Journal of Chromatography A, 1225 (2012) 193–195

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Discussion

Reply to Comments on the separation efficiency of asymmetrical Flow Field-Flow fractionation in channels of constant channel and crossflow velocities leading to constant separation efficiency

P. Déjardin*

Institut Européen des Membranes, Université Montpellier 2 (ENSCM, UM2, CNRS), CC047, 2 Place Eugène Bataillon, F-34095 Montpellier Cedex 5, France

ARTICLE INFO

Article history:
Received 2 November 2011
Received in revised form
15 December 2011
Accepted 19 December 2011
Available online 31 December 2011

Keywords:
Flow Field-Flow fractionation
Membrane
Channel geometry
Constant separation efficiency
Asymmetric

ABSTRACT

The membrane or cross-flow velocity in asymmetric Flow Field-Flow fractionation is not constant in usual geometries. Previously theoretical models however were developed with the hypothesis of a constant membrane velocity. The argument about peak broadening in the comments of K.-G. Wahlund (J. Chromatogr. A 1218 (2011) 6848) is based on this kind of model. Such an assumption was not included in the recently proposed model used to determine the conditions of constant velocities. The model goes beyond this approximation and anyway can provide the two velocity fields in various geometries.

1. Introduction

The two recent papers [1,2] analyzing the conditions to obtain constant channel and crossflow velocities in asymmetric Flow Field-Flow fractionation were aimed to go beyond the simple idea that such result could be obtained only by decreasing the channel breadth. It was demonstrated that, according to the model, the exponential breadth variation was a necessary condition, but moreover it has to be associated with variation of membrane resistance or permeate channel height as a function of distance. The core of the papers was the model developed to provide the field of pressure in the channels as a function of distance. Contrary to the affirmation in [3]: “Both designs lead to almost, but not perfectly [1], uniform channel flow velocity and crossflow velocity”, both designs lead to perfectly constant velocities, of course according to the chosen model. It was also suggested in [1] that the constant separation efficiency “might contribute reducing the presently observed peak broadening”, a point which is criticized in [3] and presented wrongly as the main claim. In those two papers indeed, we did not analyze the band broadening as it is dependent on many parameters. At least however, as far as the aim of experimentalists was to get a constant channel velocity to compare with other conditions, it seemed useful to propose the conditions of an experimental setup where the claimed condition of constant velocity would be really satisfied. We will comment below the analysis about peak broadening in [3] after recalling some background about theoretical models.

2. Background

In a hydraulic (electric) circuit with derivations, one cannot determine the local flow rates (currents or current densities) without any knowledge of the hydraulic (electric) resistances. The model developed in [1,2] was precisely used to determine if there existed a combination of resistances allowing constant velocities; and if yes, what was this combination.

It was recalled in [3]: “It has been shown that a constant mean channel flow velocity may be obtained in asymmetrical FlFFF with a channel of exponential geometry and with suitable volumetric flow rates at inlet and outlet [4]”. The model developed in [1,2] leads to a result somewhat different as, in addition, the membrane resistance or permeate channel section is a function of distance to entrance. The difference between both approaches originates from the absence of the assumption of constant cross-flow or membrane velocity in the recent model, whereas it is assumed to be constant in [4] for the three channel geometries (rectangular, trapezoidal and exponential) and in [5] for the analysis of zone broadening with rectangular and trapezoidal geometries. Formally, with the

* Tel.: +33 467149121; fax: +33 467149119.
E-mail address: dejardin@iemm.univ-montp2.fr

