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Novel general expressions that describe the behavior of the height equivalent of a theoretical plate in chromatographic systems involving electrically-driven and pressure-driven flows

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Abstract

Novel general expressions are constructed and presented that describe the behavior of the height equivalent of a theoretical plate (plate height), H , as a function of the linear velocity, V_x , along the axis, x , of the column and the kinetic parameters that characterize the mass transfer and adsorption mechanisms in chromatographic columns. Open tube capillaries as well as columns packed with either non-porous or porous particles are studied. The porous particles could have unimodal or bimodal pore-size distributions and intraparticle convective fluid flow and pore diffusion are considered. The expressions for the plate height, H , presented in this work could be applicable to high-performance liquid chromatography (HPLC) and capillary electrochromatography (CEC) systems, and could be used together with experimental plate height, H , versus linear velocity, V_x , data to determine the values of the parameters that characterize intraparticle convective fluid flow and pore diffusion. Furthermore, chromatographic systems under unretained as well as under retained conditions are examined. The experimental values of the plate height, H , versus the linear velocity, V_x , for a CEC system involving charged porous silica C_8 particles and an uncharged analyte are compared with the theoretical results for the plate height, H , obtained from the expressions presented in this work. The agreement between theory and experiment is good, and the results indicate that the magnitude of the intraparticle electroosmotic flow (EOF) in the pores of the particles is substantial while the pore diffusion coefficient was of small magnitude. But the overall intraparticle mass transfer resistance in these particles was low because of the significant contribution of the intraparticle EOF. Simulation results are also presented (i) for a hybrid HPLC–CEC system, and (ii) for different CEC systems involving open capillaries as well as packed columns having non-porous or porous particles. The analysis of the results indicates (a) the reasons for the superior performance exhibited by the hybrid HPLC–CEC system over the performance obtained when the system is operated only in the HPLC mode, and (b) the operational configuration and the properties that the structure of the porous particles would have to have in CEC systems involving uncharged or charged analytes under unretained or retained conditions in order to obtain high CEC efficiency (low values of the plate height, H).

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1. Introduction

Analytical and preparative scale chromatography processes are commonplace in industrial practice such as in the analysis and processing of biochemical and pharmaceutical compounds. Furthermore, it is well established that the overall mass transfer resistance in chromatographic columns can be substantially reduced when there is convection (fluid flow) in the pores of the adsorbent particles [1–19]; the enhanced mass transfer rate due to intraparticle fluid flow leads to small values for the reduced plate height. Intraparticle fluid flow in chromatographic systems involving pressure-driven flows, occurs when the macropores of the adsorbent particles have large enough diameters that could allow fluid flow [1–13,15–17]. In capillary electrochromatography (CEC) systems [14,18–22] which involve electrically-driven flows, intraparticle fluid flow always occurs even when the micropore diameter is small enough that overlapping of the electrical double layers is significant and could lead to substantial reduction in the magnitude of intraparticle convective flow [18,19]; the theoretical models for CEC systems of Liapis and Grimes [18], Grimes and Liapis [21,22], and Grimes et al. [19] can be used to determine the magnitude of the intraparticle velocity in a pore as well as in networks of pores (porous particles or monoliths).

The accurate design of a chromatographic process demands that the mathematical model employed for process design, could describe the quantitative dynamic behavior of the chromatographic process of interest properly, and this requires the determination of the kinetic parameters that characterize the mass transfer mechanisms involved [4,6,9,10,15–28]. When the mathematical model is complex, especially for systems involving intraparticle fluid flow, the determination of the kinetic parameters entails extensive and tedious numerical computations. A simple method for the determination of kinetic parameters of complex mathematical models that could also account for the mass transfer effect of intraparticle fluid flow along the radial and angular directions in the porous particles, is via the Laplace transformation method [15,26,29] proposed by Liapis et al. [26] and Heeter and Liapis [15]. This method uses two regressions in order to estimate the kinetic parameters. The first regression capturing the experimental

data is done in the time domain, and the determined function is Laplace transformed. Subsequent non-linear regression in the Laplace domain between this Laplace transformed function and the exact Laplace transform of the mathematical model that describes the chromatographic process, facilitates the estimation of the kinetic parameters. While this method is simple, it suffers from the need for two regressions and each regression has its own error associated with it.

In the present work, the first and second moments of the response of the chromatographic column to a pulse injection of a given analyte are determined from the exact Laplace transform of the solution of the mathematical model of a chromatographic process having either pressure-driven or electrically-driven flow that involves (i) an unpacked column (open capillary), or (ii) a column packed with non-porous particles, or (iii) a column packed with porous particles that could have either a unimodal or bimodal pore-size distribution; these moments are employed to obtain an explicit expression that can be used to determine the height equivalent of a theoretical plate (HETP) for the chromatographic system of interest as a function of the kinetic parameters and the velocity of the mobile phase in the open tube or in the interstitial channels for bulk flow of the packed bed. The use of this explicit HETP equation, along with experimentally determined values of the HETP as a function of the velocity of the mobile phase, could facilitate the estimation of the desired kinetic parameters by employing a single appropriate parameter estimation method.

2. Mathematical formulation

In the chromatographic systems considered in this work, an uncharged analyte is fed by a pulse injection (analytical chromatography) to a chromatographic column of length L and radius R_c . The chromatographic columns considered in this work could be (i) unpacked (open capillary), or (ii) packed with spherical non-porous adsorbent particles, or (iii) packed with spherical porous adsorbent particles that could have a unimodal or bimodal pore-size distribution, and the flow through the open capillary or packed bed could be generated by an applied pressure difference per unit length of the column (pres-

sure-driven flow) or by an applied potential difference per unit length of the column (electrically-driven flow). The mass transport of the uncharged analyte in the interstitial channels of a packed chromatographic column or in the open capillary, is considered to occur by axial dispersion and convection. Furthermore, when the chromatographic system of interest is packed with porous adsorbent particles, the possibility of having mass transport to occur by both pore diffusion and intraparticle convection in all levels of the pore hierarchy (for particles having a unimodal or bimodal pore-size distribution) of the porous particles is considered. In all systems studied in this work, the interaction between the analyte and the active sites on the surface of the stationary phase is considered to occur infinitely fast, the analyte concentration is considered to be dilute, and the adsorption mechanism is taken to be described by a linear equilibrium adsorption isotherm.

2.1. Expression for the plate height, H , in unpacked chromatographic columns (open capillaries)

When film mass transfer resistance in the hydrodynamic boundary layer enveloping the inner surface of the open capillary is considered, the differential mass balance for the analyte in the flowing liquid stream of the open cylindrical capillary and the differential mass balance for the analyte adsorbed on the inner surface of the open capillary, are given, respectively, by the following expressions:

$$\frac{\partial C_d}{\partial t} + V_x \cdot \frac{\partial C_d}{\partial x} - D_L \cdot \frac{\partial^2 C_d}{\partial x^2} + \frac{2}{R_c} \cdot K_f \cdot \left(C_d - \frac{C_s}{K} \right) = 0 \tag{1}$$

$$\frac{\partial C_s}{\partial t} = \frac{2}{R_c} \cdot K_f \cdot \left(C_d - \frac{C_s}{K} \right) \tag{2}$$

The initial and boundary conditions of Eqs. (1) and (2) are given by expressions (3)–(6) as follows:

$$\text{at } t = 0, C_d = 0, \text{ for } 0 \leq x \leq L \tag{3}$$

$$\text{at } t = 0, C_s = 0 \tag{4}$$

$$\text{at } x = 0, V_x C_d \Big|_{x=0} - D_L \cdot \frac{\partial C_d}{\partial x} \Big|_{x=0} = V_x \delta(t), \text{ for } t > 0 \tag{5}$$

$$\text{at } x = L, \frac{\partial C_d}{\partial x} \Big|_{x=L} = 0, \text{ for } t > 0 \tag{6}$$

In Eqs. (1)–(6), C_d denotes the concentration of the analyte in the flowing liquid stream of the open capillary, C_s is the concentration of the analyte in the adsorbed phase, V_x represents the linear velocity of the mobile phase along the axis, x , of the open capillary, K is the equilibrium adsorption constant, R_c denotes the radius of the open cylindrical capillary, t is the time, x is the axial coordinate of the open capillary, and $\delta(t)$ represents the Dirac delta function. In Eqs. (1) and (5), D_L denotes the axial dispersion coefficient; for electrically-driven flows, the expression presented by Griffiths and Nilson [30] could be used to determine the value of D_L and its form [30] is given by Eq. (7),

$$D_L = D_{mf} \cdot \left[1 + \left(\frac{4}{192 + 4 \left(\frac{R_c}{\lambda} \right)^3 + 8 \left(\frac{R_c}{\lambda} \right)^2} \right) \cdot \left(\frac{R_c V_x}{D_{mf}} \right)^2 \right] \tag{7}$$

where D_{mf} denotes the free molecular diffusivity of the analyte, and λ represents the thickness [18] of the electrical double layer (Debye length). In Eqs. (1) and (2), K_f represents the film mass transfer coefficient; for electrically-driven flows, the expression derived by Liapis and Grimes [20] could be used to determine the value of K_f and its form [20] is given by Eq. (8),

$$K_f = \alpha_4 (D_{mf})^{2/3} \cdot \left(\frac{1}{\mu} \right)^{1/3} \cdot \left(\frac{1}{\left(\frac{R_c}{\lambda} \right)} \right)^{2/3} \cdot \left[\left(-\epsilon \epsilon_0 \zeta_w E_x \frac{1}{\lambda^2} \right) \cdot \left(1 - \frac{2I_1 \left(\frac{R_c}{\lambda} \right)}{\left(\frac{R_c}{\lambda} \right) \cdot I_0 \left(\frac{R_c}{\lambda} \right)} \right) \right]^{1/3} \tag{8}$$

where α_4 represents a constant of proportionality [20], μ denotes the viscosity of the mobile liquid phase, ϵ is the dielectric constant, ϵ_0 denotes the permittivity of free space ($\epsilon_0 = 8.854 \cdot 10^{-12} \text{ C}^2/(\text{N} \cdot \text{m}^2)$), ζ_w represents the zeta potential at the surface

of the charged cylindrical capillary, J_n ($n=0, 1$) is the n th order modified Bessel function of the first kind, and E_x denotes the applied potential difference per unit length along the axial direction of the capillary. It should be noted that the expressions for D_L and K_f derived by Griffiths and Nilson [30] (Eq. (7) above) and Liapis and Grimes [20] (Eq. (8) above), respectively, also account for the effect of overlap of the electrical double layer. The expression for D_L [30] in Eq. (7) indicates that the value of D_L in electrically-driven flows could be substantially smaller in magnitude relative to the value of D_L obtained in pressure-driven flows, when the magnitude of the ratio of the capillary radius to the thickness, λ , of the electrical double layer (R_c/λ) is much greater than unity ($R_c/\lambda \gg 1$) due to the plug-flow nature of the electroosmotic flow (EOF) field under these conditions. With respect to the expression for K_f [20] in Eq. (8), the results [20] indicate that the value of K_f in electrically-driven flows can be substantially larger in magnitude relative to the value of K_f obtained in pressure-driven flows, when the magnitude of the ratio of the capillary radius to the thickness, λ , of the electrical double layer (R_c/λ) is much greater than unity due to the plug-flow nature of the electroosmotic flow (EOF) field under these conditions.

