Analysis of Liquid Chromatography with Nonuniform Crystallite Particles

A mathematical analysis for the pulse responses of a liquid chromatographic column packed with crystal powders having a particle size distribution and a nonlinear adsorption isotherm is presented. The mathematical model is solved numerically by the orthogonal collocation method. Based on the parametric analysis of the model, the effects of a symmetrical and moderately asymmetric PSD on the LC responses are shown to be negligible in comparison with the effects of other parameters, such as isotherm nonlinearity, whose effects are much more profound. The simulated responses are compared with the experimental response data for an LC column packed with silicalite crystals, and a good agreement is found between the theoretical and experimental results. Using the nonlinear LC model, the simultaneous determination of nonlinear adsorption isotherms and intraparticle diffusivities from LC pulse responses is demonstrated for liquids in porous adsorbents.

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Introduction

With extensive applications of chromatographic techniques in bulk separations, purifications and physico-chemical parameter determinations (Conder and Young, 1979; Ruthven, 1984; Wankat, 1986), many mathematical models have been developed and solved for the mass transfer in chromatographic columns packed with porous particles. These studies include: the analytical solutions for the problems of chromatography with simpler mathematical models which neglect either axial dispersion or intraparticle diffusion (e.g., Rosen, 1952; Masamune and Smith, 1964); the modeling and analytical solutions for chromatography with the consideration of both intraparticle diffusion and axial dispersion (Deisler and Wilhem, 1953; Rasmuson and Nerenieks, 1980; Rasmuson, 1981); and the development of many more complex models for chromatography such as the macro-micropore diffusion models for the chromatographic columns packed with bidisperse structured adsorbents (Ma and Mancel, 1973; Hashimoto and Smith, 1973; Haynes and Sarma, 1973). Most of these models, however, were developed for gas chromatographic columns under the assumption of a linear adsorption isotherm.

Nonlinear adsorption isotherms are more frequently encountered in liquid chromatographic systems. The mathematical analysis of nonlinear chromatography was studied by many authors including: Houghton (1963) on the effects of a polynomial isotherm on the shape of chromatographic response peaks with an infinite adsorption rate; Tien and Thodos (1959, 1965) on ion exchange and adsorption kinetics in chromatography with the Freundlich isotherm equation; and Garg and Ruthven (1972) on computing the theoretical breakthrough curves for a molecular sieve chromatographic column using the pore diffusion model with the Langmuir isotherm equation. Many other nonlinear models using either the Langmuir equation or the Freundlich equation have also been reported for the adsorption of single- or multicomponent liquids in activated carbon chromatographic columns (Liapis and Rippin, 1978; Weber and Liu, 1980; Mansour et al., 1982; Seidel and Gelbin, 1986). However, previous studies on the nonlinear chromatography focused mainly on the prediction of breakthrough curves and the design of adsorbers for purifications. Numerical solutions for the chromatographic pulse responses considering the Langmuir isotherm and axial dispersion and assuming instantaneous equilibrium were reported by Smit et al. (1980) and Jacobson et al. (1989). But their treatment does not include the kinetic parameters.

Most commercial porous particles such as zeolite crystals are usually in nonuniform size, but with a specific particle size distribution (PSD). The PSD effects on the prediction of sorption uptake curves in a batch system have been investigated by Ruthven and Loughlin (1971) and later by Moharir et al.

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(1980a) in an attempt to resolve the discrepancy between the theoretical and experimental sorption uptake curves. In those studies, the effects of a combined average particle size and size distribution were examined, and therefore the effects of the PSD alone might have been overestimated. The consideration of a PSD in the mathematical modeling for chromatographic columns appears to be first reported by Moharir et al. (1980b) on the prediction of breakthrough curves from a zeolite column using a swelling crystal model to indirectly describe the zeolite crystal PSD. Since then, incorporating a PSD in the mathematical modeling has been reported by many investigators to determine adsorption and diffusion parameters (Hsu and Haynes, 1981; Boniface and Ruthven, 1985; Hyun and Danner, 1985; Fu et al., 1986). Hsu and Haynes (1981) pointed out that the common usage of an average particle size in parameter determinations could cause substantial errors in the diffusivity calculation. However, in these studies the PSD was only incorporated in the models and appeared in the second moment equations. No detailed simulation results were reported to examine explicitly the effects of a PSD alone on the chromatographic response peaks and parameter determinations. Recently, Carta and Bauer (1990) analyzed the effects of a PSD on chromatographic responses using a simple linear model and concluded that the PSD has significant effects on the chromatographic responses. Nevertheless, their conclusion was based mainly on simulation results for a discrete bimodel PSD and an extremely asymmetric PSD which is not commonly encountered in the particles used for chromatographic operations. Furthermore, they did not compare the effects of a PSD with other parameters (e.g., the isotherm nonlinearity).