0021-9673/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2011.12.067

axial flow in the z direction, the new model treats differently the condition:

$$dq_c(z) + q_m(z) = 0 \quad (1)$$

where $q_c(z)$ is the flow rate in the sample channel at distance z from the entrance, and $q_m(z)$ is the cross flow rate through the membrane (+support) at position z, with the convention of being positive when the flow occurs from sample channel to permeate compartment. A positive flow rate through the membrane is associated with a negative variation $dq_c(z)$. For a sample channel of height w_1 and constant breadth, the mean axial velocity $v_c(z)$ in the channel and the velocity through the membrane $v_m(z)$ at distance z, are then linked by the relation:

$$v_m(z) = -w_1 \frac{dv_c}{dz} \quad (2)$$

In previous works [4–7], the membrane velocity was always assumed to be constant over the channel length L, thus for a channel of constant breadth:

$$v_m = -w_1 \frac{dv_c}{dz} = -w_1 \frac{v_c(z) - v_c(0)}{z} = -w_1 \frac{v_c(L) - v_c(0)}{L} \quad (3)$$

Let Λ_1 and Λ_2 be the characteristic lengths of the membrane (+support)/channel assembly for the sample and permeate channels respectively [2]. Index 1 is relative to the sample channel, index 2 to the permeate channel. We consider a membrane of constant characteristics over the length of the channels. Entrance of the channels is positioned at $z=0$, exit at $z=L$. Let us use the dimensionless variables $Z=z/L$ and $L_i^* = L/\Lambda_i$. $P_i(Z)$ is the pressure difference between the pressure at position Z and a reference like the atmospheric pressure P_0 for instance. We have for channels of constant breadth and height (from Eqs. (10)–(11) in [2] with $s=0$ and the ratio $W_2=w_2/w_1$ of the two heights constant):

$$\frac{d^2P_1}{dz^2} - L_1^{*2}(P_1 - P_2) = 0 \quad (4a)$$

$$\frac{d^2P_2}{dZ^2} + L_2^{*2}(P_1 - P_2) = 0 \quad (4b)$$

The difference of the two equations lead directly to the differential equation for the pressure difference $\Delta P(Z)=P_1(Z)-P_2(Z)$ between both channels which is proportional to the membrane velocity $v_m(z)$:

$$\frac{d^2\Delta P}{dZ^2} - (L_1^{*2} + L_2^{*2})\Delta P = 0 \quad (4c)$$

It is clear that the solution of Eq. (4c) is not $\Delta P(Z)=$Constant. If the breadth $b(Z)$ is not constant *and the same in both channels*, we arrive at the same conclusion from the equation:

$$\frac{d^2\Delta P}{dZ^2} + \frac{1}{b}\left(\frac{db}{dZ}\right)\frac{d\Delta P}{dZ} - (L_1^{*2} + L_2^{*2})\Delta P = 0 \quad (5)$$

and to different solutions depending of the function $b(z)$. As a summary, the membrane velocity is not constant over the length of the cell. It can be evaluated as well as the sample channel velocity by the analytical solutions of the preceding equations with the appropriate boundary conditions. Recently, the method was applied to the analysis of the void-time determination [8] for a classical rectangular channel: taking into account the resistances, it is clear that the cross-flow velocity is not constant over the cell length, even if the mean value is null. It presents a "reversal point": before that point, the cross-flow occurs from sample channel to the permeate or reservoir compartment, whereas after that point it occurs from the reservoir compartment to the sample channel. It is expected that the reversal point moves when allowing a fraction of the entrance flow rate to flow out via the permeate compartment exit.

This model allows the description of various conditions which may occur in experiments for instance when programming the exit flow rates. As stated in [5] "a good theoretical description is important for the optimizations of the separation conditions". The mean velocity of the fluid in the sample channel $v_c(z)$ and the velocity through the membrane $v_m(z)$ are related to the field of pressure by the following expressions, where η is the viscosity of the fluid and Λ_m the characteristic length of the membrane [2]:

