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The effect of the frictional heat on retention and efficiency in thermostated or insulated chromatographic columns packed with sub-2- μm particles

Nándor Lambert^a, Attila Felinger^{a,b,c,*}

^a MTA–PTE Molecular Interactions in Separation Science Research Group, Ifjúság útja 6, H–7624 Pécs, Hungary

^b Department of Analytical and Environmental Chemistry and Szentágotthai Research Center, University of Pécs, Ifjúság útja 6, H–7624 Pécs, Hungary

^c Institute of Bioanalysis, Medical School, University of Pécs, Szigeti út 12, H–7624 Pécs, Hungary

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ABSTRACT

The mass-transfer properties of a core-shell packing material with 1.6 μm particle diameter, and that of a fully porous packing material with 1.7 μm particle diameter were investigated and compared. The first absolute and the second central moments of the peaks of the homologous series of alkylbenzenes, over a wide range of mobile phase velocities were measured and used for the calculation of the mass-transfer coefficients. For the evaluation of the band broadening caused by the thermal dissimilarities, the measurements were carried out under thermostated conditions and also at near adiabatic insulation of the columns.

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1. Introduction

High separation efficiency and the simultaneous reduction of analysis time in liquid chromatography can be achieved by decreasing the particle diameter of the column packing material [1–3]. Although, the efficiency that can be reached on a column is inversely proportional with the particle size, the operating back pressure is inversely proportional with the square of the particle diameter. The use of smaller particles leads to elevated operation pressure and optimum mobile phase velocity combined with the use of higher flow-rate, which results in thermal dissimilarities in the column through the generated frictional heat of the mobile phase [4].

Previous findings show the difference in efficiency loss using different thermostating procedures such as the still air, forced air or water bath thermostating [5]. Although there are studies that assume that still air thermostating is almost adiabatic, in reality, significant difference can be observed between the still-air ther-

mostated and the near adiabatic measurements [6]. More recent studies of Gritti et al. characterize the effect of frictional heat by applying high vacuum and using low-emissivity surface material to minimize the heat loss. Nevertheless, the method provides the ability to control heat dissipation through the column wall, it requires quite difficult technical solutions and sufficient instrumentation [7,8].

When the column is thermostated, and the temperature of the column wall is kept constant, a radial temperature gradient can be observed in the column between the center and the wall. Therefore, the velocity of the mobile phase will be higher at the middle of the column than near the wall. Several studies demonstrate that the efficiency loss caused by the thermal effects can be significant in case of very fine packing materials [9,10]. The effect of the frictional heating on the retention of small molecules and protein mixtures was studied also extensively in the previous years [11–13], while more recently the visualization of the evolving thermal heterogeneities was solved using infrared thermal imaging [14]. However, the identification of the contribution of the frictional heating to the band broadening is rather difficult.

With the insulation of the column, the radial temperature gradient can be eliminated. In this study the role of the efficiency loss due to the thermal dissimilarities in the mobile phase will be evaluated using the general rate model of chromatography, employing

* Corresponding author at: Department of Analytical and Environmental Chemistry and Szentágotthai Research Center, University of Pécs, Ifjúság útja 6, H–7624 Pécs, Hungary.

E-mail address: felinger@ttk.pte.hu (A. Felinger).

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various methods for the evaluation of the different mass-transfer contributions to the theoretical plate heights that are observable on the examined columns.

2. Theory

As it is shown by Eq. (1) the generated heat power depends on the mobile phase velocity and the pressure drop along the column. Therefore, frictional heat becomes substantial at elevated mobile phase flow rates, when working at high inlet pressure:

$$P_f = F_V \times \frac{\Delta P}{L}, \quad (1)$$

where P_f is the frictional power given in W/m, ΔP is the pressure drop, L is the column length and F_V is the flow-rate.

The generated heat leads to temperature increase inside the column (especially when heat is poorly dissipated) and forms both radial and longitudinal temperature gradients that affects the retention and the band broadening of the analyte as well [11,15]. Experiments show that an efficiency loss due to the frictional heat takes place when the friction power exceeds about 4 W/m [16].

Under perfectly adiabatic conditions, only axial temperature gradients would exist, resulting in only the decrease of the apparent retention factor with the increase of the flow rate. In actual chromatographic systems, a part of the generated heat is lost through the heat convection of the mobile phase, and thermal diffusion across the column cross-section. As the column reaches thermal equilibrium, a radial temperature gradient will be formed, causing radial gradients of eluent viscosity and velocity and also radial variation of the retention factors of the solutes [17,18]. The effect of the radial retention gradient is more pronounced in case of well retained compounds, since their migration velocity is larger in the column center where the temperature is higher than close to the column wall [16].

2.1. The general rate model

The general rate model of chromatography assumes that diffusion drives the sample molecules from the stream of the mobile phase into the particles and inside the pores of the stationary phase particles. The mobile phase is stagnant in the pores of the particles, and the adsorption–desorption process take place between the still mobile phase region and the surface of the pores [19].