This paper reports an explicit approach for the analysis of the effects of a PSD and isotherm nonlinearity on the chromatographic responses based on the numerical solution of the LC (liquid chromatographic) model by the orthogonal collocation method. Since, in practice, it is much easier to have particles with a symmetrical PSD or moderately asymmetric than to have particles with an uniform PSD and a nonlinear isotherm is often encountered in LC, our analysis will focus on the examination of the effects of a symmetrical PSD and moderately asymmetric and isotherm nonlinearity on the LC responses. Furthermore, using the nonlinear model, a method for the simultaneous determination of intraparticle diffusivities and nonlinear adsorption isotherms from LC pulse responses will be demonstrated.

Mathematical Analysis

The intraparticle diffusion, axial dispersion, nonlinear adsorption isotherm, and PSD are considered in the model for an LC column packed with zeolite crystals. The following partial differential equation (PDE) can be derived to describe the mass transfer in the mobile phase:

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial Z} + \frac{(1-\epsilon_b)}{\epsilon_b}\dot{q} = D_1\frac{\partial^2 C}{\partial Z^2} \tag{1}$$

with the corresponding initial and boundary conditions (BC) (Dankwert type) for Eq. 1:

$$C(Z,t) = 0 \quad \text{at} \quad t = 0 \tag{2}$$

$$\frac{\partial C}{\partial Z} = 0 \quad \text{at} \quad Z = L \tag{3}$$

and

$$C(Z,t) = C_0(t) + \frac{D_1}{U}\frac{\partial C}{\partial Z} \quad \text{at} \quad Z = 0 \tag{4a}$$

where $C_o(t)$ is a square function depending on the sample injectors for most LC instruments:

$$C_o(t) = \begin{cases} C_o & 0 \le t \le t_{\text{in}} \\ 0 & \text{otherwise} \end{cases} \tag{4b}$$

In Eq. 1, $\dot{q}$ is the average rate of adsorption by the adsorbent particles in a differential volume. The rate of adsorption for a single particle with a radius of R can be written as:

$$\dot{q}_R = 4\pi R^2 \cdot D_c \frac{\partial C_p}{\partial r}\bigg|_{r=R} \tag{5}$$

where D_c is the intracrystalline diffusivities; C_p is the adsorbate concentration in the adsorbent pores, defined as: C_p = adsorbate mass/pore volume of particle. The average adsorption rate in the particles with different sizes can be obtained by:

$$\dot{q}_{av} = \int_0^\infty P(R)\, 4\pi R^2 \cdot D_c \frac{\partial C_p}{\partial r}\bigg|_{r=R} dR \tag{6}$$

where $P(R)$ is the number PSD function. On the basis of the volume of the particles packed, the rate of adsorption in Eq. 1 can be written as:

$$\dot{q} = \dot{q}_{av}\left[\int_0^\infty P(R)\frac{4}{3}\pi R^3\, dR\right]^{-1} \tag{7}$$

Inserting Eq. 6 into Eq. 7 gives:

$$\dot{q} = 3D_c \int_0^\infty P_v(R)\frac{1}{R}\frac{\partial C_p}{\partial r}\bigg|_{r=R} dR \tag{8}$$

where $P_v(R)$ is the volume PSD function. $P_v(R)dR$ has the physical meaning of the ratio of the volume of particles with radius from R to $(R + dR)$ to the total volume of the particles.

The pore diffusion model (Lin and Ma, 1989) can be used to describe the diffusion in the zeolite crystal particle:

$$D_c\left[\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r}\frac{\partial C_p}{\partial r}\right] = \epsilon_p \frac{\partial C_p}{\partial t} \tag{9}$$

with the IC and BC at the crystal center:

$$C_p = 0 \quad \text{at} \quad t = 0 \tag{10}$$

and

$$\frac{\partial C_p}{\partial r} = 0 \quad \text{at} \quad r = 0 \tag{11}$$

Since the mass transfer resistance at the external particle surface has negligible effects on the overall mass transfer in the GC and LC column packed with small particles (Chiang et al., 1984; Lin and Ma, 1989), local equilibrium at the external surface can thus be assumed to simplify the mathematics involved in the numerical solution. Thus, the nonlinear adsorption isotherm equation, $C_p = g(C)$, is directly employed as the other boundary equation for the crystals as:

$$C_p = g(C) \quad \text{at} \quad r = R \tag{12}$$

Introducing the dimensionless variables as defined in the nomenclature into Eqs. 1, 8 and 9, and the corresponding initial and boundary equations result in the following dimensionless equations for the model:

Mass transfer in the mobile phase:

$$\frac{\partial X}{\partial \Theta} + \frac{\partial X}{\partial \Phi} + \dot{Q} = \alpha \frac{\partial^2 X}{\partial \Phi^2} \tag{13}$$

where

$$\dot{Q} = \int_0^\infty \beta(R) \cdot P_v(R) \left. \frac{\partial Y}{\partial \phi} \right|_{\phi=1} dR \tag{14}$$

and the diffusion in zeolite crystals:

$$\frac{\partial Y}{\partial \phi} = \tau(R) \left[\frac{\partial^2 Y}{\partial \phi^2} + \frac{2}{\phi} \frac{\partial Y}{\partial \phi} \right] \tag{15}$$

with the initial conditions:

$$X = 0 \quad \text{at} \quad \Theta = 0 \tag{16}$$

$$Y = 0 \quad \text{at} \quad \Theta = 0 \tag{17}$$

and the boundary conditions:

$$\frac{\partial X}{\partial \Phi} = 0 \quad \text{at} \quad \Phi = 1 \tag{18}$$

$$X = \Gamma + \alpha \frac{\partial X}{\partial \Phi} \quad \text{at} \quad \Phi = 0 \tag{19}$$

$$\frac{\partial Y}{\partial \phi} = 0 \quad \text{at} \quad \phi = 0 \tag{20}$$

$$Y = G(X) \quad \text{at} \quad \phi = 1 \tag{21}$$

with

$$\Gamma = \begin{cases} 1/\Theta_{\text{in}} & (0 \le \Theta \le \Theta_{\text{in}}) \\ 0 & \text{otherwise} \end{cases} \tag{22}$$

and

$$G(X) = \frac{1}{C_{\#}} g(C_{\#} \cdot X) \tag{23}$$

The coupled integral PDE's in the dimensionless form were solved by the orthogonal collocation numerical method (Michelsen and Villadsen, 1972; Villadsen and Michelsen, 1978). The key step in the derivation of the collocation equations, which was elaborated in the Supplementary Material (Lin, 1988), is the descretization of the integral Eq. 14 using Gauss-Legendre quadrature (Carnah et al., 1977; Villadsen and Michelsen, 1978). The resulting collocation equations are a set of $(N + NMP)$ ordinary differential equations (ODE's) with N and M being the total numbers of the internal collocation points along the axial direction of the LC column and the particle radial direction, respectively, and P being the total number of internal quadrature points for the integral in Eq. 14. These ODE's were solved by the IMSL routine DGEAR to give one simulated response peak. In the computation, experimentally determined PSD data or any proposed PSD data were interpolated to give a continuous PSD function $P_v(R)$ for the evaluation of the value of $P_v(R_i)$ at any given quadrature point. In the numerical solution of the ODE's by the IMSL routine DGEAR, it was found that using the stiff method of Gear as the basic method and the chord method with Jacobian calculated internally by finite differences as the iteration method gave the shortest CPU time required to solve the ODE's in comparison with other methods. The internal collocation numbers of $M = 8$, $N = 3$, and $P = 5$ were used in the numerical computation, thus resulting in a total of 128 ODE's for the nonlinear LC problem. These collocation numbers gave the least CPU time, with a similar accuracy to those with larger values for N, M, and P.

Parametric Study

The Langmuir-type equation is used as the nonlinear isotherm in the parametric analysis:

$$q = \frac{n \cdot b \cdot C}{1 + b \cdot C} \tag{24}$$

where q and C are usually in the units of (g/g or mol/g) and (g/mL or mol/mL), respectively. $q = C_{ap} v_p$. Equation 24 can be converted to the following dimensionless form:

$$Y = \frac{K_e \cdot X}{1 + b \cdot C_{\#} \cdot X} \tag{25}$$

where

$$K_e = n \cdot b / v_p \tag{26}$$

To study the effects of the PSD alone rather than the effects of a combined average size and PSD, symmetrical and asymmetric PSD functions with the same average particle size are used in the numerical computations. Figure 1 gives the three symmetrical PSD functions (a) and two moderately asymmetric PSD functions (b). The vertical straight line #4 in Figures 1a and 1b is the delta function for the PSD, representing the uniform particle size at $R = 1.5 \times 10^{-4}$ cm. All the PSD functions as given in Figure 1 have the same average particle size with $R_{av} = 1.5 \times 10^{-4}$ cm. Other parameter values used in the parameter analysis are listed in Table 1.