$$v_m(z) = \Delta P(z)\frac{\Lambda_m}{12\eta} \quad (6a)$$

$$v_c(z) = -\frac{dP_1}{dz}\frac{w_1^2}{12\eta} \quad (6b)$$

3. Peak broadening

In previous works of the literature it was always implicit that the membrane velocity was constant, the problem being the variations of the channel velocity, and the analyses of the peak broadening were performed in accordance with this framework. However, such an analysis would benefit from knowing both velocities all along the cell when performing experiments in constant or varied (programming) conditions of flow. The criticism in [3] is based on the assumption of constant membrane velocity, which is not realized in usual cell geometries. However, an improved interpretation would be to include these variations and determine the conditions of application of the approximations. Following the method of Litzen and Wahlund (Eq. (22) in [5]), where the factor χ is here dependent of the non constant membrane velocity, with the sample velocity averaged over its exponential distribution in the high retention limit $V=(6D/w_1)(v_c/v_m)$, D being the diffusion coefficient of the solute, the plate height is:

$$\bar{H} = L\frac{w_1^2}{D}\frac{\int_0^L \chi(v_m)\frac{v_m^2}{v_c}dz}{\left(\int_0^L \frac{v_m}{v_c}\,dz\right)^2} \quad (7)$$

and using the relation (2) for a channel of constant breadth:

$$\bar{H} = L\frac{1}{D}\frac{\int_0^L \chi(v_m)\frac{v_m^2}{v_c}dz}{\left(\ln\frac{v_c(L)}{v_c(0)}\right)^2} \quad (8)$$

Assuming $\chi \approx 24\lambda^3$ in the high retention limit, with $\lambda=l/w_1$ where l is the characteristic length of the exponential distribution of the sample ($l=D/v_m$), this expression becomes:

$$\bar{H} = L\frac{24D^2}{w_1^3}\frac{\int_0^L \frac{dz}{v_c v_m}}{\left(\ln\frac{v_c(L)}{v_c(0)}\right)^2} \quad (9)$$

provided the assumptions are verified over the full length of the channel. Otherwise, it may be needed to change the integration domain. Let us note that, for channels of non constant breadth $b(z)$, the relation (2) becomes:

$$v_m(z) = -w_1\left(\frac{dv_c}{dz} + \frac{1}{b}\frac{db}{dz}v_c\right) \quad (10)$$

The integral of the denominator takes then the more general expression

$$\int_0^L \frac{v_m}{v_c}\,dz = w_1 \ln\left(\frac{q_{c,in}}{q_{c,out}}\right) \quad (11)$$

where $q_{c,in}$ and $q_{c,out}$ are the flow rates at entrance and exit of the sample channel respectively.

4. Conclusion

Contrary to chromatography, the two fields of separation and transport are not independent in asymmetric Flow Field-Flow fractionation. The normal separation field (or v_m) and the longitudinal separation and transport field (or v_c) are interdependent through the relation (10) all over the length of the channels. The proposition in [1] about the possible improvement of separation, which was not at all the main claim, was very prudent ("might help"), being aware that many parameters are determining the resolution power. Contrary to what is written in [3], the aim was not in those papers to evaluate, discuss and predict the overall efficiency of asymmetrical Flow-FFF channels. It was to determine the experimental conditions to obtaining constant velocities, hence providing a better experimental model for comparison with theory. Anyway replying to those comments is a good opportunity to position the model with respect to previous ones and claim as in [8] that a sound interpretation of the experiments would require the knowledge of the characteristics of channels and overall of membranes and supports. In addition, the model can be applied to any simple geometry and provide the velocity fields all over the length of the channel. Of course, the model remains a model and contains its own level of approximations. It has however the advantage to provide analytical solutions and to go beyond the simple assumption of constant membrane velocity.

References

[1] P. Dejardin, J. Chromatogr. A 1187 (2008) 209.
[2] P. Dejardin, J. Chromatogr. A 1203 (2008) 94.
[3] K.-G. Wahlund, J. Chromatogr. A 1218 (2011) 6848.
[4] P.S. Williams, J. Microcolumn Sep. 9 (1997) 459.
[5] A. Litzen, K.G. Wahlund, Anal. Chem. 63 (1991) 1001.
[6] A. Litzen, Anal. Chem. 65 (1993) 461.
[7] K.G. Wahlund, J.C. Giddings, Anal. Chem. 59 (1987) 1332.
[8] M. Martin, M. Hoyos, J. Chromatogr. A 1218 (2011) 4117.