The Laplace transform domain solution to the system of equations given by expressions (1)–(6) and the first and second moments of the column response to the pulse injection can be found in Ref. [31]. The equation describing the height equivalent of a theoretical plate (plate height), H , for the open capillary system described by Eqs. (1) and (2) is given by Eq. (9) and its derivation is found in Ref. [31],

$$H = \frac{2D_L}{V_x} + \frac{d_c K^2}{2K_f(1+K)^2} \cdot V_x \quad (9)$$

where d_c denotes the diameter of the open cylindrical capillary ($d_c = 2R_c$).

2.2. Expression for the plate height, H , in chromatographic columns packed with spherical non-porous adsorbent particles

When film mass transfer resistance in the hydro-

dynamic boundary layer surrounding the non-porous particles packed in the chromatographic column is considered, the differential mass balance for the analyte in the flowing liquid stream in the interstitial channels of the packed chromatographic column and the differential mass balance for the analyte adsorbed on the surface of the non-porous particles, are given, respectively, by the following expressions:

$$\frac{\partial C_d}{\partial t} + V_x \cdot \frac{\partial C_d}{\partial x} - D_L \cdot \frac{\partial^2 C_d}{\partial x^2} + \frac{(1 - \epsilon_b)}{\epsilon_b} \cdot \frac{3}{R_p} \cdot K_f \cdot \left(C_d - \frac{C_s}{K} \right) = 0 \quad (10)$$

$$\frac{\partial C_s}{\partial t} = \frac{3}{R_p} \cdot K_f \cdot \left(C_d - \frac{C_s}{K} \right) \quad (11)$$

The initial and boundary conditions of Eqs. (10) and (11) are given by Eqs. (3)–(6) where C_d denotes the concentration of the analyte in the interstitial channels of the packed bed, C_s is the concentration of the analyte in the adsorbed phase, V_x represents the linear velocity of the mobile phase in the interstitial channels along the axis, x , of the packed column, R_p denotes the radius of the non-porous particles, and ϵ_b is the void fraction of the packed bed. For electrically-driven flows, the values of D_L [30] and K_f [20] could be determined by Eqs. (12) and (13), respectively:

$$D_L = D_{mf} \cdot \left[\chi \cdot \left[1 + \left(\frac{4}{192 + 4 \left(\frac{R_{ic}}{\lambda} \right)^3 + 8 \left(\frac{R_{ic}}{\lambda} \right)^2} \right) \cdot \left(\frac{R_{ic} V_x}{D_{mf}} \right)^2 \right] \right] \quad (12)$$

$$K_f = \alpha_4 (D_{mf})^{2/3} \cdot \left(\frac{1}{\mu} \right)^{1/3} \cdot \left(\frac{1}{\left(\frac{R_{ic}}{\lambda} \right)} \right)^{2/3} \cdot \left[\left(-\epsilon \epsilon_0 \zeta_w E_x \frac{1}{\lambda^2} \right) \cdot \left(1 - \frac{2I_1 \left(\frac{R_{ic}}{\lambda} \right)}{\left(\frac{R_{ic}}{\lambda} \right) \cdot I_0 \left(\frac{R_{ic}}{\lambda} \right)} \right) \right]^{1/3} \quad (13)$$

In Eqs. (12) and (13), R_{ic} denotes the radius of the

interstitial channels for bulk flow in the packed column, while the parameter χ represents the conductivity factor [18,32,33] which is equal to the ratio of the effective conductivity of the packed capillary column filled with the electrolyte solution to the conductivity of the unpacked capillary column filled with the electrolyte solution [18]. The value of χ can be determined experimentally from the procedures reported in Refs. [18,32,33]. The Laplace transform domain solution to Eqs. (10) and (11) along with the first and second moments of the column response to the pulse injection can be found in Ref. [31]. The equation for the plate height, H , for a chromatographic column packed with non-porous adsorbent particles described by Eqs. (10) and (11), is given by Eq. (14) whose derivation is presented in Ref. [31]:

$$H = \frac{2D_L}{V_x} + \frac{\epsilon_b(1 - \epsilon_b)d_p K^2}{3K_f(\epsilon_b + (1 - \epsilon_b)K)^2} \cdot V_x \quad (14)$$

In Eq. (14), d_p denotes the diameter of the non-porous particles ($d_p = 2R_p$).

2.3. Expression for the plate height, H, in chromatographic columns packed with porous adsorbent particles having a unimodal pore-size distribution

The differential mass balance for the analyte in a porous adsorbent particle having a unimodal pore-size distribution, when external film mass transfer resistance in the hydrodynamic boundary layer surrounding the spherical porous adsorbent particle is not considered, is given by Eq. (1) in the work of Heeter and Liapis [15], and its initial and boundary conditions are given by Eqs. (2)–(7) of Ref. [15]. The solution to Eq. (1) of Ref. [15] in the Laplace transform domain when film mass transfer resistance is neglected is given by Eq. (24) of Ref. [15]. When film mass transfer resistance is considered, Eq. (4) of Ref. [15] should be replaced by the following expression [34]:

$$\text{at } R = R_p, \quad K_f(C_d - C_p|_{R=R_p}) - \epsilon_p D_p$$

$$\cdot \frac{\partial C_p}{\partial R} \Big|_{R=R_p} + \epsilon_p v_{pR} C_p|_{R=R_p} = 0,$$

$$\text{for } t > 0, \quad 0 \leq \theta \leq \pi \quad (15)$$

In Eq. (15), C_d denotes the concentration of the analyte in the interstitial channels for bulk flow, C_p is the concentration of the analyte in the pores of the porous particle, R denotes the radial direction in the porous particle, θ represents the angular direction in the porous particle, R_p denotes the radius of the porous adsorbent particle, K_f is the film mass transfer coefficient, ϵ_p represents the porosity of the porous particle, v_{pR} represents the radial component of the intraparticle convective velocity, and D_p denotes the pore diffusion coefficient. The value of D_p can be determined through pore network modelling theory [15–17,19,28].

The Laplace transform of the solution to Eq. (1) of Ref. [15] when film mass transfer resistance is considered, is given by Eq. (16) which is reported in the work of Heeter [34],

$$C'_p = C'_d \exp\left(\frac{R_p V_{pore}}{2D_p} \cdot \rho\eta\right) \sum_{n=0}^{\infty} d_{5n} P_n(\eta) \sum_{i=0}^{\infty} \frac{A_2^i \rho^{2i+n}}{b_{ni}} \quad (16)$$

where

$$A_2 = s \cdot \frac{R_p^2}{D_p} \cdot \left(1 + \frac{K}{\epsilon_p}\right) + \left(\frac{R_p V_{pore}}{2D_p}\right)^2 \quad (17)$$

$$\mathbf{d}_5 = \mathbf{B}_5^{-1} \mathbf{S} \quad (18)$$

$$B_{5jk} = -\frac{R_p V_{pore}}{2D_p} \int_{-1}^1 \eta P_j(\eta) P_k(\eta) d\eta \sum_{i=0}^{\infty} \frac{A_2^i}{b_{ki}},$$

for $j \neq k$ (19)

$$B_{5jj} = \left(\frac{2}{2j+1}\right) \sum_{i=0}^{\infty} \left(\frac{K_f R_p}{\epsilon_p D_p} + 2i + j\right) \cdot \frac{A_2^i}{b_{ji}} - \frac{R_p V_{pore}}{2D_p} \int_{-1}^1 \eta [P_j(\eta)]^2 d\eta \sum_{i=0}^{\infty} \frac{A_2^i}{b_{ji}} \quad (20)$$

$$S_j = \frac{K_f R_p}{\epsilon_p D_p} \int_{-1}^1 \exp\left(-\frac{R_p V_{pore}}{2D_p} \cdot \eta\right) \cdot P_j(\eta) d\eta \quad (21)$$

In Eqs. (16)–(21), C'_p denotes the Laplace transform of the concentration of the analyte in the pores of the adsorbent particles, C'_d represents the Laplace transform of the concentration of the analyte in the

interstitial channels for bulk flow in the packed bed, ϵ_p is the particle porosity, $P_j(\eta)$ is a j th order Legendre polynomial of the first kind, V_{pore} denotes the velocity of the liquid in the pores of the porous particles along the axial direction of the packed column and the magnitude of V_{pore} can be determined from pore network modelling theory [15–17,19,28]. The expressions for ρ , η , and b_{ji} are given by Eqs. (11), (12) and (23) of Ref. [15], respectively. Due to the fact that the effect of the external film mass transfer resistance is negligible [15,34,35] compared to the effect of the intraparticle (internal) mass transfer resistance in the pores of the particles, the effect of the external film mass transfer resistance in columns packed with porous particles will not be further considered in this work and, thus, Eq. (15) of this work where $K_f \rightarrow \infty$ (negligible film mass transfer resistance) should be replaced by Eq. (4) of Ref. [15].