It should be pointed out that the effects of an extremely asymmetric PSD on LC response peaks are not examined here due to the fact that particles with an extremely asymmetric PSD are not of practical interest as chromatographic packings. For most industrially available or laboratory synthesized zeolite crystals, e.g., the silicalite sample from Union Carbide Corp. (its

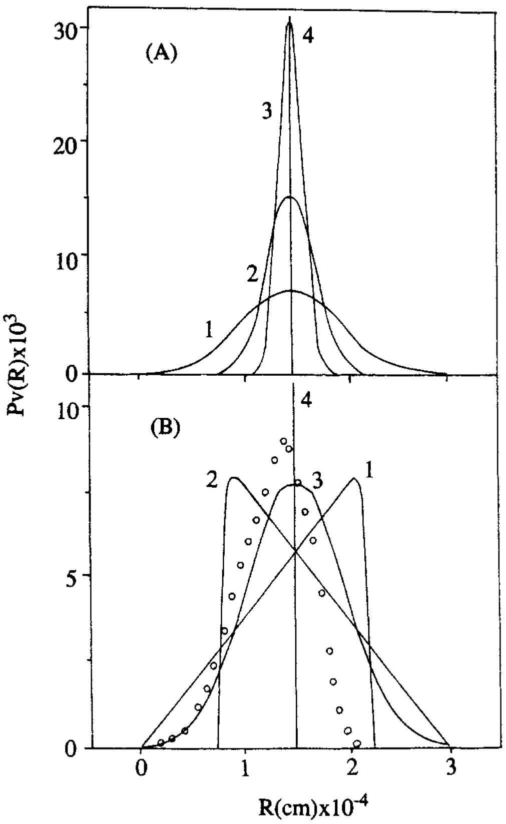

Figure 1. PSD functions used for the simulation (——) and the experimentally determined PSD of the silicalite crystals (O).

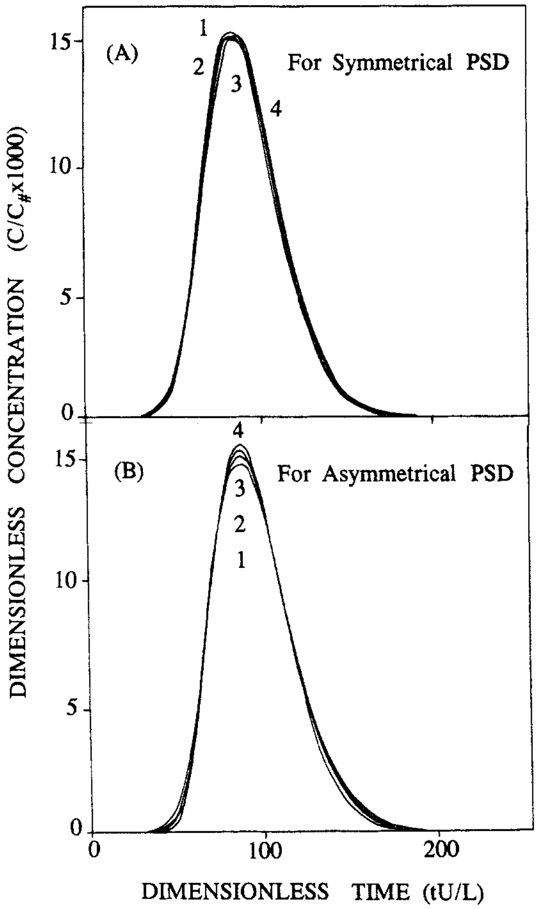

Figure 2. Effects of the PSD on LC response peaks.

PSD is also shown in Figure 1), the PSD is generally more symmetrical than the two moderately asymmetric PSD as given in Figure 1b. The present model in the dimensionless form includes the two simple models: the uniform PSD model when PSD function is a delta function and the linear model when b or $C_\#$ is set to zero (see Eq. 25, with $b = 0$ or $C_\# = 0$, Eq. 25 becomes linear as $Y = K_e X$).

The simulated response peaks with the different PSD's are shown in Figure 2. The symmetrical PSD with the same average size, but different broadness (curves #1, 2, 3 in Figure 1a), only slightly affects the shape of the LC response peaks (Figure 2a). The negligible effect of a symmetrical PSD on the response peaks appears to be the result of the compensation on the mass transfer rate in the portion of particles with the size larger than the average and the portion of the particles with the size smaller than the average. The larger particles result in a low mass transfer rate while the small particles give a high mass transfer rate. The effects of a moderately asymmetric PSD on the LC response peaks are shown in Figure 2b, where the four response peaks correspond to the PSD functions as given in Figure 1b. Comparing the response peaks in Figures 2a and 2b shows that the effects of the moderately asymmetric PSD on the response peaks are more severe than those of the symmetrical PSD but still negligible in comparison with the effects of other parameters to be discussed later. The effects of an extremely nonuniform PSD, such as a bimodel PSD, on chromatographic responses could probably be much more significant, as recently shown by Carta and Bauer (1990).

Table 1. Parameter Values in Parametric Analysis*

L (cm)	ID (cm)	V_c (cm^3)	V_l (mL)	ϵ_p	ϵ_b
2.0	0.21	0.0692	0.02	0.33	0.466
K_e (mL/mL)	b (mL/g)	R_{av} (cm)	D_l (cm^2/s)	D_c (cm^2/s)	U (cm/s)
250	1,000	1.5×10^{-4}	1.0×10^{-4}	0.5×10^{-10}	1.0

*Used in the parameter analysis unless otherwise specified in the figures.

