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# Prediction of Chromatographic Separation of Eugenol by the Fast Fourier Transform Method

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**ABSTRAK**

Masa pensuisan atau penukaran antara jerapan dan nyah-erapan dalam kromatografi cecair, iaitu ketika kepekatan aliran keluar mencapai nilai bulus, amatlah penting dalam pengendalian, peningkatan skala dan pengoptimuman pemisahan secara kromatografi. Masa pensuisan boleh dianggar dengan simulasi komputer turus kromatografi jerapan. Dalam karya ini, simulasi teori turus kromatografi oleh Chen dan Hsu berdasarkan kaedah jelmaan Fourier pantas (JFP) yang dicadangkan pertama kali oleh Hsu untuk sistem kromatografi, yang menggunakan anggaran pekali resapan paksian, pekali pemindahan jisim, dan keresapan liang yang diperolehi daripada pemisahan peringkat analisis, dibandingkan dengan data uji kaji pemisahan kromatografi eugenol. Teknik JFP digunakan untuk menyelesaikan model ini. Penggunaan JFP dan bukan teknik yang lebih anggun seperti kaedah beza terhingga atau penempatan bersama ortogonal adalah beralaskan pengiraan yang lebih mudah dan kedapatan teknik menyongsang yang lebih baik. Model ini disahkan oleh data uji kaji daripada pemisahan kromatografi eugenol pada turus analisis μBondapak $C_{18}$, fasa bergerak metanol-air (80:20), kadar alir 0.5 ml/min, pada penyuntikan larutan berlainan kepekatan pada keadaan keseimbangan. Data sifat fizik yang diperlukan untuk pengesahan ini seperti data penjerapan keseimbangan sesuhu ditentukan secara uji kaji, dan data pemindahan jisim dihitung dengan korelasi lazim dan daripada pemisahan peringkat analisis. Simulasi ini mengesahkan data uji kaji pada nombor Peclet 6000, parameter panjang lapisan 3.0 dan bilangan sampel 90.

**ABSTRACT**

The switching time to change from adsorption to desorption in liquid chromatography, which is the time at which the concentration of the effluent reaches the breakthrough value, is important in the operation, scale-up, and optimisation of chromatographic separation. The switching time can be estimated by computer simulation of the chromatographic adsorption column. In this paper, the theoretical simulation of the chromatographic column of Chen and Hsu (1987) based on the Fast Fourier Transform (FFT) method originally proposed for chromatographic systems by Hsu using estimated axial diffusivity, film mass transfer coefficient and pore diffusivity obtained from analytical scale separation, is compared with experimental data of chromatographic separation of eugenol. The use of FFT over more sophisticated techniques such as finite difference or orthogonal collocation methods was dictated by the simpler

computation and the availability of better inverting techniques. The model was validated by experimental data on chromatographic separation of eugenol on μBondapak $C_{18}$ analytical column, mobile phase methanol-water (80:20), and flow rate 0.5 ml/min, at different solution concentration injection at equilibrium condition. Physical property data required for validation such as equilibrium adsorption isotherm data was determined experimentally, and mass transfer data was calculated from normal correlations and from analytical scale separation. The simulation agreed with experimental data at a Peclet number of 6000, a bed length parameter of 3.0 and number of samples 90.