The differential mass balance for the analyte in the interstitial channels of the packed column is given by Eq. (22),

$$\frac{\partial C_d}{\partial t} + V_x \cdot \frac{\partial C_d}{\partial x} - D_L \cdot \frac{\partial^2 C_d}{\partial x^2} + \frac{(1 - \epsilon_b)}{\epsilon_b} \cdot \frac{\partial \bar{C}_p}{\partial t} = 0 \tag{22}$$

The initial and boundary conditions of Eq. (22) are given by Eqs. (3)–(6) above, where now the variable C_d denotes the concentration of the analyte in the interstitial channels of the packed bed, \bar{C}_p is the average concentration of the analyte in the adsorbent particle and the Laplace transform of \bar{C}_p is given by Eq. (24) of Ref. [15], V_x represents the linear velocity of the mobile phase in the interstitial channels along the axis, x , of the packed column, the parameter R_p denotes the radius of the porous particles, and ϵ_b is the void fraction of the packed bed. For electrically-driven flows, the values of D_L [30] and K_f [20] are determined, respectively, from Eqs. (12) and (13) above. The Laplace transform domain solution of Eq. (22) along with the first and second moments of the column response to the pulse injection can be found in Ref. [31]. The equation for the height equivalent of a theoretical plate, H , for columns packed with spherical porous adsorbent particles having a unimodal pore-size distribution is given by Eq. (23),

$$H = \frac{2D_L}{V_x} - \frac{\chi''}{(\chi')^2} \cdot \frac{L^2}{D_L} V_x \tag{23}$$

where

$$\chi' \frac{L^2}{D_L} + \frac{3}{2} \cdot \frac{(1 - \epsilon_b)}{\epsilon_b} \cdot \frac{L^2}{D_L} \cdot (K + \epsilon_p) \sum_{n=0}^{\infty} d_{1n} \sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}} \int_0^1 \int_{-1}^1 \rho^{2i+n+2} e^{\alpha \rho \eta} P_n(\eta) d\eta d\rho \tag{24}$$

$$\chi'' = 3 \frac{(1 - \epsilon_b)}{\epsilon_b} \cdot \frac{L^2}{D_L} \cdot (K + \epsilon_p) \left[\left(\sum_{n=0}^{\infty} d_{2n} \sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}} \times \int_0^1 \int_{-1}^1 \rho^{2i+n+2} e^{\alpha \rho \eta} P_n(\eta) d\eta d\rho \right) + \left(\sum_{n=0}^{\infty} d_{1n} \sum_{i=0}^{\infty} \frac{i \left(\frac{R_p^2 (\epsilon_p + K)}{\epsilon_p D_p} \right) (\alpha^2)^{i-1}}{b_{ni}} \times \int_0^1 \int_{-1}^1 \rho^{2i+n+2} e^{\alpha \rho \eta} P_n(\eta) d\eta d\rho \right) \right] \tag{25}$$

$$\alpha = \frac{1}{2} \cdot \frac{V_{\text{pore}} R_p}{D_p} \tag{26}$$

$$d_{1n} = \left(\frac{2n + 1}{2} \right) \cdot \left[\frac{\int_{-1}^1 e^{-\alpha \eta} P_n(\eta) d\eta}{\sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}}} \right] \tag{27}$$

$$d_{2n} = - \left(\frac{2n + 1}{2} \right) \cdot \left(\int_{-1}^1 e^{-\alpha \eta} P_n(\eta) d\eta \right) \cdot \frac{\left(\sum_{i=0}^{\infty} \frac{i \left(\frac{R_p^2 (\epsilon_p + K)}{\epsilon_p D_p} \right) (\alpha^2)^{i-1}}{b_{ni}} \right)}{\left(\sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}} \right)^2} \tag{28}$$

2.4. Expression for the plate height, H , in chromatographic columns packed with porous adsorbent particles having a bimodal pore-size distribution

The differential mass balance for the analyte in the micropores of a porous adsorbent particle [15] is given by the following expression:

$$\begin{aligned} & \left[1 + \left(\frac{K}{\epsilon_{pm}(1 - \epsilon_p)} \right) \right] \cdot \frac{\partial C_{pm}}{\partial t} + v_{pmr} \cdot \frac{\partial C_{pm}}{\partial r} \\ & + \frac{v_{pm\phi}}{r} \cdot \frac{\partial C_{pm}}{\partial \phi} \\ & = D_{pm} \left[\frac{1}{r^2} \cdot \frac{\partial}{\partial r} \cdot \left(r^2 \cdot \frac{\partial C_{pm}}{\partial r} \right) + \frac{1}{r^2 \sin \phi} \cdot \frac{\partial}{\partial \phi} \right. \\ & \quad \left. \times (\sin \phi) \cdot \frac{\partial C_{pm}}{\partial \phi} \right] \end{aligned} \tag{29}$$

The initial and boundary conditions of Eq. (29) are as follows:

$$\begin{aligned} & \text{at } t = 0, C_{pm} = 0, \quad \text{for } 0 \leq r \leq r_{pm}, \\ & 0 \leq \phi \leq \pi \end{aligned} \tag{30}$$

$$\text{at } \phi = 0, \left. \frac{\partial C_{pm}}{\partial \phi} \right|_{\phi=0} = 0, \quad \text{for } t > 0, 0 \leq r \leq r_{pm} \tag{31}$$

$$\text{at } \phi = \pi, \left. \frac{\partial C_{pm}}{\partial \phi} \right|_{\phi=\pi} = 0, \quad \text{for } t > 0, 0 \leq r \leq r_{pm} \tag{32}$$

$$\text{at } r = 0, C_{pm} \text{ is finite, for } t > 0, 0 \leq \phi \leq \pi \tag{33}$$

$$\begin{aligned} & \text{at } r = r_{pm}, C_{pm} = C_p(t, R, \theta), \quad \text{for } t > 0, \\ & 0 \leq \phi \leq \pi \end{aligned} \tag{34}$$

In Eqs. (29)–(34), ϵ_p is the porosity of the macroporous region of the adsorbent particles having a bimodal pore-size distribution, ϵ_{pm} denotes the porosity of the microporous region of the adsorbent particles having a bimodal pore-size distribution, C_{pm} represents the concentration of the analyte in the microporous region of the porous adsorbent particles, C_s denotes the concentration of the uncharged analyte in the adsorbed phase per unit volume of the particle, v_{pmr} is the radial component of the velocity in the pores of the microporous region of the adsorbent particles, $v_{pm\phi}$ is the angular component of the velocity in the pores of the microporous region of the adsorbent particles, D_{pm} represents the pore diffusion coefficient of the analyte in the microporous region of the porous adsorbent particles (the value of D_{pm} can be obtained through pore network modelling theory [15–17,19,28]), r denotes the radial coordinate of the microporous region of the

adsorbent particles, ϕ denotes the angular coordinate of the microporous region of the adsorbent particles, R represents the radial coordinate of the macroporous region of the adsorbent particles, and θ denotes the angular coordinate of the macroporous region of the adsorbent particles.

The Laplace transform domain solution [31] to the system of equations given by expressions (29)–(34) is given by Eq. (35),

$$\begin{aligned} C'_{pm} &= C'_p \exp\left(\frac{V_{micro} r_{pm}}{2D_{pm}} \cdot \rho_m \eta_m\right) \\ & \times \sum_{n=0}^{\infty} d_{3n} P_n(\eta_m) \sum_{i=0}^{\infty} \frac{A_3^i \rho_m^{2i+n}}{b_{ni}} \end{aligned} \tag{35}$$

where

$$\rho_m = \frac{r}{r_{pm}} \tag{36}$$

$$\eta_m = \cos \phi \tag{37}$$

$$A_3 = s \cdot \frac{r_{pm}^2}{D_{pm}} \cdot \left(1 + \frac{K}{\epsilon_{pm}(1 - \epsilon_p)} \right) + \left(\frac{V_{micro} r_{pm}}{2D_{pm}} \right)^2 \tag{38}$$

$$\begin{aligned} d_{3n} &= \left(\frac{2n+1}{2} \right) \\ & \frac{\int_{-1}^1 \exp\left(-\frac{V_{micro} r_{pm}}{2D_{pm}} \cdot \eta_m\right) P_n(\eta_m) d\eta_m}{\sum_{i=0}^{\infty} \frac{A_3^i}{b_{ni}}} \end{aligned} \tag{39}$$

The parameter V_{micro} denotes the velocity of the fluid along the axial direction of the column in the microporous region of the adsorbent particles. It should be noted that for chromatographic systems having no flow in the micropores, the value of V_{micro} should be set equal to zero.

The differential mass balance for the analyte in the macroporous region of the adsorbent particles is given by Eq. (43) of Ref. [15] and its initial and boundary conditions are given by Eqs. (2) and (4)–(7) of Ref. [15]. The Laplace transform domain solution to the differential mass balance equation for the analyte in the macroporous region of the adsorbent particle is given by Eq. (48) of Ref. [15] where the term A_4 in Eq. (48) of Ref. [15] should be replaced by the following expression,

$$A_4 = \left(\frac{V_{\text{pore}} R_p}{2D_p} \right)^2 + \frac{R_p^2}{D_p} \cdot s \cdot \left[1 + \left(\frac{3}{2} \cdot (K + \epsilon_{\text{pm}}(1 - \epsilon_b)) \sum_{n=0}^{\infty} d_{3n} \sum_{i=0}^{\infty} \frac{A_3^i}{b_{ni}} \cdot J_{ni} \right) \right] \quad (40)$$

where

$$J_{ni} = \int_0^1 \int_{-1}^1 \rho_m^{2i+n+2} \exp\left(-\frac{V_{\text{micro}} r_{\text{pm}}}{2D_{\text{pm}}} \cdot \rho_m \eta_m \right) \times P_n(\eta_m) d\eta_m d\rho_m \quad (41)$$

The differential mass balance for the analyte in the interstitial channels of the packed column is given by Eq. (42) as follows:

$$\frac{\partial C_d}{\partial t} + V_x \cdot \frac{\partial C_d}{\partial x} - D_L \cdot \frac{\partial^2 C_d}{\partial x^2} + \frac{(1 - \epsilon_b)}{\epsilon_b} \cdot \frac{\partial \bar{C}_{\text{ps}}}{\partial t} = 0 \quad (42)$$

The initial and boundary conditions of Eq. (42) are given by Eqs. (3)–(6) above. In Eq. (42), the average concentration, \bar{C}_{ps} , of the analyte in the porous adsorbent particle is given by Eq. (51) of Ref. [15], and the value of the axial dispersion coefficient, D_L , can be determined from Eq. (12) presented above. The Laplace transform domain solution of Eq. (42) along with the first and second moments of the column response to the pulse injection can be found in Ref. [31]. The expression for the height equivalent of a theoretical plate, H , for columns packed with spherical porous adsorbent particles having a bimodal pore-size distribution, is given by Eq. (43),

$$H = \frac{2D_L}{V_x} - \frac{\chi''}{(\chi')^2} \cdot \frac{L^2}{D_L} \cdot V_x \quad (43)$$

where

$$\chi' = \frac{L^2}{D_L} + \frac{(1 - \epsilon_b)}{\epsilon_b} \cdot \frac{L^2}{D_L} \cdot A_6 \sum_{n=0}^{\infty} d_{4n} \sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}} \times \int_0^1 \int_{-1}^1 \rho^{2i+n+2} e^{\alpha\rho\eta} P_n(\eta) d\eta d\rho \quad (44)$$

$$\chi'' = 2 \cdot \frac{(1 - \epsilon_b)}{\epsilon_b} \cdot \frac{L^2}{D_L} \cdot \left[\left(A_8 \sum_{n=0}^{\infty} d_{4n} \sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}} \times \int_0^1 \int_{-1}^1 \rho^{2i+n+2} e^{\alpha\rho\eta} P_n(\eta) d\eta d\rho \right) + \left(A_6 \sum_{n=0}^{\infty} d_{6n} \sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}} \int_0^1 \int_{-1}^1 \rho^{2i+n+2} e^{\alpha\rho\eta} P_n(\eta) d\eta \cdot d\rho \right) \times \left(A_6 \sum_{n=0}^{\infty} d_{4n} \sum_{i=0}^{\infty} A_7 \cdot \frac{i(\alpha^2)^{i-1}}{b_{ni}} \int_0^1 \int_{-1}^1 \rho^{2i+n+2} e^{\alpha\rho\eta} P_n(\eta) d\eta d\rho \right) \right] \quad (45)$$

