*-butane/zeolite NaY (Fu et al., 1986). The apparatus employed sensitive flame ionization detectors and thus allowed the injection of highly diluted samples of *n*-butane into the column. The system behaved linearly as demonstrated by experiments in which input pulse size and concentration were varied. In these experiments a particle-associated transport resistance was clearly evident. The question arose as to whether this transport resistance might be due to a thermal effect.

Experimental conditions and estimated parameters for run FURM 1-1 are summarized in Table 1. The carrier gas was pure helium. Consequently C_o and α are zero for this experiment and no contribution to the pulse broadening from heat transfer is expected. Nevertheless it is of interest to calculate temperature variations in the column using our model to test the isothermality assumption. Two plots, one near the entrance and one at the exit, are presented in Figures 1 and 2. As the concentration pulse approaches a given point in the column, a small temperature rise above baseline is experienced due to the exothermic sorption heat. This is followed immediately by a small decrease in temperature as the component desorbs. The temperature variations are greatest near the column entrance where the concentration pulse is steepest. The important point, however, is that for these experiments, maximum temperature variations are only of the order of thousandths of a degree. The isothermality assumption is evidently quite good in these experiments.

Table 1. Column Parameters for Run FURM 1-1*

Bed porosity, ϵ_z	0.350
Particle macroporosity, ϵ_y	0.486
Particle heat capacity, $\rho_s c_s$	0.25 cal/mL · K
Particle radius, r_y	0.03575 cm
Column length, L	30.48 cm
Heat transfer coefficient, h	0.0151 cal/cm^2 · s · K
Baseline temperature, T_o	471.2 K
Baseline concentration, C_o	0
Superficial velocity, u	4.54 cm/s
Axial dispersion coefficient, D_z	0.772 cm^2/s
Henry's law constant, $K_{c,o}$	178.5
Heat of sorption, ΔH_s	−10,300 cal/gmol

*Fu et al. (1986).

The temperature variations calculated from this model, which does not account for particle-associated mass transport resistances, are expected to provide bounds on the actual temperature deviations. Under a finite mass transport resistance, the particle may not equilibrate with the gas phase concentration wave with correspondingly less heat evolved. Also, finite mass transport resistances serve to broaden the concentration pulse with a similar reduction in height of the temperature wave. One possibility, which seems remote but may nevertheless deserve further attention, is that of localized heating at the particle

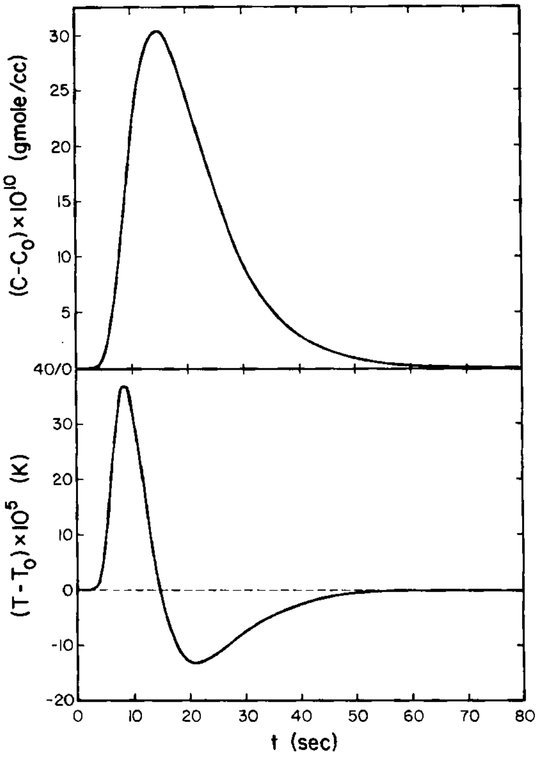

Figure 1. Response curves at $z/L = 0.05$.

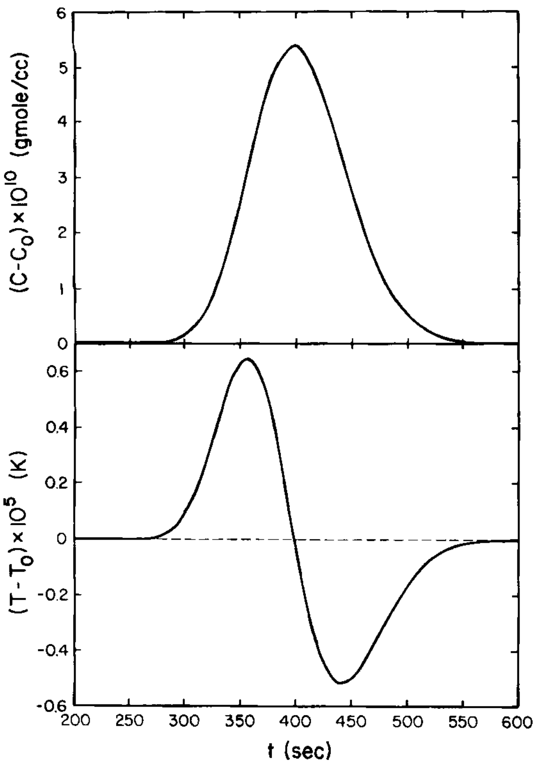

Figure 2. Response curves at $z/L = 1$.

external surface when intraparticle heat and mass transfer resistances are both finite. Cerro and Smith (1969) suggested this possibility in connection with their experiments on the *n*-butane/silica gel system.

Notation

a = quantity, Eq. 13
b = quantity, Eq. 14, gmol/mL.K
C = gas phase concentration, gmol/mL
C' = concentration deviation from baseline, gmol/mL
$\tilde{C}'$ = Laplace transform c', gmol.s/mL
c_s = particle heat capacity, cal/g.K
d = quantity, Eq. 15, cal/mL.K
D_z = axial dispersion coefficient, cm^2/s
e = quantity, Eq. 16, cal/gmol
E = residence time distribution curve, s^{-1}
f = quantity, Eq. 20 s^{-1}
h = external heat transfer coefficient, cal/s.cm^2.K
K_c = Henry's law constant
L = bed length, cm
n = quantity, Eq. 12, gmol.mL/s
q = sorbed phase concentration, gmol/mL
q^* = sorbed phase concentration in equilibrium with gas phase, gmol/mL
R = gas constant, cal/gmol.K
r_y = particle radius, cm
s = Laplace transform variable, s^{-1}
t = time, s
T = temperature, K
T' = temperature deviation from baseline, K
$\tilde{T}'$ = Laplace transform of T', K.s
u = superficial velocity, cm/s
v = volumetric flow rate, cc/s
w = amount of diffusant injected, gmol
z = axial distance coordinate, cm

Greek letters

α = quantity, Eq. 4 gmol/mL.K
β = quantity, Eq. 4
ΔH_s = heat of sorption, cal/gmol
ϵ_y = macroporsity
ϵ_z = bed porosity
μ = mean of residence time distribution, s
ρ_s = particle density, g/mL
σ^2 = variance about the origin, s^2
ω = frequency, s^{-1}

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