**Keywords: separation, high performance liquid chromatography, Fast Fourier Transform**

## INTRODUCTION

In practice, liquid chromatography is operated in a cyclic manner alternating between adsorption and desorption. During adsorption, the feed containing a solute at certain concentration is introduced into the bed as a band. During desorption or elution, a carrier fluid free of solute is fed into the system until the solute adsorbed on the adsorbent particles is completely recovered. Desorption of the solute is usually initiated when the solute concentration in the effluent stream reaches or passes the breakthrough value; in other words, before the bed is completely saturated. Therefore, the switching time to change from adsorption to desorption, and vice versa, is important in the operation, scale-up, and optimisation of a chromatographic separation. The switching time can be estimated by computer simulation of the chromatographic adsorption column. The simulation model requires equilibrium sorption data which is determined experimentally and mass transfer data including inter-particle mass-transfer coefficients and effective diffusivities for transport within the porous adsorbent particles which are determined from available correlations. In this paper, the theoretical simulation of the chromatographic column of Chen and Hsu (1987) based on the Fast Fourier Transform (FFT) method originally proposed for chromatographic systems by Hsu (1979) using estimated axial diffusivity, film mass transfer coefficient and pore diffusivity obtained from analytical scale separation, is compared with experimental data of chromatographic separation of eugenol.

## MATHEMATICAL MODEL

Chen and Hsu (1987) used the fixed bed adsorber model of Rasmuson and Neretnieks (1980) to describe an isothermal adsorption column packed with porous spherical particles of radius $a$ adopted for this simulation work. At time zero, a step change in the concentration of an adsorbable species was introduced into the flowing stream. The adsorption column was subjected to axial dispersion, pore diffusion resistance, and external film diffusion resistance. After introducing dimensionless variables as suggested by Raghavan and Ruthven (1983), the fixed-bed adsorber may be described by the following set of equations. Mass

balance in the mobile phase is given by

$$\frac{\partial U}{\partial \tau} + \psi_1 \delta \frac{\partial U}{\partial x} - \frac{1}{P_e} \psi_1 \delta \frac{\partial^2 U}{\partial x^2} = -3\psi_1 \xi (U - Q|_{\eta=1}) \tag{1}$$

Particle diffusion is given by

$$\frac{\partial Q}{\partial \tau} = \frac{\partial^2 Q}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial Q}{\partial \eta} \tag{2}$$

Initial and boundary conditions are as follows:

$U(x,\tau = 0) = 0$ (3)

$U(x = 0,\tau) = 1$ (4)

$U(x = \infty,\tau) = 0$ (5)

$Q(\eta,x,\tau = 0) = 0$ (6)

$Q(\eta = 0,x,\tau) \neq \infty$ (7)

$$\frac{1}{K_1} \frac{\partial Q}{\partial \eta} \Big|_{\eta=1} = \xi \left( U - \frac{Q|_{\eta=1}}{K_1} \right) \tag{8}$$

where

$$U = C / C_0, Q = \frac{C_P}{C_0}, x = \frac{z}{L}, \tau = \frac{D\theta}{a^2}, \eta = \frac{r}{a}, \psi_1 = \frac{K_1}{m}, \delta = \frac{Va^2 m}{LDK_1}, \xi = \frac{k_f a}{DK_1}$$

and $P_e = \frac{LV}{D_L}$. The Laplace domain solution of $U$ is

$$\overline{U}(x,s) = \frac{1}{s} \exp\left\{ \left[ \frac{P_e}{2} - \sqrt{\frac{P_e^2}{4} + \frac{P_e s}{\psi_1 \delta} + \frac{3\xi P_e \phi(s)}{\delta}} \right] x \right\} \tag{9}$$

where $\phi(s) = \dfrac{\sqrt{s}Cosh\sqrt{s} - Sinh\sqrt{s}}{\sqrt{s}Cosh\sqrt{s} - Sinh\sqrt{s} + \xi Sinh\sqrt{s}}$

Multiplying Equation (9) by $s$ gives a transfer function $F(s)$ of the corresponding chromatography system

$$F(s) = \exp\left\{ \left[ \frac{P_e}{2} - \sqrt{\frac{P_e^2}{4} + \frac{P_e s}{\psi_1 \delta} + \frac{3\xi P_e \phi(s)}{\delta}} \right] x \right\} \tag{10}$$

where $F(s) = \exp(-\sigma x)$

$$\sigma = \frac{P_e}{2} - \sqrt{\frac{P_e^2}{4} + \frac{P_e s}{\psi_1 \delta} + \frac{3\xi P_e \phi(s)}{\delta}} \tag{11}$$