The moments of a chromatographic peak, calculated from the general rate model allow the derivation of a detailed plate height equation [20,21].

The retention time, or first absolute moment (μ_1) of a chromatographic peak can be written as

$$\mu_1 = \frac{\int C(t)t dt}{\int C(t)dt} = \frac{L}{u_h}(1 + k_1), \quad (2)$$

with

$$k_1 = F[\varepsilon_p + K(1 - \varepsilon_p)] \quad (3)$$

and

$$F = \frac{1 - \varepsilon_e}{\varepsilon_e} \quad (4)$$

where $C(t)$ is the chromatographic band profile, L the length of the column, u_h the interstitial velocity of the mobile phase, ε_e and ε_p the external and internal porosities respectively, K is the equilibrium constant of the adsorption or partition, and F is the column phase ratio.

The second central moment calculated via the general rate model is expressed as follows:

$$\mu_2 = \frac{\int C(t)(t - \mu_1)^2 dt}{\int C(t)dt} = \frac{2L}{u_h} \left[\frac{D_L}{u_h^2} (1 + k_1)^2 + \frac{Fa^2}{u_h} \left(\frac{r_p}{3k_{ext}} + \frac{r_p^2}{15D_p} \right) \right] \quad (5)$$

where D_L is the axial dispersion coefficient, k_{ext} the external mass-transfer coefficient, D_p the intraparticle diffusion coefficient, and r_p is the average particle radius. The moments calculated from the general rate model allow the derivation of the following plate height equation:

$$H = L \frac{\mu_2'}{\mu_1^2} = \frac{2D_L}{u_h} + \frac{2u_h}{F} \left(\frac{k_1}{k_1 + 1} \right)^2 \left(\frac{r_p}{3k_{ext}} + \frac{r_p^2}{15D_p} \right). \quad (6)$$

In case of core–shell particles, the plate height equation (Eq. (6)) must be corrected, because of the altered geometry of diffusion paths inside the particles. Due to the presence of the solid core, the plate height equation will take the following form [22,23]:

$$H = L \frac{\mu_2'}{\mu_1^2} = \frac{2D_L}{u_h} + \frac{2u_h}{F} \left(\frac{k_1}{k_1 + 1} \right)^2 \left(\frac{r_p}{3k_{ext}} + \frac{r_p^2}{15D_p} R \right) \quad (7)$$

where R is expressed as follows:

$$R = \frac{r_p^4 + 2r_p^3 r_i + 3r_p^2 r_i^2 - r_p r_i^3 - 5r_i^4}{(r_p^2 + r_p r_i + r_i^2)^2}, \quad (8)$$

where r_i and r_p are the internal, and the external radii of the porous shell of the superficially particles. For a fully porous particle $R = 1$.

The axial dispersion coefficient, D_L , must be known to characterize the band broadening in the interstitial volume of the column. Gunn's correlation [24] is widely used to estimate the axial dispersion coefficient. In this study a simplified form of the Gunn correlation was used, written with convenient chromatographic terms resulting in the following equation [20,21]:

$$\frac{2D_L}{u_h d_p} = \frac{2\gamma}{v} + \frac{2\lambda\omega v/F}{2\lambda + \omega v/F} \quad (9)$$

where γ was determined via peak parking (arrested flow) and was found as $\gamma = 0.67$ and $\gamma = 0.84$ for the Cortecs and the BEH column, respectively, $\lambda = 2.586$, $\omega = 0.0712$, F is the phase ratio (Eq. (4)) and v the reduced interstitial velocity is given as:

$$v = \frac{u_h d_p}{D_m}. \quad (10)$$

The numerical values of the parameters were determined by the fitting Eq. (9) to the Gunn correlation over a wide range of reduced interstitial velocities [20]. For the systems investigated in this study, the axial dispersion calculated by Eq. (9) resulted in values rather similar to those that can be obtained by the protocol suggested by Gritti and Guiochon [25].

The external mass transfer coefficients were calculated using the Wilson–Geankoplis equation [26]:

$$k_{ext} = \frac{1.09}{\varepsilon_e} u_h^{1/3} \left(\frac{D_m}{d_p} \right)^{2/3} \quad (11)$$

where D_m is the molecular diffusion coefficient which can be derived for small molecules with the Scheibel equation [27]:

$$D_m = \frac{8.2 \times 10^{-8} T}{\eta_B V_a^{1/3}} \left[1 + \left(\frac{3V_b}{V_a} \right)^{2/3} \right] \quad (12)$$

where D_m is given in cm^2/s , the viscosity of the mobile phase (η_B) is given in cP, T is the absolute temperature and V_a and V_b are the molar volumes (mL/mol) of the solute and the solvent at their normal boiling points.

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