It should be noted that the PSD for most industrially available zeolite samples is more symmetrical than the moderately asymmetric PSD as shown in Figure 1b. For particles with an extremely nonuniform PSD, it can generally be fractionated in practice to a narrow size distribution which would normally have a symmetrical or moderately asymmetric PSD. It is very difficult, if not impossible, and probably very costly, to have particles with an absolutely uniform PSD for chromatographic applications. Therefore, the present analysis provides evidences that, for most cases, the PSD can be neglected in the mathematic model to reduce the complexity of the model and analysis. On the other hand, some other parameters, which will be discussed next, should be more carefully controlled.

The numerical solutions of the nonlinear model with an uniform PSD are used to examine the effect of isotherm nonlinearity on the LC response peaks. As shown in Eq. 25, the isotherm nonlinearity is mathematically represented by the product of ($b \cdot C_\#$). (Note that $C_\#$ is directly related to the injection sample concentration as $C_\# = C_o V_1 / V_c \epsilon_b$.) Therefore, the smaller the isotherm constant b or injection sample concentration C_o, the more linear the Langmuir isotherm becomes. The constants b and C_o are equivalent in affecting the isotherm nonlinearity. Figure 3 shows that the LC response peaks with different injection sample concentrations. It is obvious that a larger value of C_o results in a less symmetrical response peaks with a shorter retention time (mean). This evidence is generally true regardless of different values of the other parameters. It is very interesting to note that with C_o of about 0.04 ~ 0.05 g/mL, as given in Figure 3a, the studied LC system gives twin-peak response peaks with a sharp peak front followed by a broad tailing. With further increasing C_o, as shown in Figure 3b, the response peaks become even more asymmetric, characterized by a very quick and sharp peak front and a long peak tail.

For the Langmuir-type equation, an increase in the injection sample concentration is equivalent to the decrease in the average slope of adsorption isotherm (average equilibrium constant, $K_{e(\mathrm{av})}$). Therefore, as $K_{e(\mathrm{av})}$ decreases, the response peaks become less symmetrical with a shorter retention time. In the case of a higher C_o which results in a smaller $K_{e(\mathrm{av})}$, less adsorbate molecules may be adsorbed and desorbed in adsorbent particles and more may remain in the mobile phase. Thus, the portion of the adsorbate in the mobile phase may just pass right through the column, forming the quick and sharp part of the response peak with the elution time of the peak front approximately equal to the residence time ($\Theta_{\mathrm{res}} = tU/L = 1$). The broad and tailing part of the response peak at higher C_o is formed by the other portion of the adsorbate due to the adsorption and desorption in the column packing. These parametric analyses suggest that to obtain a better response peak with a low value of HETP (longer retention time and less broadness) the injection sample concentration should be as low as possible.

The effect of the parameter K_e, the equilibrium constant at infinite dilution for nonlinear isotherms is shown in Figure 4 (with b = 1,000 mL/g, C_o = 0.03 g/mL for Figure 4a). For the linear LC, the parameter K_e (adsorption equilibrium constant) affects mainly the mean and broadness of the response peak. For the nonlinear LC, a variation of the K_e influences the mean and broadness as well as the symmetry of the LC response peaks. For a given value of b, a smaller value of K_e indicates less linearity of an adsorption isotherm. Thus, decreasing K_e results in less symmetrical response peaks with a shorter retention time.

Figure 5a shows the effect of the intraparticle diffusivity D_c on the nonlinear LC response peaks. A smaller value of D_c gives a less symmetrical response peak. Unlike the linear LC (Lin and Ma, 1989) in which the mean of a response peak is independent of D_c, decreasing D_c for a nonlinear LC seems to reduce the mean of the response peak as well. The effects of interstitial flow velocity on the response peaks are similar to those of D_c, as shown in Figure 5b. An increase in U results in a less symmetrical response peak. It should be noted that Figure 5 is plotted in