## ADSORPTION ISOTHERM

Adsorption isotherm was generated by pumping solutions of different concentrations of eugenol into a new clean column until it is fully saturated. A standard analytical $C_{18}$ μ Bondapak column 0.39 cm I.D. and 30 cm height, was used in the experiments. The adsorbent particles size is 10 μm. The mobile phase used was a mixture of HPLC grade methanol and doubled distilled water having a ratio of 80:20 by volume. Low pressure column experiments were conducted with a flow rate of 0.5 ml/min. Concentration of eugenol in the fluid leaving the bed was determined from its absorbance at 280 nm. The column was stabilised after each experiment by varying the methanol flow rate for about 5 hours followed by a constant low flow rate of 0.1 ml/min for half a day. When the inlet and outlet concentrations became identical, the amount of eugenol retained on the adsorbent particles could easily be determined from mass balance, knowing the total amount of eugenol which had been fed to the bed. The linearity of the adsorption system was examined by replicate experiments in which the concentration of pumping solution was varied from 0.1 ml to 0.5 ml eugenol/100 ml solvent. The capacity ($q_a$) is plotted against the equilibrium solution concentrations ($C^*$) as shown in *Figure 1.* The isotherm is linear in the working range and the expression for the isotherm at room temperature is

$$q_a = 1.8703C^* \qquad (12)$$

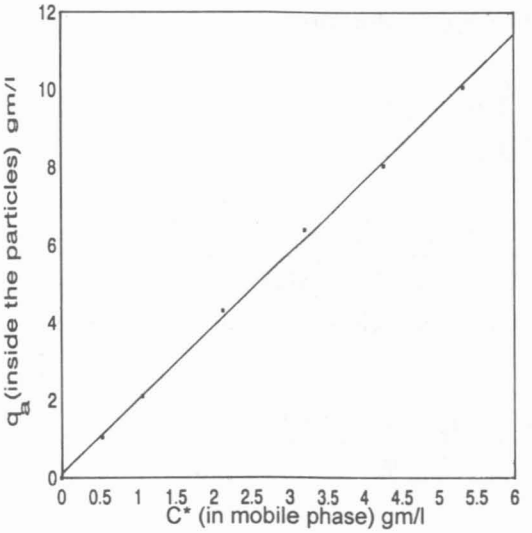


*Fig 1. Adsorption isotherm of eugenol at room temperature from packed bed equilibrium adsorption experiments on $C_{18}$ μ Bondapak column (30 cm × 3.9 mm i.d.); mobile phase, methanol/water (80:20); flowrate, 0.5 ml/min.*

## PARAMETER ESTIMATION

The molecular diffusivity, $D_m$, of eugenol in methanol-water mixture was estimated by Wilke and Chang (1955) correlation:

$$D_m = \frac{1.173 \times 10^{-16} (\psi_2 M_2)^{0.5} T}{\mu V_1^{0.6}} \tag{13}$$

where $M_2$ is the molecular weight of the solvent, $T$ is the temperature in ° K, $\mu$ is the solvent viscosity (Pa s), $\psi_2$ is the association factor and $V_l$ is the molal volume (km³/kg mole). The dependence of external film mass-transfer coefficient $k_f$ on flow rate may be obtained from the following Wilson and Geankoplis correlation (Geankoplis, 1983) for Reynolds number between 0.0015 and 55.

$$k_f = \frac{1.09u}{\varepsilon} \left[\mathrm{ReSc}\right]^{-2/3} \tag{14}$$

The axial dispersion coefficient of liquid flowing through fixed beds can be obtained from the correlation equation of Wen and Fan (1975):

$$\frac{1}{\mathrm{Sc}} = \frac{D_L \rho}{\mu} = \frac{\mathrm{Re}}{0.2 + 0.011 \mathrm{Re}^{0.48}} \tag{15}$$

For systems in which the main mechanism of intraparticle diffusion is molecular diffusion within the macropores, intrapore diffusivity Raghavan and Ruthven, 1983) is given as

$$D \approx \varepsilon_P D_m / \chi \tag{16}$$

## SIMULATION OF THE PACKED BED SYSTEM

Parameters used in the simulation estimated from the defined data from experimental analytical scale separation are assigned as shown in Table 1.