$$\alpha = \frac{1}{2} \cdot \frac{V_{\text{pore}} R_p}{D_p} \quad (46)$$

$$\beta = \frac{1}{2} \cdot \frac{V_{\text{micro}} r_{\text{pm}}}{D_{\text{pm}}} \quad (47)$$

$$d_{4n} = \left(\frac{2n + 1}{2} \right) \cdot \left[\frac{\int_{-1}^1 e^{-\alpha\eta} P_n(\eta) d\eta}{\sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}}} \right] \quad (48)$$

$$d_{5n} = \left(\frac{2n + 1}{2} \right) \cdot \left[\frac{\int_{-1}^1 e^{-\beta\eta_m} P_n(\eta_m) d\eta_m}{\sum_{i=0}^{\infty} \frac{(\beta^2)^i}{b_{ni}}} \right] \quad (49)$$

$$d_{6n} = - \left(\frac{2n + 1}{2} \right) \cdot \left(\int_{-1}^1 e^{-\alpha\eta} P_n(\eta) d\eta \right) \frac{\left(\sum_{i=0}^{\infty} A_7 \cdot \frac{i(\alpha^2)^{i-1}}{b_{ni}} \right)}{\left(\sum_{i=0}^{\infty} \frac{(\alpha^2)^i}{b_{ni}} \right)^2} \quad (50)$$

$$d_{7n} = - \left(\frac{2n + 1}{2} \right) \frac{\left(\int_{-1}^1 e^{-\beta\eta_m} P_n(\eta_m) d\eta_m \right) \left(\sum_{i=0}^{\infty} A_5 \cdot \frac{i(\beta^2)^{i-1}}{b_{ni}} \right)}{\left(\sum_{i=0}^{\infty} \frac{(\beta^2)^i}{b_{ni}} \right)^2} \quad (51)$$

$$A_5 = \frac{r_{pm}^2}{D_{pm}} \cdot \left(1 + \frac{K}{\epsilon_{pm}(1 - \epsilon_p)} \right) \quad (52)$$

$$A_6 = \frac{3}{2} \cdot \epsilon_p + \frac{9}{4} \cdot (K + \epsilon_{pm}(1 - \epsilon_p)) \sum_{n=0}^{\infty} d_{5n} \sum_{i=0}^{\infty} \frac{(\beta^2)^i}{b_{ni}} \\ \times \int_0^1 \int_{-1}^1 \rho_m^{2i+n+2} e^{\beta \rho_m \eta_m} P_n(\eta_m) d\eta_m d\rho_m \quad (53)$$

$$A_7 = \frac{R_p^2}{D_p} \cdot \left[1 + \frac{3}{2} \cdot (K + \epsilon_{pm}(1 - \epsilon_p)) \sum_{n=0}^{\infty} d_{5n} \right. \\ \left. \times \sum_{i=0}^{\infty} \frac{(\beta^2)^i}{b_{ni}} \int_0^1 \int_{-1}^1 \rho_m^{2i+n+2} e^{\beta \rho_m \eta_m} P_n(\eta_m) d\eta_m d\rho_m \right] \quad (54)$$

$$A_8 = \frac{9}{4} \cdot (K + \epsilon_{pm}(1 - \epsilon_p)) \left[\left(\sum_{n=0}^{\infty} d_{7n} \sum_{i=0}^{\infty} \frac{(\beta^2)^i}{b_{ni}} \right) \right. \\ \left. \times \int_0^1 \int_{-1}^1 \rho_m^{2i+n+2} e^{\beta \rho_m \eta_m} P_n(\eta_m) d\eta_m d\rho_m \right) \\ + \left(\sum_{n=0}^{\infty} d_{5n} \sum_{i=0}^{\infty} A_5 \cdot \frac{i(\beta^2)^{i-1}}{b_{ni}} \int_0^1 \int_{-1}^1 \right. \\ \left. \times \rho_m^{2i+n+2} e^{\beta \rho_m \eta_m} P_n(\eta_m) d\eta_m d\rho_m \right) \quad (55)$$

Frey et al. [6] developed an expression for the reduced plate height, h ($h = H/d_p$), in chromatographic columns packed with porous adsorbent particles having a bimodal pore-size distribution; Frey et al. [6] considered that mass transport in the macroporous region of the particles occurs by diffusion and convective flow while in the microporous region of the particles mass transport was considered to occur only by diffusion. But the model of Frey et al. [6] assumes that the concentration gradients in the macroporous and microporous regions of the particle are linear; this assumption of Frey et al. [6] is actually physically unrealistic because the assumption that there are linear concentration gradients in the macroporous and microporous regions of the particle forces the concentration distribution of the analyte in the macroporous and microporous regions of the particle to equilibrate infinitely fast when there is a change in the concentration of the analyte in the interstitial channels for bulk flow and in the macropores of the particles, respectively. In effect, their [6] assumption of linear concentration gradients in the

macroporous region of the particles indicates that the analyte would pass through the macroporous region of the particles much faster than it would if the concentration gradient in the macroporous region of the particles was non-linear which leads to an underestimation of the value of the reduced plate height, h , while their [6] assumption of linear concentration gradients in the microporous region of the particles indicates that the total mass of the analyte that enters the microporous region of the particles would be larger than one would obtain by considering non-linear driving forces in the microporous region of the particles. Thus, their [6] assumption of linear concentration gradients in the microporous region of the particles can lead to an overestimation of the value of the reduced plate height, h , as the value of the equilibrium adsorption constant, K , increases. Furthermore, Frey et al. [6], apart from having considered linear concentration gradients in the macroporous region of the particles, also considered the intraparticle velocity only along the axial direction of the column, and this requires the minimum value of the concentration of the analyte in the particle to occur at the downstream edge of the particle. But when intraparticle fluid flow occurs it has been shown [9–13,36] that the fluid velocity components along the radial, R , and angular, θ , directions of the macroporous region of the particles have to be considered and this causes [9–13,36] (i) the minimum concentration of the analyte in the particles to shift downstream from the center of the particles, but the minimum concentration of the analyte remains in the particle interior, and (ii) the isoconcentration profiles of the analyte in the pore fluid and in the adsorbed phase are asymmetric; consequently, the total mass of the analyte in the particle will be larger under the latter conditions than when the concentration gradients of the analyte in the macroporous and microporous regions of the particle are taken to be linear and the intraparticle flow occurs only along the axial direction of the column, and therefore, one would obtain an underestimate of the value of the plate height from the expression of Frey et al. [6]. In contrast, the equations for the plate height, H , developed in this work [Eqs. (23) and (43)] can account for non-linear concentration gradients in the macroporous and microporous regions of the particle as well as for

intraparticle fluid flow along the radial, R , and angular, θ , directions of the particle and, thus, the equations for the plate height, H , presented in this work could provide physically meaningful values of the parameters that characterize the chromatographic separation system when compared to experimentally obtained H versus V_x curves.

3. Results and discussion

In Fig. 1, the theoretical results obtained from Eq. (23) developed in this work for the determination of the plate height, H , in a capillary column packed with porous particles of diameter $d_p = 1.0 \mu\text{m}$ and having a unimodal pore-size distribution are compared to the experimental data measured by Lütcke [37]. The charged particles used in the experiment [37] were porous silica C_8 particles whose porosity, ϵ_p , was estimated to be equal to 0.49; these particles were packed in a fused-silica capillary of radius $R_c = 50 \mu\text{m}$ and length $L = 8.5 \text{ cm}$, and the system was such that the value of the void fraction, ϵ_b , in the packed bed was estimated to be 0.35. The mobile phase used in the experiment [37] was acetonitrile–25 mM Tris–HCl (80:20) at pH 8.0 and temperature $T = 20^\circ\text{C}$, while the value of the free molecular diffusivity, D_{mf} , of the analyte (uracil) used in the experiment was estimated by Lütcke [37] to be $1.0 \cdot 10^{-9} \text{ m}^2/\text{s}$ and the value of the equilibrium

adsorption constant, K , was equal to zero (the chromatographic system was operated under unretained conditions); also, Lütcke [37] estimated that the value of the conductivity factor, χ , of the packed column (see Eq. (12) above) is equal to 0.61. If one were to consider that the intraparticle diffusion coefficient could be expressed by the empirical relationship $D_p = (\epsilon_p D_{mf})(\beta/\tau)$ [16,17,19,28], where β denotes the hindrance parameter [38] for the analyte in the pores of the porous medium and τ represents the average tortuosity of the porous medium, then the values of the ratios β/τ and V_{pore}/V_x could be obtained from experimentally measured H versus V_x curves by employing Eq. (23) and a single appropriate parameter estimation method. Through non-linear regression of the experimental data of Lütcke [37] with Eq. (23) developed in this work, the value of the ratio, β/τ , was found to be 0.07155, and the value of the ratio of the intraparticle velocity along the axial direction of the packed column, V_{pore} , to the interstitial velocity, V_x , was found to be equal to 0.2387 ($V_{\text{pore}}/V_x = 0.2387$). The results in Fig. 1 indicate that the agreement between theory and experiment is good; the value of the correlation factor that indicates the degree of agreement between the experimental data for the plate height, H , and the theoretical results was 0.99986. The value of the ratio V_{pore}/V_x indicates that a significant amount of EOF occurs in the pores of the particles, while the value of the ratio β/τ suggests that the magnitude of the intraparticle diffusion coefficient, D_p , of the analyte is substantially smaller than the value of its free molecular diffusion coefficient, D_{mf} . Meyers et al. [28] employed pore network modelling theory to obtain values for the pore-size distribution, pore connectivity, and pore spatial distribution of similar silica C_8 particles having a different (larger) particle diameter, and they found that intraparticle pores having a diameter slightly greater than 100 \AA constituted most of the pore volume, but a significant majority of the total number of intraparticle pores had a diameter that was less than or equal to 20 \AA . Therefore, the results of Meyers et al. [28] suggest that one would expect to obtain a reasonably high magnitude of the intraparticle EOF in the porous particles (considering that the surface charge density of the intraparticle pores is large in magnitude [18]), because EOF is generated

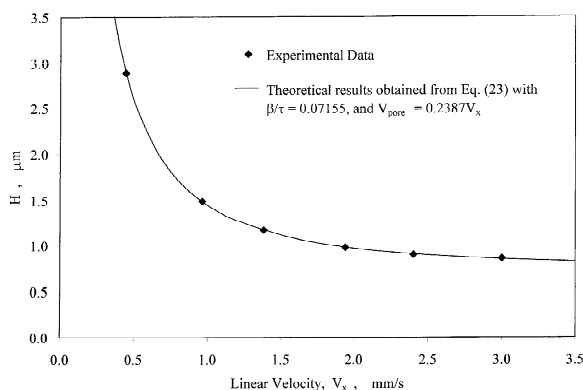


Fig. 1. Comparison between the experimental data of the plate height, H , for a fused-silica CEC column packed with porous silica C_8 particles having a unimodal pore-size distribution and the theoretical results obtained from Eq. (23).