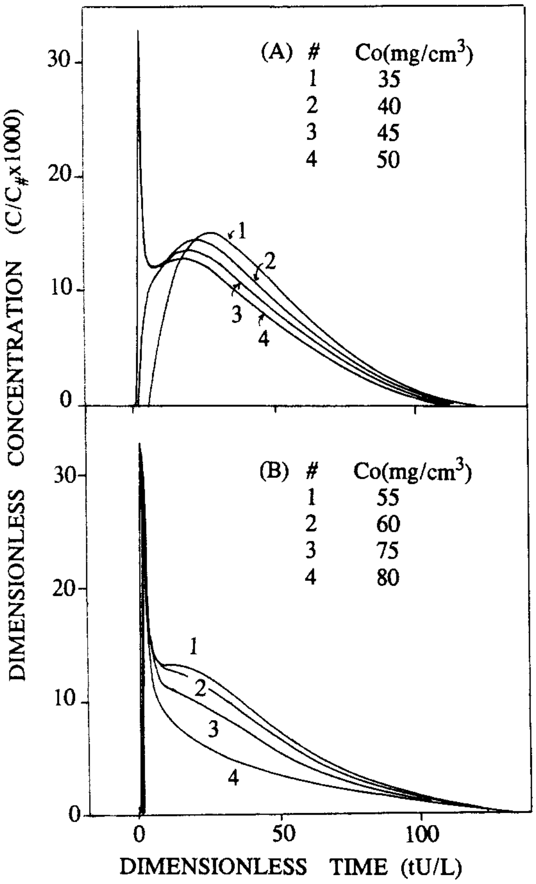

Figure 3. Effects of the injection sample concentration on LC response peaks.

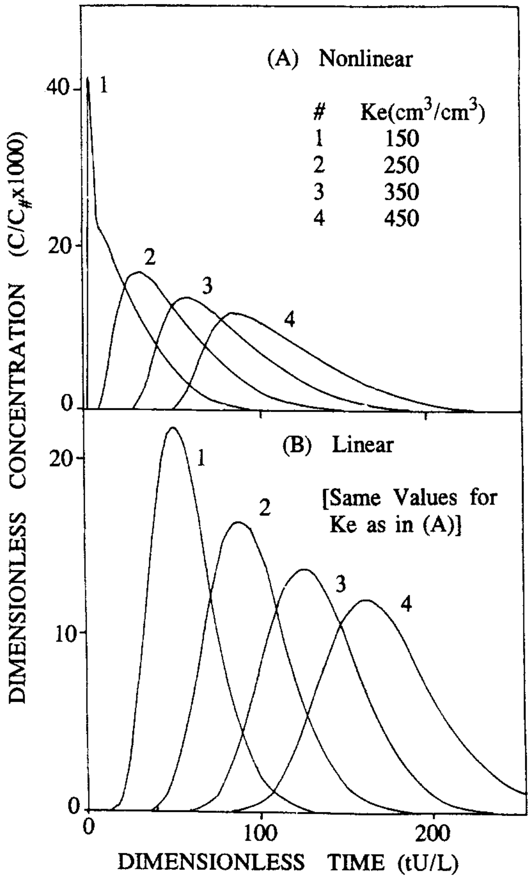

Figure 4. Effects of the equilibrium constant on LC response peaks.

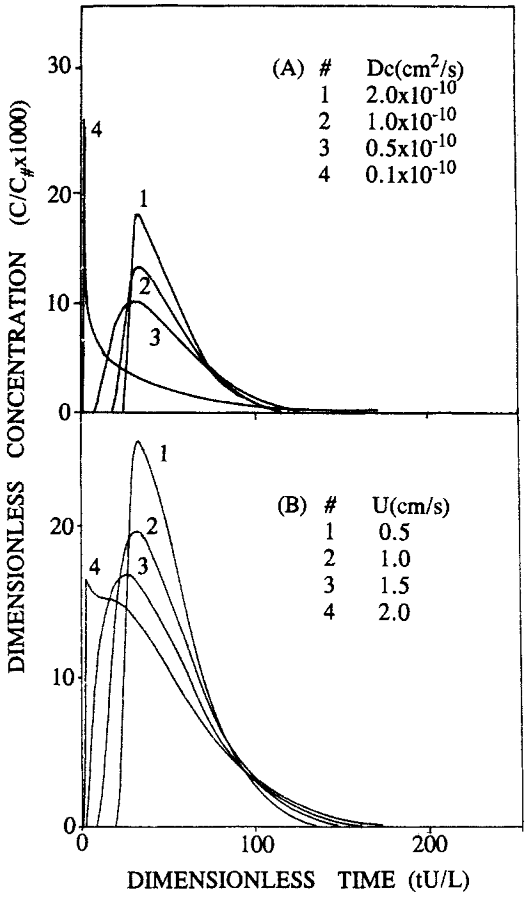

Figure 5. Effects of the intracrystalline diffusivity and the flow rate on response peaks.

the dimensionless time ($\Theta = tU/L$). As U increases, the invariable location of the response peaks in the dimensionless time domain is equivalent to a decrease in the mean of the response peaks in the real time domain. This is consistent with the fact that at a lower carrier flow rate, the response peak emerges from the column outlet more slowly. The axial dispersion has small effects on both the nonlinear and linear LC response peaks. It is found that with D_l smaller than 0.001 cm²/s, a variation on D_l essentially does not affect the LC response peaks.