TABLE 1

| Parameter | Value |
|---|---|
| $T$ | 298 K |
| $\chi$ | 3.385 |
| $\varepsilon_P$ | 0.3385 |
| $m$ | 0.5117 |
| $k_f$ | $4.4076 \times 10^{-2}$cm²/sec |
| $D_L$ | $4.89 \times 10^{-4}$cm²/sec |
| $D$ | $5.168 \times 10^{-7}$cm²/sec |
| $\xi$ | 0.045 |
| $P_e$ | 6000 |

Following the methods of Hsu (1979), Hsu and Dranoff (1987) and Chen and Hsu (1987), the Fast Fourier Transform was applied to solve the fixed-bed

adsorption problem equation (1) to (10). If inversion of $F(s)$ in equation (11), named $f(\tau)$ can be found, then $U$ at bed length $x$ and time $\tau$ can be obtained by integrating $f(\tau)$ from zero to $\tau$ with respect to $\tau$. The inversion of $F(s)$ by FFT is given by

$$f(t) = f(\tau) = f(j\Delta T') \tag{17}$$

$$= \frac{1}{2T}\sum_{k=0}^{N-1} F\left(ik\frac{\pi}{T'}\right)\exp\left(\frac{2\pi jk}{N_s}\right) \tag{18}$$

where $j = 0,1,2,\ldots\ldots, N_s - 1$

## RESULTS AND DISCUSSION

*Figure 2* shows effluent concentration profile for injection of different solution concentration to an initially new clean bed versus different length of elution time. It also shows that the effluent concentration first approached the feed concentration and then is reduced to zero at the end of the period. The breakthrough curves at different injection concentration were presented in *Figure 3.*

*Figure 4* to *Figure 7* show the theoretical simulation results of the adsorption of a single component eugenol onto a fixed bed of ( Bondapak C18 analytical column. The parameters used in the calculation are all estimated from the optimum analytical scale separation. Figure 4 displays the chromatographic elution curves at different bed length parameters calculated from the proposed model. It shows that the elution curves peak height is dependent on the bed length parameter.

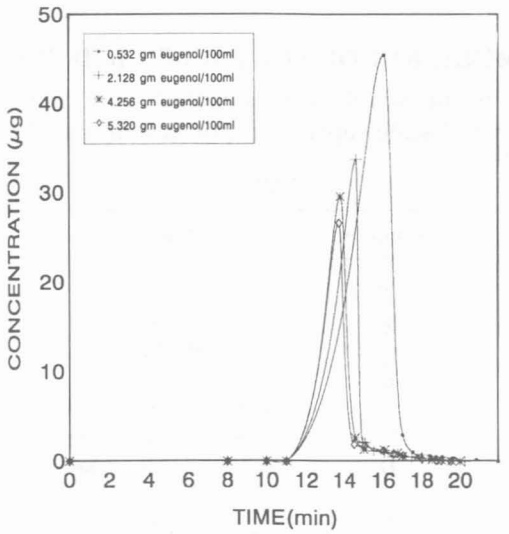


*Fig 2. Chromatogtaphic elution curves of eugenol on µ Bondapak $C_{18}$ analytical column, mobile phase methanol-water (80:20), flow rate 0.5 ml/min, at different solution concentration injection at equilibrium condition*