by an external body force acting on the space charge density in the electrical double layers adjacent to the surface of the intraparticle pores and the majority of the pore volume that EOF passes through is in pores whose radius [28] is greater than the thickness, λ , of the electrical double layer ($\lambda = 14.88 \text{ \AA}$) and, thus, there could be a significant electroosmotic fluid velocity in a majority of the pore volume. It is worth noting that when the radii of the intraparticle pores are significantly greater than the value of λ , the magnitude of the velocity of the EOF in the pores of the particles will begin to approach the magnitude of the EOF in the interstitial channels for bulk flow ($V_{\text{pore}}/V_x \rightarrow 1$) [39–42], and this situation could lead to even further reductions in the value of the plate height, H [39–42]. In contrast to EOF, pore diffusion is a transport process that is path dependant, and since a majority of the total number of pores could have a pore diameter equal to or less than 20 \AA , a molecule diffusing through the particle will have to pass through many small pores where frictional resistance [16,17,19,28] can significantly slow down the diffusion process and cause the value of D_p to become much less than the value of D_{mf} . The results in Fig. 1 also indicate that there is a long, shallow minimum in the H versus V_x curve which suggests that the value of the time constant for mass transfer in the pores of the particles is similar in magnitude to the time constant for mass transport in the interstitial channels for bulk flow and, furthermore, the value of the plate height, H , can be less than the value of the particle diameter, d_p , which indicates that there is very little intraparticle (internal) mass transfer resistance due to the significant magnitude of the intraparticle EOF ($V_{\text{pore}} = 0.2387V_x$); this small intraparticle mass transfer resistance causes the width (variance) of the solute band migrating through the column to be less than one particle diameter.

In Fig. 2, simulation results for the H versus V_x curves are presented for chromatographic columns packed with porous adsorbent particles having a unimodal pore-size distribution in order to determine the effects that retention (adsorption) of an uncharged analyte has on the plate height, H . The system parameters employed to obtain the results presented in Fig. 2 are identical to those shown in Fig. 1, and theoretical results obtained from Eq. (23) developed in this work are presented at four different

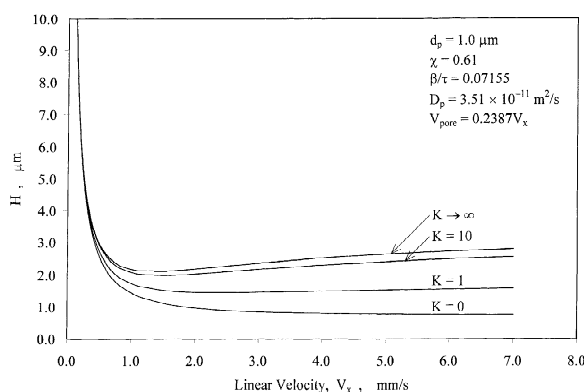


Fig. 2. Theoretical results for the plate height, H , versus the linear velocity, V_x , for a CEC column packed with porous particles having a unimodal pore-size distribution at four different values of the equilibrium adsorption constant K ; $K=0$, $K=1$, $K=10$, and $K \rightarrow \infty$.

values of the equilibrium adsorption constant, K ($K=0$, $K=1$, $K=10$, and $K \rightarrow \infty$). The results in Fig. 2 indicate that as the value of the equilibrium adsorption constant, K , increases, the value of the plate height, H , increases because the adsorption of the analyte in the pores of the particles, which provide the majority of the total surface area for adsorption in the packed column, slows down the intraparticle mass transfer rate considerably relative to the mass transfer rate in the interstitial channels for bulk flow. Furthermore, the results in Fig. 2 indicate that as the value of K becomes very large ($K \rightarrow \infty$), the H versus V_x curve reaches an asymptotic limit, because the affinity of the analyte for adsorption becomes so strong that the effect of the adsorption mechanism on the mass transfer rate in the intraparticle pores relative to the effect of the adsorption mechanism on the mass transfer rate in the interstitial pores becomes indistinguishable. It should be noted that the results presented in Fig. 2 apply only to capillary electrochromatography columns employing uncharged analytes; if the analyte is charged and its charge is opposite to that of the surface, the value of H should approach infinity as the value of the equilibrium adsorption constant, K , of a linear equilibrium adsorption isotherm becomes very large, because the increased adsorption of the charged analyte will cause the surface charge density of the particles to approach zero, or reverse its

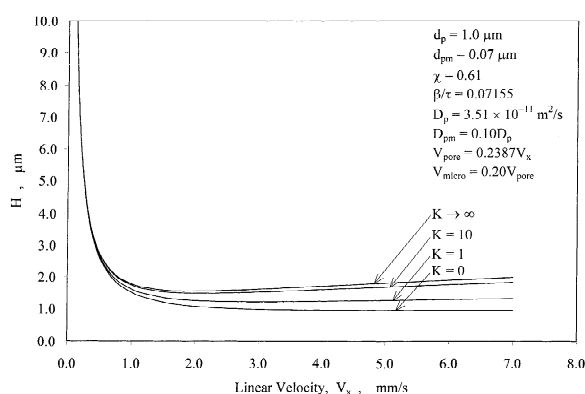


Fig. 3. Theoretical results for the plate height, H , versus the linear velocity, V_x , for a CEC column packed with porous particles having a bimodal pore-size distribution at four different values of the equilibrium adsorption constant K ; $K=0$, $K=1$, $K=10$, and $K \rightarrow \infty$.

charge, and the velocity of the EOF will go to zero, or reverse direction, respectively [18,21,22].

In Fig. 3, theoretical results for the H versus V_x curves are presented for CEC columns packed with porous particles having a bimodal pore-size distribution where EOF can occur in the macroporous and microporous regions of the adsorbent particles [Eq. (43)]. In the results presented in Fig. 3, the particle diameter, d_p , was considered to be equal to 1.0 μm , the diameter, d_{pm} ($d_{pm}=2r_{pm}$), of the subsidiary [4,6,9–13,15] particles (microspheres) was estimated to be 0.07 μm , the porosity, ϵ_p , of the macroporous region of the particles was considered to be equal to 0.49, the porosity, ϵ_{pm} , of the microporous region was taken to be 0.6, the total porosity of the particle was 0.796 (the porous particles having a bimodal pore-size distribution employed to obtain the results presented in Fig. 3 have a porosity, ϵ_p ($\epsilon_p=0.49$), for the macroporous region of the particle whose value is equal to the total porosity, ϵ_p , of the particles having a unimodal pore-size distribution and whose results were presented in Fig. 2), the value of the conductivity factor, χ , of the packed bed was considered to be equal to 0.61, the value of the free molecular diffusion coefficient, D_{mf} , of the analyte was taken to be equal to $1.0 \cdot 10^{-9} \text{ m}^2/\text{s}$, the value of the effective diffusion coefficient, D_p , of the analyte in the macroporous region of the particles was taken to be equal to

$3.51 \cdot 10^{-11} \text{ m}^2/\text{s}$, the value of the effective diffusion coefficient, D_{pm} , of the analyte in the microporous region of the particle was taken to be 10% of the value of the effective diffusion coefficient, D_p , of the analyte in the macroporous region of the particle ($D_{pm}=0.10D_p$), and the value of the velocity, V_{micro} , of the EOF in the microporous region of the particle was considered to be 20% of the value of the velocity, V_{pore} , of the EOF in the macroporous region of the particle ($V_{micro}=0.20V_{pore}$). Similar to the results presented in Fig. 2, the results presented in Fig. 3 clearly show that for a given value of V_x , the value of the plate height increases as the value of the equilibrium adsorption constant, K , increases and that the H versus V_x curve reaches an asymptotic limit as the value of K becomes very large. Furthermore, if one compares the results presented in Fig. 2 to the results shown in Fig. 3 for the CEC systems studied, it can be seen that, for a given value of V_x , (i) the value of the plate height, H , under unretained conditions ($K=0$) is larger in the CEC columns packed with porous particles having a bimodal pore-size distribution than the value of the plate height, H , in the CEC columns packed with porous particles having a unimodal pore-size distribution (where flow is considered to occur in all of the intraparticle pores and, thus, on average $V_{pore}=0.2387V_x$ in each pore of the porous particles having a unimodal pore-size distribution), and (ii) the value of the plate height, H , under retained conditions ($K \neq 0$) is smaller in the CEC columns packed with porous particles having a bimodal pore-size distribution than the value of the plate height, H , in the CEC columns packed with porous particles having a unimodal pore-size distribution (where flow is considered to occur in all of the intraparticle pores and, thus, on average $V_{pore}=0.2387V_x$ in each pore of the porous particles having a unimodal pore-size distribution). When there is EOF in the microporous region of the particles, the throughput of the analyte in the particles having a bimodal pore-size distribution can be increased relative to the throughput of the analyte in porous particles having a unimodal pore-size distribution [4] where the total porosity, ϵ_p , of the porous particle having a unimodal pore-size distribution is equal to the porosity, ϵ_p , of the macroporous region of the porous particles having a bimodal pore-size distribution and, furthermore, under these conditions the

internal surface area of the particles having a bimodal pore-size distribution would be larger than the internal surface area of the porous particles having a unimodal pore-size distribution, but because the value of the effective diffusion coefficient, D_{pm} , of the analyte in the microporous region of the particles was taken to be an order of magnitude less than the value of the effective diffusion coefficient, D_p , of the analyte in the macroporous region of the particles ($D_{pm}=0.1D_p$), the value of the pore connectivity [16,17,19,28] in the microporous region of the particles could be considered to be low and, thus, the effective path length for mass transport in the porous particle having a bimodal pore-size distribution could be considered to be larger than the effective path length for mass transfer in the porous particles having a unimodal pore-size distribution. Under retained conditions ($K \neq 0$), the increase in throughput of the analyte and the increased surface area for adsorption in the particles having a bimodal pore-size distribution provide the positive effect of reducing the mass transfer resistance [4] in the pores of the particles because the increased throughput and the larger internal surface area could increase [4] the dynamic utilization of the active sites for adsorption, while the larger effective path length for mass transport in these particles (due to the low value of the pore connectivity that was considered in the microporous region of the particles) leads to the negative effect of increasing the intraparticle mass transfer resistance. In the CEC systems shown in Fig. 3, the radius, r_{pm} , of the subsidiary particles (microspheres) is small enough such that the positive effect, with regard to increasing the dynamic utilization of the active sites for adsorption, of the increased throughput and larger internal surface area in the particles having a bimodal pore-size distribution outweigh the negative effect of the increased path length for mass transfer (due to the low value of the pore connectivity that was considered in the microporous region of the particles) in these particles and, thus, the porous particles having a bimodal pore-size distribution provide a net residence time of the analyte in these particles which is less than the net residence time of the analyte in the adsorbent particles having a unimodal pore-size distribution. Thus, under retained conditions the CEC columns packed with porous particles having a bimodal pore-

size distribution studied in this work (Fig. 3) will provide smaller values for the plate height, H , than the CEC columns packed with porous particles having a unimodal pore-size distribution for the systems studied in this work (Fig. 2). However, under unretained conditions ($K=0$), due to the fact that a low value of the pore connectivity was considered in the microporous region of the particle having a bimodal pore-size distribution which suggests that the effective path length for mass transfer is larger in the particles having a bimodal pore-size distribution than the effective path length for mass transfer in the porous particles having a unimodal pore-size distribution and, since there is no retention, the intraparticle mass transfer resistance will be dominated by dispersive effects which are directly related to the effective path length for mass transfer in the particles and, furthermore, due to the fact that on average $V_{pore}=0.2387V_x$ in each pore of the porous particle having a unimodal pore-size distribution, the positive effect of the increased throughput in the particles having a bimodal pore-size distribution cannot on its own (without the effect of retention) compensate for the negative effect of the increased path length for mass transfer. Thus, under unretained conditions, the net residence time of the analyte in the adsorbent particles having a bimodal pore-size distribution will be larger than the net residence time of the analyte in the particles having a unimodal pore-size distribution, which indicates that under unretained conditions ($K=0$) the value of the plate height, H , will be larger for the CEC columns considered in this work (Fig. 3) packed with porous particles having a bimodal pore-size distribution relative to the value of H for the CEC columns considered in this work (Fig. 2) packed with porous particles having a unimodal pore-size distribution.