Comparison with Experiments

The simulated response peaks are compared with the experimental results for an LC column packed with molecular sieve silicalite crystals (obtained from Union Carbide Co.). Some of the column parameters are listed in Table 2. The experiments for the determination of the LC response peaks were performed in a Beckman HPLC system with a UV-Vis spectrometer as the detector. The details on the experiments such as verification of the column performance and negligible dead volume effects are given elsewhere (Lin and Ma, 1988; Ma et al., 1989). Water was used as the carrier solvent and *n*-propanol and *i*-propanol were used as the tracer adsorbates. It has been shown that the adsorption isotherms for alcohols from aqueous solution in silicalite could be well fitted by the Langmuir equation (Milestone and Bibby, 1983; Lin and Ma, 1988). The particle size distribution of the silicalite sample measured by the Electrozone particle size analyzer is given in Figure 1b. It is obvious that the PSD function for the silicalite sample is more symmetrical and narrower than the PSD's as shown in Figure 1b; and therefore, the effect of the particle size distribution can be neglected.

Table 2. Parameter Values for Response Peaks from Silicalite Column

Particle and Column Parameter

R(μm)	ϵ_p	v_p(mL/g)	L(cm)	ID(cm)	ϵ_b
1.17	0.33	0.19	2.0	0.2	0.46

Isotherm and Rate Parameter

	T (°C)	K_e* (mL/mL)	b* (mL/g)	$D_c^* \times 10^{10}$ (cm²/s)
ETOH	70	106 ± 2	250 ± 2	4.01 ± 0.01
IPOH	70	271 ± 2	591 ± 4	2.10 ± 0.02

*Data after ± are the 95% confidence interval.

Recently Onyegbado and Susu (1990) showed a method of simultaneously determining nonlinear and sorption rate parameters by fitting one simulated response peak to one experimentally measured peak using a simple nonlinear model. This one peak fitting method, however, resulted in more than one set of the optimum parameter values and another method had to be used to eliminate the estimated parameters which had no physical meaning. In this paper, it has been demonstrated that for adsorption systems with nonlinear adsorption isotherm, the variation on the injection sample concentration C_o or the carrier solvent flow rate Q (i.e., the interstitial velocity U) can drastically affect both the shape and location of LC response peaks. This indicates that the LC response peaks are rather sensitive to these two experimentally measurable variables. Furthermore, the simulation results also show that the effects of C_o and U on LC responses are similar to those of the isotherm constant b and diffusivity D_c. Thus, it is possible to determine the nonlinear adsorption isotherm parameters and intraparticle diffusivity by fitting the simulated response peaks with the experimentally measured response peaks at different C_o and Q. The multiple-peak fitting can generally ensure the uniqueness of a set of the determined values for the isotherm parameters and diffusivity.

The multiple-peak fitting was done by minimizing the following objective function with IMSL routine ZXSSQ:

$$F(K_e, b, D_c) = \sum_{\text{pks}} \sum_{\text{pts}} [C(L, t_i)_{\text{cal}} - C(L, t_i)_{\text{exp}}]^2 \quad (27)$$

In a preliminary computation for one of the studied systems from the silicalite column, it was found that the fitted values of the three parameters K_e, b, and D_c using the model with a PSD and the one without a PSD were essentially the same. This is because the PSD of the silicalite sample was not extremely asymmetric. However, the computation time with PSD was over 20 times larger than the case with uniform PSD. Therefore, the model with an uniform PSD was used in most cases of this work to reduce the computation time while retaining the similar accuracy. The detailed results for the adsorption and diffusion of various aqueous alcohols in silicalite by the multiple-peak fitting method were reported by Lin and Ma (1988). Figure 6 shows

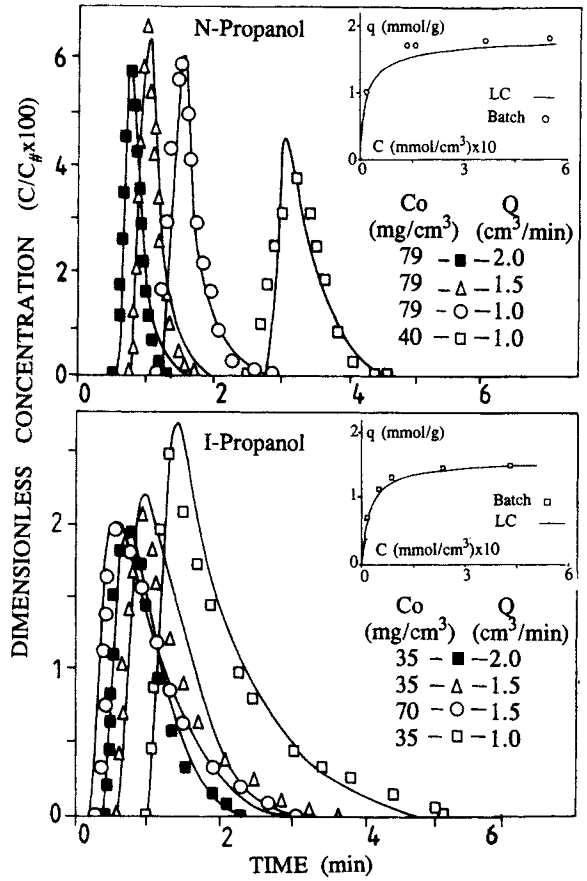

Figure 6. Comparison of simulated and experimental peaks.