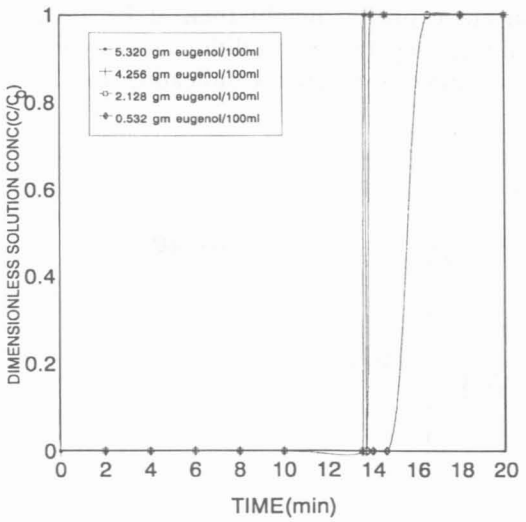


*Fig 3. Experimental breakthrough curves at different eugenol injection concentration on μ Bondapak $C_{18}$ analytical column, mobile phase methanol-water (80:20), flow rate 0.5 ml/min*

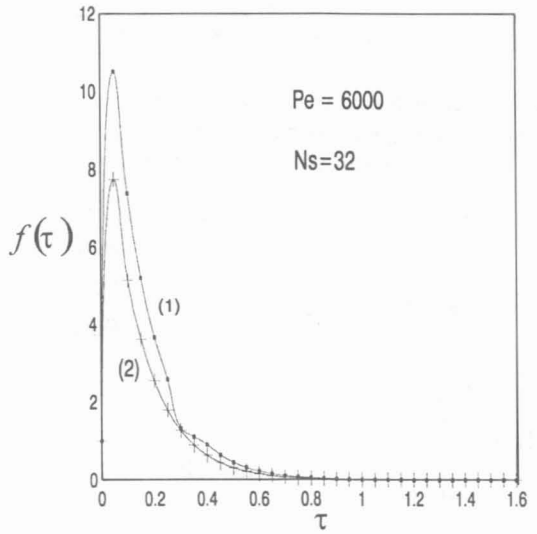


*Fig 4. Theoretical chromatographic evution curves of eugenol on μ Bondapak $C_{18}$ analytical column, mobile phase methanol-water (80:20), flow rate 0.7 ml/min, at different bed length parameters, (1) δ=3.0, (2) δ=0.3*

*Figure 5* shows the effect of number of sampling points on the elution curves at Peclet number 6000 for analytical column. Increasing the sample numbers to 64 gives a higher peak height and vary smoothly than that computed at sample number 32. *Figure 6* shows the theoretical chromatographic curves of eugenol at different Peclet number. Increasing the Peclet number to 10,000 shows a

little difference in curve profile height than at Peclet number 6000 of the optimum analytical scale separation condition. At very low Peclet number 60, the elution curve is skewed and shallow indicating very slow saturation.

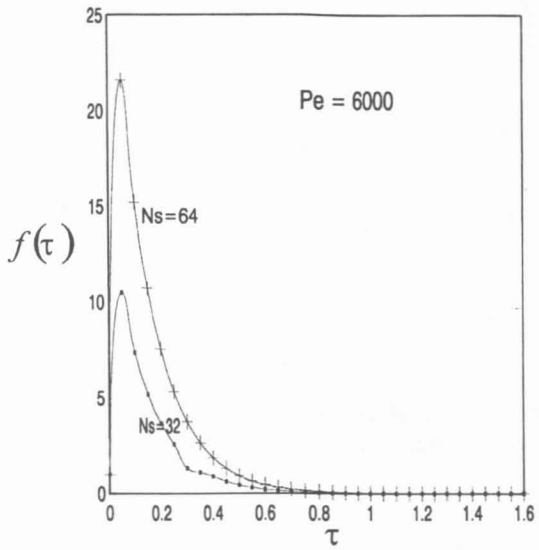


*Fig 5. Theoretical chromatographic elution curve of eugenol on μ Bondapak $C_{18}$ analytical column, mobile phase methanol-water (80:20), flow rate 0.7 ml/min, δ=0.3, at different sample points(N)*

