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Influence of cross-section geometry on band broadening in plug-flow microchannels

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Abstract

An expression is derived for the plate height attributed to an analyte band transported with uniform flow through a narrow straight microchannel having arbitrary cross-section geometry. The derived expression represents the plate height as a function of the retention factor, parameters describing the adsorption dynamics, and bulk and interfacial diffusion coefficients of the analyte. Additionally, the plate height depends on a dimensionless geometrical factor, for which an expression is obtained to be valid for arbitrary cross-section geometry. Considering different examples (circle, parallel planes, annulus, arbitrary circumscribed polygon, rectangle and ellipse), it is shown that cross-section geometry strongly affects the band broadening. It is discussed how the plate height depends on the system parameters.

Keywords: Microchannels

1. Introduction

In recent years, there have been a growing progress in developing high performance and fast analytical techniques, which employ microchannels for separation and transportation of substances, analytes (Huang et al., 1999; Krylov and Dovichi, 2000; Malik, 2002; Pesek and Matyska, 2000). To a large extent, in these studies, success was achieved due to the ability to drive analyte molecules with a relatively high (of order of 10^{-3} m/s) and, simultaneously, nearly uniform velocity. By creating a uniform (plug) flow of an analyte, one can avoid the Taylor dispersion (longitudinal band broadening due to flow non-uniformity within a cross-section, Taylor, 1953) thereby, increasing the resolution, efficiency and productivity of analytical devices (Gas et al., 1995; Gas and Kenndler, 2000, 2002).

In microchannels, a nearly uniform flow of an analyte is produced by applying an electric field to the channel ends. The latter gives rise to an electrically driven hydrodynamic (electroosmosis) flow having a uniform velocity within the channel except for the thin double layer regions adjacent to the wall. Such an electro-osmotic flow provides nearly uniform convective flow of analyte. The charged analyte molecules are additionally involved in a migration motion—electrophoresis that, under certain conditions, has nearly uniform velocity as well. For many cases of great practical importance, the weak non-uniformities of the electroosmotic and electrophoretic flows do not lead to a noticeable band broadening. For such cases, the plug-flow model yields a good description of the behavior of an electrically driven band of an analyte (Gas et al., 1995; Gas and Kenndler, 2000, 2002).

Dealing with uniform flow of an analyte, the major mechanism of band broadening is associated with a violation of the thermodynamic equilibrium of the analyte adsorption at the channel walls (Aris, 1959; Giddings, 1961, 1965; Gas et al., 1995; Gas and Kenndler, 2000, 2002) The band broadening due to the incomplete adsorption equilibrium strongly affects performance of the open electrochromatographic and electrophoretic columns.

The influence of adsorption kinetic on the band broadening was analyzed by many authors (Aris, 1959; Giddings, 1961, 1965; Liu et al., 1992; McEldoon and Datta, 1992; Martin and Guiochon, 1984; Martin et al., 1985; Gas et al., 1995; Rathore and Horvath, 1996; Schure and Lenhoff, 1993;

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Koutny et al., 1996; Poppe, 2002; Dutta and Leighton, 2003a; Paces et al., 2003). Most of these studies were concerned with circular and plane parallel channels. For such cross-section geometries, considering a linear equation of adsorption dynamics, the analytical expressions for the plate height were obtained in the classic publications of Giddings (1961, 1965). Among the few studies dealing with other types of geometries, there is the classic paper of Aris (1959), who considered an annulus with one adsorbing wall. Recently, Poppe (2002) conducted numerical analysis of the band broadening in rectangular channels. Using the plug-flow model, Dutta and Leighton (2003a) derived an analytical expression for the dispersion coefficient attributed to rectangular cross-sections.

It should be noted that, very often, the channels employed in microfluidic techniques have cross- section geometries substantially different from the already analyzed examples, Huang et al. (1999); Koutny et al. (1996), Bianchi et al. (2001). Some authors, Dutta and Leighton (2001, 2002, 2003b), Lim et al. (2004), consider a variation of the cross-section geometry as a mean of improving performance of microfluidic devices. Thus, a theory is required which would be capable of addressing the band broadening in a plug-flow channel having an arbitrary cross-section geometry. In the present paper, using a modification of the plate height approach developed by Giddings (1961, 1965), we will describe the band broadening of an analyte moving with uniform velocity through a channel with an arbitrary cross-section and interacting with the channel walls according to linear adsorption dynamics.