In Fig. 4, simulation results for the H versus V_x curves for CEC columns packed with porous particles having a bimodal pore-size distribution are presented under conditions of no retention ($K=0$) and maximum retention ($K \rightarrow \infty$), where the value of the ratio of the velocity, V_{micro} , of the EOF in the microporous region of the particles to the velocity, V_{pore} , of the EOF in the macroporous region of the particles, is varied between 0.0 and 0.80 ($0.0 \leq V_{micro}/V_{pore} \leq 0.80$), and the values of all the other system parameters are identical to those used to

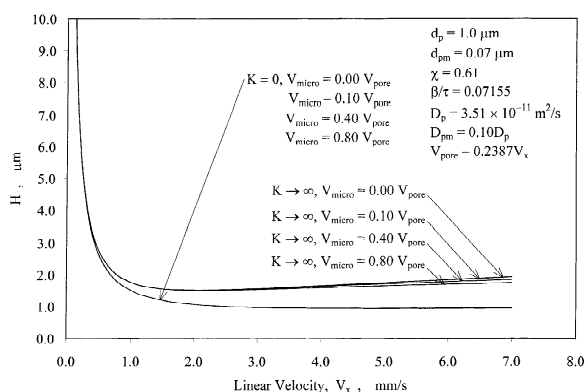


Fig. 4. Theoretical results for the plate height, H , versus the linear velocity, V_x , for a CEC column packed with porous particles having a bimodal pore-size distribution at conditions of no retention ($K=0$) and maximum retention ($K \rightarrow \infty$) for four different values of the electroosmotic velocity, V_{micro} , in the microporous region of the particles; $V_{\text{micro}} = 0.0$, $V_{\text{micro}} = 0.10V_{\text{pore}}$, $V_{\text{micro}} = 0.40V_{\text{pore}}$, and $V_{\text{micro}} = 0.80V_{\text{pore}}$, where V_{pore} denotes the linear velocity in the macroporous region of the particles.

obtain the results presented in Fig. 3. The results in Fig. 4 clearly indicate that under unretained conditions, convective flow in the microporous region has an insignificant effect on the value of the plate height, H , because for the system shown in Fig. 4 the positive effect of the convective velocity in the microporous region (increased throughput) alone cannot outweigh the negative effect of the increased path length for mass transfer (the value of the connectivity of the pores in the microporous region of the particles was considered to be small because $D_{\text{pm}} = 0.1D_{\text{p}}$). Under retained conditions the results in Fig. 4 show that convective flow in the microporous region of the particles along with the larger surface area for adsorption can reduce the intraparticle mass transfer resistance because the increased throughput of the analyte through the particle can increase the dynamic utilization of the active sites for adsorption in the particle [4]. It should be noted that the positive effect of convective flow in the microporous region could be more significant in larger in diameter, d_p , particles, when such particles could be constructed by employing subsidiary particles (microspheres) with a larger radius, r_{pm} , because a larger value of r_{pm} would cause the value of the time constant for mass transfer by convective flow in the subsidiary particles to decrease relative to the diffu-

sive time constant for mass transfer in the subsidiary particles; however, the value of the pore connectivity in the larger in radius, r_{pm} , subsidiary particles should be large in order to avoid creating a longer path length for mass transfer in the larger in diameter, d_p , particles. It is important to note here that experimentally measured values of the plate height, H , versus the linear interstitial velocity, V_x , for chromatographic columns packed with porous particles having a bimodal pore-size distribution could be used to obtain the values for (i) the ratio (V_{pore}/V_x) of the magnitude of the convective velocity, V_{pore} , in the macroporous region of the particles to the magnitude of the linear interstitial velocity, V_x , and (ii) the ratio ($V_{\text{micro}}/V_{\text{pore}}$) of the magnitude of the convective velocity, V_{micro} , in the microporous region of the particles to the magnitude of the convective velocity, V_{pore} , in the macroporous region of the particles, by employing Eq. (43) developed in this work and an appropriate parameter estimation method, while the values of the effective diffusion coefficients, D_p and D_{pm} , of the analyte in the macroporous and microporous regions of the particle, respectively, could be determined from the pore network models developed by Meyers and Liapis [16,17], Grimes et al. [19], and Meyers et al. [28] along with experimental data from the experiments described by Meyers et al. [28].

In Fig. 5, theoretical H versus V_x curves are presented for a chromatographic column packed with porous adsorbent particles of diameter $d_p = 30 \mu\text{m}$ and having a bimodal pore-size distribution, at conditions of no retention ($K=0$) and of maximum retention ($K \rightarrow \infty$). The conductivity factor, χ , of the packed bed was considered to be equal to 0.61, the porosity, ϵ_p , of the macroporous region of the particles was taken to be equal to 0.35, the porosity, ϵ_{pm} , of the microporous region of the particles was considered to be equal to 0.49, the total porosity of the particle was 0.67, the diameter, d_{pm} ($d_{\text{pm}} = 2r_{\text{pm}}$), of the subsidiary particles was taken to be equal to $1.0 \mu\text{m}$, the value of the free molecular diffusion coefficient, D_{mf} , of the analyte was considered to be equal to $1.0 \cdot 10^{-9} \text{ m}^2/\text{s}$, the value of the effective diffusion coefficient, D_p , of the analyte in the macroporous region of the particles was taken to be equal to $3.51 \cdot 10^{-10} \text{ m}^2/\text{s}$, and the value of the effective diffusion coefficient, D_{pm} , of the analyte in

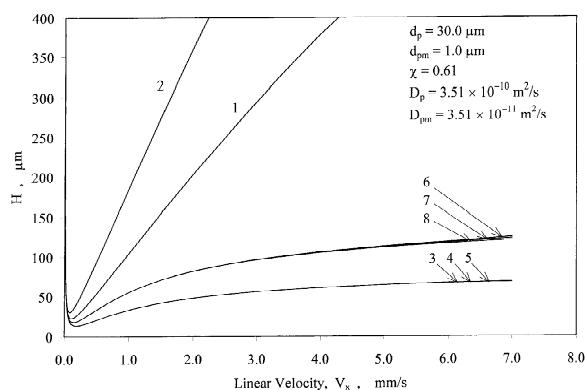


Fig. 5. Theoretical results for the plate height, H , versus the linear velocity, V_x , for an HPLC column and a hybrid HPLC–CEC column packed with porous particles having a bimodal pore-size distribution at conditions of no retention ($K=0$) and maximum retention ($K \rightarrow \infty$). V_{pore} and V_{micro} denote the linear velocity in the macroporous and microporous regions of the particles, respectively. 1=HPLC system where $K=0.0$; 2=HPLC system where $K \rightarrow \infty$; 3=hybrid HPLC–CEC system where $K=0.0$ and $V_{\text{micro}} = 0.10V_{\text{pore}}$; 4=hybrid HPLC–CEC system where $K=0.0$ and $V_{\text{micro}} = 0.40V_{\text{pore}}$; 5=hybrid HPLC–CEC system where $K=0.0$ and $V_{\text{micro}} = 0.80V_{\text{pore}}$; 6=hybrid HPLC–CEC system where $K \rightarrow \infty$ and $V_{\text{micro}} = 0.10V_{\text{pore}}$; 7=hybrid HPLC–CEC system where $K \rightarrow \infty$ and $V_{\text{micro}} = 0.40V_{\text{pore}}$; 8=hybrid HPLC–CEC system where $K \rightarrow \infty$ and $V_{\text{micro}} = 0.80V_{\text{pore}}$.

the microporous region of the particles was considered to be equal to $3.51 \cdot 10^{-11} \text{ m}^2/\text{s}$ ($D_{\text{pm}} = 0.1D_p$). When the value of the ratio of the velocity, V_{pore} , of the mobile phase in the macroporous region of the particles to the velocity, V_x , of the mobile phase in the interstitial channels for bulk flow is equal to 0.01 ($V_{\text{pore}} = 0.01V_x$) and there is no fluid flow in the subsidiary (microporous region) particles, the column system in Fig. 5 can be thought of as a high-performance liquid chromatography (HPLC) column employing perfusive particles [4,6,9–13,15,43–45]; when the value of the ratio V_{pore}/V_x is equal to 0.09 ($V_{\text{pore}} = 0.09V_x$) and there is convective flow in the subsidiary particles, the column system in Fig. 5 can be thought of as an HPLC system employing perfusive particles having in addition a small applied electrical potential difference per unit length along the column that could promote flow in both the macroporous and microporous regions of the particles (a hybrid HPLC–CEC system considering pressure-driven flow together with electrically-driven flow). The results presented in Fig. 5 indicate that

fluid flow in the microporous region will not have a significant impact on the plate height, H , when the radius, r_{pm} , of the subsidiary particles is substantially larger than the value of r_{pm} employed to obtain the results presented in Fig. 4, but the additional convective flow that occurs in the macroporous region of the particles that is considered to occur due to the application of a small electrical potential difference per unit length along the axial direction of the column has a considerable effect on reducing the value of the plate height, H , and, thus, especially under retained conditions, small values of the plate height could be achieved if one applies a small electrical potential difference per unit length along the axial direction of the column in addition to the pressure-driven flow in the HPLC column, which increases the fluid velocity both in the macroporous and microporous regions of the particles having a bimodal pore-size distribution.