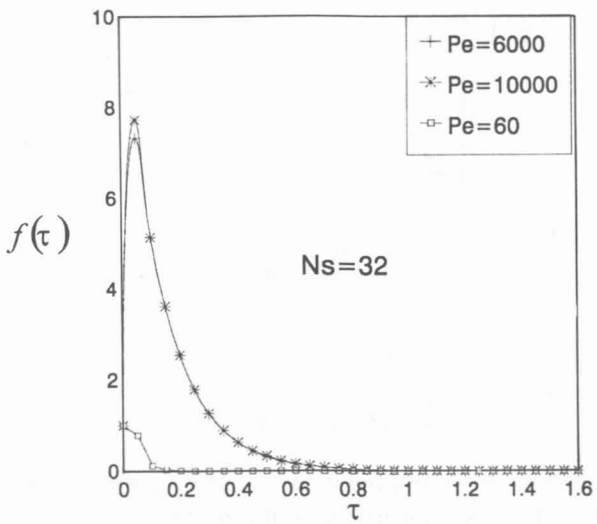


*Fig 6. Theoretical chromatographic elution curve of eugenol on μ Bondapak $C_{18}$ analytical column, mobile phase methanol-water (80:20), flow rate 0.7 ml/min, δ=0.3, at different Peclet number*

*Figure 7* demonstrates the breakthrough curves at different Peclet numbers of 6000 and 10,000 showing initial sharp rise of the curves due to the small particle size of the packing material, followed by a much more gradual increase towards the feed concentration during the later part of the curves. In Figure 8 the experimental elution curve of eugenol at real elution time 0.42 minutes (Figure 5.3.3) was compared with the theoretical simulation data at various Peclet numbers. The results show that the experimental data agree with the theoretical model of Chen and Hsu (1987) well at Peclet number ($P_e$) near 6000 and sample number ($N_s$) 90.

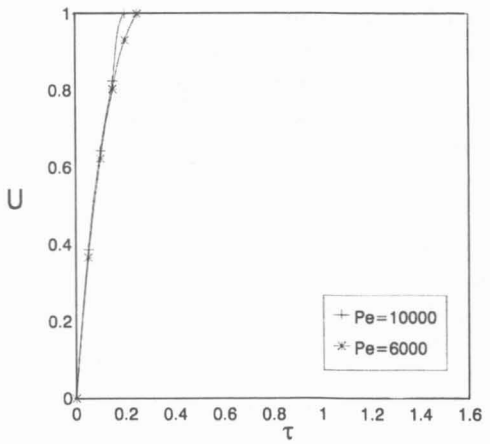


*Fig 7. Theoretical breakthrough curve of eugenol on μ Bondapak $C_{18}$ analytical column, mobile phase methanol-water (80:20), flow rate 0.7 ml/min, δ=0.3, at different Peclet number*

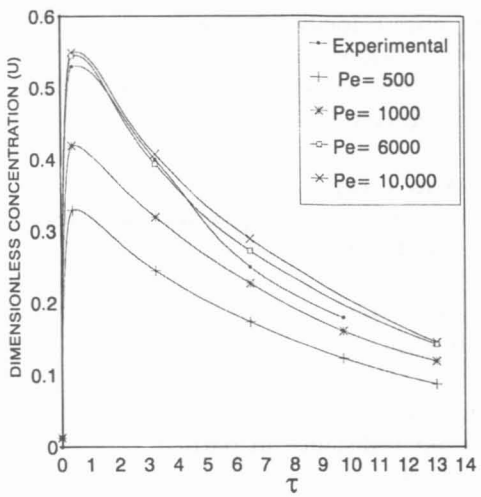


*Fig 8. Experimental elution curve of eugenol superimposed on theoretical predictions elution curve at different Peclet numbers. (Experimental conditions μ Bondapak $C_{18}$ analytical column, mobile phase methanol-water [80:20], flow rate 0.7 ml/min. Simulation parameters δ=3.0, $N_s$=90)*

## CONCLUSION

The elution profile and the breakthrough curves depend on Peclet number ($P_e$), bed length parameters ($\delta$) and number of sample points ($N_s$). The proposed model of Cheng and Hsu (1987) and the accuracy and high computing speed of the FFT technique of Hsu (1979) gives satisfactory agreement between theoretical model and experimental data of chromatographic separation of eugenol.