2. Plate height approach and previous results

In this section, we will give some comments regarding the plate height approach and present three expressions derived in literature for the plate height attributed to the plug-flow channels with circular, plane parallel, Giddings (1961, 1965), and rectangular cross-sections, Dutta and Leighton (2003a).

For sufficiently long and narrow channels, mathematical modeling of the concentration band behavior is often conducted in terms of the plate height, H. The corresponding analysis is based on the fact that, under certain conditions, the time-dependent longitudinal distribution of the analyte concentration, $C(x,t)$, is approximated by a solution of

$$\frac{\partial C}{\partial t}+u_c\left(\frac{\partial C}{\partial x}-\frac{1}{2}H\frac{\partial^2 C}{\partial x^2}\right)=0, \tag{1}$$

where x and t are the longitudinal coordinate and time, respectively. Under certain conditions, Eq. (1) can be used for describing both the convective and electrophoretic transport of an analyte.

For a given initial distribution, $C(x,0)$ solving Eq. (1) one obtains the concentration distribution for any given time, t, $C(x,t)$. Typical behavior of the solution of Eq. (1) is illustrated in Fig. 1 where the movement of the concentration band is accompanied by its broadening. It can be shown that, in Eq. (1), the parameter u_c is the velocity of analyte band center of mass. The parameter H, the plate height, describes the change in the concentration distribution squared variance, σ^2 while moving the band for a unit distance (Fig. 1). Thus, the importance of the parameter, H, is that, for any given transportation distance, using a known value of H one can predict the expected changes in the band variance.

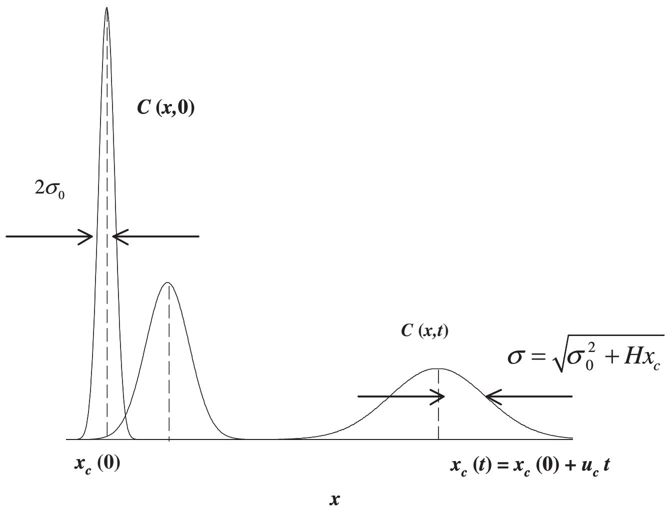

Fig. 1. Illustration of the behavior of the solution of Eq. (1).

For any particular system, obtaining an expression for the plate height amounts to rearranging the analyte mass balance equations in order to reduce them to Eq. (1). Automatically, such a rearrangement yields the required inter-relation between the plate height and the parameters employed in the original mass balance equations. In the next sections, such an approach will be used for obtaining the plate height for an analyte transported through a plug-flow channel.

Now, we will present the earlier obtained expressions that describe the plate height, H, for the circular, plane parallel and rectangular cross-sections. In the publications of Giddings (1961, 1965) and Dutta and Leighton (2003a, b), the adsorption-desorption rate at the channel wall, q, was addressed using the following equation:

$$q=-\frac{\Gamma-k_A C_B}{\tau_A}\quad \text{at the wall,} \tag{2}$$

where Γ is the local value of adsorption, C_B, is the bulk analyte concentration; τ_A is the time scale rate constant and k_A is the adsorption equilibrium constant.

The plate heights obtained by Giddings (1961, 1965) and Dutta and Leighton (2003a, b) for the circular, plane parallel and rectangular cross-sections can be represented in a common form

$$H=\frac{2}{u}\left[D_B+\frac{1-R}{R}D_A\right] +2u\left[(1-R)^2\frac{d^2}{D_B}+R(1-R)\tau_A\right], \tag{3}$$

where D_B and D_A are the analyte diffusion coefficients in the bulk and in the adsorption layer, respectively. The dimensionless parameter R, which is referred to as the retention factor,