In Fig. 6a, the ratio of the plate height, H_{npc} (evaluated from Eq. (14)), of a column packed with non-porous particles of diameter $d_p = 1.0 \text{ }\mu\text{m}$ to the plate height, H_{ot} (evaluated from Eq. (9)), of an open cylindrical capillary of diameter $d_c = 1.0 \text{ }\mu\text{m}$ is presented for CEC systems; in Fig. 6a the void fraction of the packed bed, ϵ_p , was taken to be equal to 0.35, the conductivity factor, χ , of the packed bed was taken to be equal to 0.61, and the value of the free molecular diffusion coefficient, D_{mf} , of the analyte was considered to be equal to $1.0 \cdot 10^{-9} \text{ m}^2/\text{s}$. The results in Fig. 6a indicate that under unretained conditions, the ratio of the plate height, H_{npc} , of a column packed with non-porous particles of diameter $d_p = 1.0 \text{ }\mu\text{m}$ to the plate height, H_{ot} , of an open tube of diameter $d_c = 1.0 \text{ }\mu\text{m}$ is essentially equal to the conductivity factor, χ , because under unretained conditions ($K=0$) the only contribution to both plate heights, H_{npc} and H_{ot} , is from axial dispersion, and because the radius, R_c ($R_c = d_c/2$), of the open capillary and the radius, R_{ic} , of the interstitial channels for bulk flow (the value of R_{ic} was taken to be equal to one-third of the value of the radius of the non-porous particles ($R_{\text{ic}} = (1/3)(d_p/2)$)) are both much greater than the magnitude of the Debye length, λ (14.88 Å), the ratio of the axial dispersion coefficient of the analyte in the column system packed with non-porous particles [Eq. (12)] to the axial dispersion coefficient of the analyte in

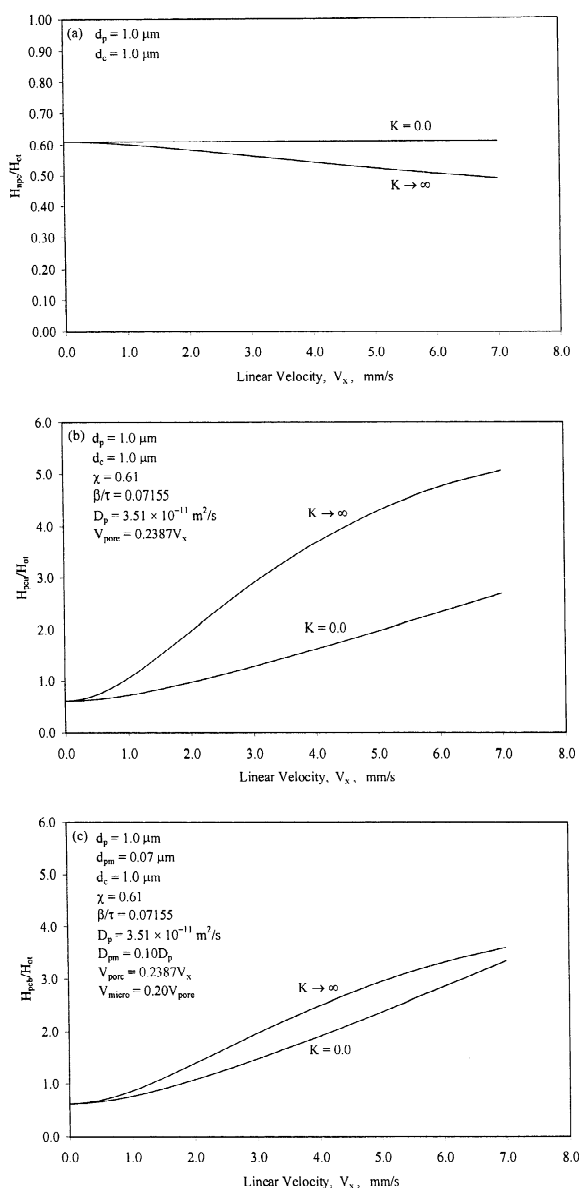


Fig. 6. (a) Ratio of the plate height, H_{npc} , for a CEC column packed with non-porous particles to the plate height, H_{ot} , of an open capillary CEC system under conditions of no retention ($K=0$) and maximum retention ($K \rightarrow \infty$). (b) Ratio of the plate height, H_{pcu} , for a CEC column packed with porous particles having a unimodal pore-size distribution to the plate height, H_{ot} , of an open capillary CEC system under conditions of no retention ($K=0$) and maximum retention ($K \rightarrow \infty$). (c) Ratio of the plate height, H_{pcb} , for a CEC column packed with porous particles having a bimodal pore-size distribution to the plate height, H_{ot} , of an open capillary CEC system under conditions of no retention ($K=0$) and maximum retention ($K \rightarrow \infty$).

the open capillary [Eq. (7)], for all practical purposes, will be equivalent to the conductivity factor, χ . However, under retained conditions, the value of the plate height, H_{npc} , for chromatographic columns packed with non-porous adsorbent particles will always be less than the value of the plate height, H_{ot} , for open capillaries whose diameter, d_c , is equal to the diameter, d_p , of the non-porous particles, because the column packed with non-porous particles can be thought of as a bundle of open capillaries whose diameter is smaller than d_p and, thus, the value of the plate height, H_{npc} , will be smaller in chromatographic columns packed with non-porous particles than the value of H_{ot} in open capillaries. In Fig. 6b, the ratio of the plate height, H_{pcu} (evaluated from Eq. (23)), of a chromatographic column packed with porous adsorbent particles having a diameter $d_p = 1.0 \mu\text{m}$ and a unimodal pore-size distribution to the plate height, H_{ot} (evaluated from Eq. (9)), of an open capillary of diameter $d_c = 1.0 \mu\text{m}$ is presented for CEC systems. The results presented in Fig. 2 for $K=0$ and $K \rightarrow \infty$ were employed in Fig. 6b for the chromatographic columns packed with porous particles having a unimodal pore-size distribution. The results presented in Fig. 6b indicate that the value of H_{pcu} is lower than the value of H_{ot} at low values of the linear interstitial velocity, V_x , where the contribution of the intraparticle mass transfer resistance to the plate height, H , is low, but as the value of V_x increases, and especially when adsorption occurs, the effect of the contribution of the intraparticle mass transfer resistance to the plate height, H , substantially increases, and thus, the open capillary provides lower values for the plate height than a column packed with porous adsorbent particles having a unimodal pore-size distribution as the value of V_x increases. In Fig. 6c, the ratio of the plate height, H_{pcb} (evaluated from Eq. (43)), of a chromatographic column packed with porous adsorbent particles having a diameter $d_p = 1.0 \mu\text{m}$ and a bimodal pore-size distribution to the plate height, H_{ot} (evaluated from Eq. (9)), of an open capillary of diameter $d_c = 1.0 \mu\text{m}$ is presented for CEC systems. The results presented in Fig. 3 for $K=0$ and $K \rightarrow \infty$ were employed in Fig. 6c for the chromatographic columns packed with porous particles having a bimodal pore-size distribution. The results shown in Fig. 6c are similar to the results presented in Fig. 6b with

respect to the dependence of the ratio $H_{\text{pcb}}/H_{\text{ot}}$ on the linear interstitial velocity, V_x . But for the reasons discussed above for Figs. 2 and 3, under unretained conditions ($K=0$) the value of the ratio $H_{\text{pcb}}/H_{\text{ot}}$ is larger than the value of the ratio $H_{\text{pcu}}/H_{\text{ot}}$ for all values of V_x , while under retained conditions ($K \neq 0$) the value of the ratio $H_{\text{pcb}}/H_{\text{ot}}$ is smaller than the value of the ratio $H_{\text{pcu}}/H_{\text{ot}}$ for all values of V_x ; therefore, for the reasons discussed above, the effect of retention on column efficiency is less significant in chromatographic columns packed with particles having a bimodal pore-size distribution than those packed with particles having a unimodal pore-size distribution (compare the results in Fig. 6b and c). It should be noted at this point that the results shown in Fig. 6a–c were obtained for uncharged analytes; if the analyte was charged and its charge was opposite to that of the stationary phase, then under retained conditions the performance of the open tube would be catastrophic [18,21,22], because in an open tube the ratio of the available surface area for adsorption to the total system volume would be very small and, thus, even the smallest amount of adsorption could cause the surface charge density of the stationary phase to approach zero or reverse its charge which would cause the EOF to stop or reverse direction, respectively [18,21,22]; this result indicates that in CEC systems employing charged solutes under retained conditions it would be desirable to employ chromatographic columns packed with adsorbent particles where the ratio of the available surface area for adsorption to the total system volume would have to be very large.

4. Conclusions and remarks

In this work, novel general expressions have been constructed and presented that describe the behavior of the height equivalent of a theoretical plate (plate height), H , as a function of the linear velocity, V_x , along the axis of the column and the kinetic parameters that characterize the mass transfer and the linear equilibrium adsorption mechanisms in chromatographic columns. Open tube capillaries as well as columns packed with either non-porous or porous particles have been studied. The porous particles could have a unimodal or a bimodal pore-size

distribution, and intraparticle convective fluid flow and pore diffusion have been considered. These expressions for H could be applicable to both HPLC and CEC systems and could be used together with experimental plate height, H , versus linear velocity, V_x , data to determine the values of the parameters that characterize intraparticle convective fluid flow and pore diffusion.

The expressions for the plate height, H , developed in this work for chromatographic columns packed with porous particles having either a unimodal or a bimodal pore-size distribution (i) account for both linear and/or non-linear concentration gradients developing in the pores of the particles, (ii) consider the intraparticle convective and diffusive mass transport mechanisms in the pores of the particles to be separate mass transport mechanisms characterized by their own individual and proper driving forces rather than considering a convection augmented diffusion coefficient [6,42–45] in the pores of the particles which has severe limitations due to the physically restricted assumption of linear concentration gradients in the pores of the particles, and (iii) consider the effects of the radial and angular components of the velocity vector of intraparticle convective flow in the pores of the spherical particles which were not considered by the authors of Refs. [6,42–45]. The results for the CEC systems studied and presented in this work have indicated that under unretained conditions porous particles having a unimodal pore-size distribution provide lower values of the plate height, H , than porous particles having a bimodal pore-size distribution where the value of the pore connectivity of the microporous region was considered to be low, while under retained conditions porous particles having a bimodal pore-size distribution where intraparticle convective flow can occur in the macroporous and microporous regions of the particles can provide lower values of the plate height, H , than porous particles having a unimodal pore-size distribution whose total porosity, ϵ_p , is equal to the porosity, ϵ_p , of the macroporous region of the particles having a bimodal pore-size distribution, if the combination of the positive effects of the increased throughput and the larger surface area for adsorption provided by the porous particles having a bimodal pore-size distribution overcome the negative effects of the longer path length for mass

transfer through the porous particle having a bimodal pore-size distribution with a low value of the pore connectivity in the microporous region; furthermore, the effect of retention on column efficiency was less significant in chromatographic columns packed with particles having a bimodal pore-size distribution than those packed with particles having a unimodal pore-size distribution. These results suggest that porous particles of diameter, d_p , having a bimodal pore-size distribution should be comprised of subsidiary particles (microspheres) whose diameter, d_{pm} , should be substantially smaller than the value of d_p and the pore connectivity of the microporous region of the particles should be large in order to obtain lower values of the plate height, H , in columns packed with porous particles having a bimodal pore-size distribution than columns packed with porous particles having a unimodal pore-size distribution.