Insets show the isotherms measured by the LC method and by the batch method.

the comparison of the theoretical and experimental response peaks for *n*-propanol and *i*-propanol for the LC column packed with silicalite crystals. The parameter values for the simulated response peaks are summarized in Table 2. For a given adsorption system, the theoretical response peaks at different Q and C_o were computed using the same set of values for the three parameters, K_e, b, and D_c. It is evident from the comparison results, as shown in Figure 6, that the nonlinear mathematical model agrees well with the experimental results. Furthermore, in the upper right corner of the Figures 6a and 6b, the adsorption isotherms computed from the LC measured K_e and b values are compared with the adsorption isotherms measured by the batch method (Lin and Ma, 1988) for the two adsorption systems. The agreement between the LC results and the batch results is quite remarkable.

Conclusion

- The mathematical model for nonlinear chromatographic column with particle size distribution (a set of coupled integral partial differential equations) was solved by the orthogonal collocation method to examine explicitly the effects of the PSD and isotherm nonlinearity on LC responses.
- Parametric analysis shows that the effects of a symmetrical or moderately asymmetric particle size distribution on chromatographic response are negligible in comparison with those of other parameters such as isotherm nonlinerity. These results are important in suggesting that: 1. to simplify the mathematics, a model using the volume average particle diameter can be applied for the analysis and parameter evaluations for most chromatographic columns packed with particles without an extremely nonuniform PSD; 2. to fractionate extremely nonuniform particles to an extent of having a symmetrical or moderately asymmetric PSD is generally sufficient to ensure the negligible effects of the PSD in most practical chromatographic operations. The effects of an isotherm nonlinearity on chromatographic response peaks, on the other hand, are much more profound, and therefore the injection sample concentration should be carefully controlled.
- The nonlinear mathematical model is used to calculate the response peaks for an LC column packed with industrial molecular sieve silicalite crystals, and a good agreement is found between the theoretical and experimental results.
- With the nonlinear LC model, the nonlinear adsorption isotherm and the intraparticle diffusivity can be simultaneously determined from impulse chromatographic response peaks at different carrier flow rate and injection sample concentrations. A good agreement was found between the isotherms measured by the LC method and by the batch method.

Notation

C = adsorbate concentration in mobile phase, mg/cm³ or mmol/g
C_o = injection sample concentration, mg/cm³
C_p = adsorbate concentration in adsorbent pore, $C_p = q/v_p$, mg/cm³
$C_\# = C_o \cdot V_l/V_c \cdot \epsilon_b$, mg/cm³
D_c = intracrystalline diffusivity, cm²/s
D_l = axial dispersion coefficient, cm²/s
ID = LC column inner diameter, cm
K_e = adsorption equilibrium constant at infinitely dilution, cm³/cm³
L = length of packing in column, cm
M = total internal collocation number in particle
N = total internal collocation number in mobile phase
n = Langmuir isotherm parameter, g/g
P = total internal quadrature number
Q = volumetric flow rate, cm³/s
q = amount adsorbed by adsorbent particle, $q = C_p v_p$, mmol/g or mg/g
$\dot{q}$ = adsorption rate by an adsorbent particle, mg/cm³/s
R = radius of adsorbent particle, cm
R_{av} = volume average particle radius, cm
r = radial position in adsorbent particle, cm
t = time, s or min
t_{in} = injection time, $t_{in} = V_l/Q$, s
U = interstitial flow velocity, cm/s
V_c = empty LC column volume, cm³
V_l = injection sample loop volume, cm³
v_p = adsorbent particle pore volume, cm³/g
Z = column axial direction position, cm
Z_i = ith guadrature point
w_i = weight of Gaussian quadrature at ith point

Greek letters

ϵ_p = porosity of zeolite crystal
ϵ_b = porosity of the packed column

Dimensionless variables

$\Theta = Ut/L$
$\Theta_{in} = V_l/V_c\epsilon_b$
$\Phi = Z/L$
$\phi = r/R$
$X = C/C_\#$
$Y = C_p/C_\#$

Dimensionless parameters

$\alpha = D_l/UL$

$\beta(R) = 3(1 - \epsilon_b)LD_c/\epsilon_b UR^2$

$\tau(R) = LD_c/U\epsilon_b R^2$

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