## NOMENCLATURE

| | |
|---|---|
| $C$ | concentration of solute at time $\theta$, ($gm$ / $ml$) |
| $C_0$ | inlet concentration in fluid($mol$ / $cm^3$) |
| $C^*$ | equilibrium solution concentration ($gm$ / l) |
| $C_p$ | inlet concentration in particle ($mol$ / $cm^3$) |
| $D$ | intrapore diffusivity ($cm^2$ / sec) |
| $D_L$ | axial diffusivity ($cm^2$ / sec) |
| $D_M$ | molecular diffusivity ($cm^2$ / sec) |
| $K_1$ | equilibrium constant |
| $L$ | length of the column ($cm$) |
| $M_2$ | molecular weight of solvent |
| $N_s$ | number of sample points |
| $P_e$ | Peclet number |
| $Q$ | volumetric mobile phase flow rate ($ml$ / sec) |
| Re | Reynolds number |
| Sc | Schmidt number |
| $T'$ | half-period of function being considered |
| $U$ | dimensionless fluid phase concentration |
| $V$ | average linear pore velocity,($cm$ / sec) |
| $V_1$ | molal volume($ml$ / $gm$ $mol$) |
| $a$ | radius of the particle, ($cm$) |
| $k_f$ | mass transfer coefficient ($cm$ / sec) |
| $m$ | = $\varepsilon$ / (1–$\varepsilon$) |
| $q_a$ | adsorbent capacity ($gm$ / $ml$) |
| $r$ | radial distance from centre of spherical particles, ($cm$) |
| $x$ | dimensionless axial distance |
| $z$ | axial distance ($m$) |
| $\varepsilon$ | bed porosity, ($m^3$ / $m3$) |
| $\varepsilon_p$ | macropore porosity |
| $\theta$ | time(sec) |
| $\phi$ | frequency function |
| $\eta$ | dimensionless radial distance in particle |
| $\mu$ | solvent viscosity ($cp$) |
| $\xi$ | film resistance parameter |
| $\psi_1$ | distribution ratio |
| $\psi_2$ | association factor |

$\tau$ contact time parameter
$\delta$ bed length parameter
$\sigma$ constant
$\chi$ tortuosity factor

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## REFERENCES

CHENG, T. L., and J. T. HSU 1987. Prediction of breakthrough curves by the application of Fast Fourier Transform. *AIChE J.* **33(8)**:1387 - 1390.

GEANKOPLIS, C. J. 1983. *Transport Process and Unit Operations.* Massachusetts: Allyn and Bacon, Massachusetts.

HSU, J. T. 1979. Computer simulation of cascade chromatography and the application of Fast Fourier Transform to distributed-parameter model. PhD. Thesis, Northwestern University.

HSU, J. T. and J. S. DRANOFF 1987. Numerical inversion of certain Laplace transform by the direct application of fast Fourier transform (FFT) algorithm. *Comput. Chem. Engng.* **11(2)**:101 - 110.

RAGHAVAN, N. S. and D. M. RUTHVEN 1983. Numerical simulation of a fixed-bed adsorption column by the method of orthogonal collocation. *AIChE J.* **29**:922.

RASMUSON, A. and I. NERETNIEKS 1980. Exact solution of a model for diffusion in particles and longitudinal dispersion in packed beds. *AIChE J.* **26**:686.

WEN, C. Y. and L. T. FAN 1975. *Models for Flow Systems and Chemical Reactors.* New York: Marcel Dekker

WILKE, C. R. and P. CHANG 1955. Correlation for diffusion coefficients in dilute solutions. *AIChE J.* **1**:264.