The results obtained from the expressions for the plate height developed in this work also indicate that a significant reduction in the value of the plate height, H , can be obtained for HPLC systems employing perfusive particles whose pore structure has a bimodal pore-size distribution, if a small electrical potential difference per unit length along the column would be applied (a hybrid HPLC–CEC system) in order to increase the magnitude of intraparticle convective flow in both the macroporous and microporous regions of the perfusive particles. Furthermore, the theoretical results of this work suggest that under unretained conditions, open capillary CEC columns and CEC columns packed with non-porous particles could provide smaller values of the plate height, H , than CEC columns packed with porous particles having either a unimodal or bimodal pore-size distribution, while under retained conditions CEC columns packed with non-porous particles will provide lower values for the plate height, H , than any of the other CEC system configurations studied in this work; however, it should be noted that these results were obtained for an uncharged analyte and, thus, one should use caution when considering these results for CEC systems employing charged analytes under retained conditions, because the adsorption of a charged analyte could cause the velocity of the EOF to be significantly reduced in magnitude or even reverse direction due to the low surface area for adsorption encountered in open

capillary columns or columns packed with non-porous particles.

The experimental values of the plate height, H , for an uncharged analyte (uracil) in a CEC system comprised of a fused-silica column packed with charged porous silica C_8 particles having a unimodal pore-size distribution were compared with the theoretical results for the plate height, H , obtained from the expression developed in this work [Eq. (23)]. The agreement between theory and experiment was found to be good and, furthermore, the results obtained in this work for the transport parameters of the uncharged analyte in the pores of the silica C_8 particles agreed with the results for the transport properties of similar silica C_8 particles obtained from pore network modelling theory [28]. The results indicate that the magnitude of the intraparticle EOF in the pores of the particles is substantial while the pore diffusion coefficient was of small magnitude. But the overall intraparticle mass transfer resistance in these particles was low because of the significant contribution of the intraparticle EOF.

It is very important to indicate again that the expressions developed in previous works [6,42–45], as well as the novel general expressions constructed and presented in this work to describe the behavior of the height equivalent to a theoretical plate in chromatographic systems, are only valid for systems involving neutral (uncharged) analytes. If the analyte is charged, then the effects of (i) the electrophoretic migration of the charged analyte and of the charged species of the electrolyte, (ii) the dynamic behavior of the charged solutes in the electrical double layer, and (iii) the charged adsorptive surface (when retention occurs), must be considered [46–48] in order to describe properly the transport of the charged solutes in the liquid solution in (a) the interstitial channels for bulk flow in the packed column, (b) the liquid film (hydrodynamic boundary layer) surrounding the adsorbent particles, and (c) the liquid in the pores of the porous particles, as well as the rate of adsorption of the charged solute on the charged adsorptive surface of the particles. The recent modelling works of Liapis et al. [46], Grimes and Liapis [47], and Grimes [48] provided important and interesting contributions to the scientific understanding of the transport of charged solutes in liquid solutions in contact with charged adsorptive surfaces, as well as

to the determination and demonstration of the effects of the dynamic behavior of the electrical double layer on the adsorption rate of the charged analyte onto the charged adsorptive surface. These works [46–48] have provided the mechanistic basis for elucidating the physical phenomena that have been experimentally observed by confocal scanning laser microscopy [49–52] with regard to the transport and adsorption of a charged analyte in porous adsorbent particles involving charged adsorptive surfaces, and at the same time these works [46–48] have clearly indicated the need for significant modelling and experimental (where the experiments are guided by modelling) research efforts in chromatographic systems involving charged analytes adsorbing onto charged adsorptive surfaces in order to further advance our scientific understanding of the dynamic and equilibrium interactions among the electrically-driven and/or pressure-driven convective flows, and diffusional, electrophoretic, and adsorption mechanisms.

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References

- [1] C.M. Guttman, E.A. DiMarzio, *Macromolecules* 3 (1970) 681.
- [2] M.E. van Kreveland, N. van den Hoed, *J. Chromatogr.* 149 (1978) 71.
- [3] A.I. Liapis, M.A. McCoy, *J. Chromatogr.* 599 (1992) 87.
- [4] A.I. Liapis, *Math. Modelling Sci. Computing* 1 (1993) 397.
- [5] M.A. McCoy, A.I. Liapis, K.K. Unger, *J. Chromatogr.* 644 (1993) 1.
- [6] D.D. Frey, E. Schweinheim, C. Horvath, *Biotechnol. Prog.* 9 (1993) 273.
- [7] A.I. Liapis, M.A. McCoy, *J. Chromatogr. A* 660 (1994) 85.
- [8] A.I. Liapis, K.K. Unger, in: G. Street (Ed.), *Highly Selective Separations in Biotechnology*, Blackie, Glasgow, UK, 1994, p. 121.
- [9] A.I. Liapis, Y. Xu, O.K. Crosser, A. Tongta, *J. Chromatogr. A* 702 (1995) 45.
- [10] G.A. Heeter, A.I. Liapis, *J. Chromatogr. A* 711 (1995) 3.
- [11] Y. Xu, A.I. Liapis, *J. Chromatogr. A* 724 (1996) 13.
- [12] G.A. Heeter, A.I. Liapis, *J. Chromatogr. A* 734 (1996) 105.
- [13] G.A. Heeter, A.I. Liapis, *J. Chromatogr. A* 743 (1996) 3.
- [14] D. Coelho, M. Shapiro, J.F. Thovert, P.M. Adler, *J. Colloid Interface Sci.* 181 (1996) 169.
- [15] G.A. Heeter, A.I. Liapis, *J. Chromatogr. A* 760 (1997) 55.
- [16] J.J. Meyers, A.I. Liapis, *J. Chromatogr. A* 827 (1998) 197.
- [17] J.J. Meyers, A.I. Liapis, *J. Chromatogr. A* 852 (1999) 3.
- [18] A.I. Liapis, B.A. Grimes, *J. Chromatogr. A* 877 (2000) 181.
- [19] B.A. Grimes, J.J. Meyers, A.I. Liapis, *J. Chromatogr. A* 890 (2000) 61.
- [20] A.I. Liapis, B.A. Grimes, *J. Colloid Interface Sci.* 229 (2000) 540.
- [21] B.A. Grimes, A.I. Liapis, *J. Chromatogr. A* 919 (2001) 157.
- [22] B.A. Grimes, A.I. Liapis, *J. Colloid Interface Sci.* 234 (2001) 223.
- [23] A.I. Liapis, *Sep. Purif. Methods* 19 (1990) 133.
- [24] M.A. McCoy, A.I. Liapis, *J. Chromatogr.* 548 (1991) 25.
- [25] A. Tongta, A.I. Liapis, D.J. Siehr, *J. Chromatogr. A* 686 (1994) 21.
- [26] A.I. Liapis, A. Tongta, O.K. Crosser, *Math. Modelling Sci. Computing* 5 (1995) 1.
- [27] B.H. Arve, A.I. Liapis, *AIChE J.* 33 (1987) 179.
- [28] J.J. Meyers, S. Nahar, D.K. Ludlow, A.I. Liapis, *J. Chromatogr. A* 907 (2001) 57.
- [29] C.L. Williams, A.R. Bhakta, P. Neogi, *J. Phys. Chem. B* 103 (1999) 3242.
- [30] S.K. Griffiths, R.H. Nilson, *Anal. Chem.* 71 (1999) 5522.
- [31] B.A. Grimes, Report No. 3, Department of Chemical Engineering, University of Missouri-Rolla, Rolla, MO, 2002.
- [32] J. Happel, H. Brenner, *Low Reynolds Number Hydrodynamics with Special Applications to Particulate Media*, Prentice-Hall, Englewood Cliffs, NJ, 1965.
- [33] D.J. Gunn, *Chem. Eng. Sci.* 42 (1987) 363.
- [34] G.A. Heeter, Ph.D. Dissertation, Department of Chemical Engineering, University of Missouri-Rolla, Rolla, MO, USA, 1997.
- [35] G. Stephanopoulos, K. Tsiveriotis, *Chem. Eng. Sci.* 44 (1989) 2031.
- [36] C. Grammling, C. Harvey, L. Miegs, in: *Proceedings of the International Groundwater Symposium*, 25–28 March, 2002, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.
- [37] S. Lüdtke, Ph.D. Dissertation, Institut für Anorganische Chemie and Analytische Chemie, Johannes Gutenberg-Universität, Mainz, 1999.
- [38] H. Brenner, L.J. Gaydos, *J. Colloid Interface Sci.* 58 (1977) 312.
- [39] R. Stol, W.T. Kok, H. Poppe, *J. Chromatogr. A* 853 (1999) 45.
- [40] R. Stol, W.T. Kok, H. Poppe, *J. Chromatogr. A* 887 (2000) 199.
- [41] R. Stol, W.T. Kok, H. Poppe, *J. Chromatogr. A* 914 (2001) 201.

- [42] R. Stol, H. Poppe, W.T. Kok, *Anal. Chem.* 73 (2001) 3332.
- [43] A.E. Rodrigues, L. Zuping, J.M. Loureiro, *Chem. Eng. Sci.* 46 (1991) 2765.
- [44] A.E. Rodrigues, J.M. Loureiro, R.M.Q. Ferreira, *Chem. Eng. Commun.* 107 (1991) 21.
- [45] A.E. Rodrigues, J.C. Lopes, Z.P. Lu, J.M. Loureiro, M.M. Dias, *J. Chromatogr.* 590 (1992) 93.
- [46] A.I. Liapis, B.A. Grimes, K. Lacki, I. Neretnieks, *J. Chromatogr. A* 921 (2001) 135.
- [47] B.A. Grimes, A.I. Liapis, *J. Colloid Interface Sci.* 248 (2002) 504.
- [48] B.A. Grimes, Ph.D. Dissertation, Department of Chemical Engineering, University of Missouri-Rolla, Rolla, MO, USA, 2002.
- [49] A. Ljunglöf, R. Hjorth, *J. Chromatogr. A* 743 (1996) 75.
- [50] A. Ljunglöf, J. Thömmes, *J. Chromatogr. A* 813 (1998) 387.
- [51] A. Ljunglöf, P. Bergvall, R. Bhikhabhai, R. Hjorth, *J. Chromatogr. A* 844 (1999) 129.
- [52] A. Ljunglöf, Ph.D. Dissertation, Center for Surface Biotechnology, Uppsala University, Uppsala, 2002.