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## Expressions for the C-term in the presence of pore flow

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### Abstract

In the course of our work on capillary electrochromatography (CEC) we, as others, have found strong evidence that flow in pores of particles can be significant. Its magnitude relative to the interstitial flow is characterized by the flow reduction factor,  $\omega$ . Indirect evidence for pore flow was obtained much earlier by others, when it was noted that plate height, especially the C-term part, was significantly smaller in electrically driven (ED) than in pressure drive (PD) systems. This was interpreted as enhanced mass transfer, for which the intra-particle flow was held responsible. More direct evidence was produced by us when the size-exclusion (SEC) behaviour of polymers was studied in ED systems. It was found that the effect of exclusion on migration velocity could vanish entirely, and large and small molecules were co-eluted. This can only be explained if  $\omega$  approaches 1; flow within the pores being as large as the interstitial flow. Indeed, consideration of double layer overlap indicated that  $\omega$ -values close to 1 can often be expected in CEC. These large values  $\omega$  inspired us to reconsider the effect of pore flow on the mass transfer term. We have arrived at the conclusion that enhanced mass transfer cannot explain in itself the extremely small values for the reduced plate height,  $h$ , ( $<1$ ) observed especially for weakly retained solutes. In fact, when the pore flow is equal in magnitude to the interstitial flow, an unretained solute moves as fast within the particle as in the interstices; there is no non-equilibrium generated and a mass transfer term in  $h$  is not expected. For the migration of the solute the system is essentially uniform. Thus, apart from the mass transfer enhancement, another factor plays a role in the decrease of the  $h$ -values. We have attempted to derive a suitable expression for this effect. Some results are presented here. In one approach the situation is compared to that of an open tubular column with moving pseudo-stationary phase on the wall, an experiment that has actually been carried out by Krejci et al., or with micellar electrokinetic chromatography. In that case the plate height is easily derived. The result says that the plate height is proportional to the square of velocity difference between the two zones. However, the analogy is not perfect, and another approach suggests a direct proportionality rather than a square law one. Finally, a more refined treatment could be made only for a slab, not for a sphere. Extrapolation of this result to a sphere is put forward as a tentative expression for this effect. © 2002 Published by Elsevier Science B.V.

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### 1. Introduction

Plate heights in liquid chromatography (LC) with columns packed with porous particles are known to

be influenced when there is flow within the particles. As far as we know the first indications of this phenomena were obtained by size exclusion chromatographic (SEC) experiments (where large molecules and corresponding large pores are both present), by van Kreveland and van den Hoed [1,2], as well as by Kirkland [3].

In Refs. [1–3] the observed smaller plate heights

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were correctly interpreted as due to the enhanced mass transfer brought about by the convection within the particle. It is no coincidence that this phenomenon was observed with high molecular mass solutes as separated in SEC: the diffusion coefficients are very small. That is, equilibration of the particle content by diffusion is slow, and even a small enhancement by convection will speed up this process and lead to smaller plate heights. Pressure driven intraparticle convection is very small compared to the interstitial velocity; the ratio will be roughly given by the ratio of the squares of pore size and interstices. Even with 10- $\mu\text{m}$  particles and 100-nm pores this ratio is below  $100 \times (9/4) \times 2 = 2000$ .

In later years the intraparticle convection was known under the name perfusion, and perfusion chromatography [4] was developed in order to enhance speed of separation, especially of bio-molecules. This was done using particles with a bimodal pore size distribution; the group of large pores allowed fast flow through the structure, while the group of small pores allowed for sufficient surface area and sample capacity. Numerous papers have appeared on the theory of mass transfer enhancement by diffusion [5–8].

In this contribution the focus is on a particular part of the C-term, that caused by the slow mass transfer within the particle. In order to arrive at practical, not too complicated, expressions the following assumptions have been made: the particle structure is such that it can be considered from the point of view of dispersion as uniform. The phenomena in the particle can be described as if the latter consisted of a uniform phase, with a distribution coefficient,  $K''$ , towards the interstitial fluid, and a diffusion coefficient,  $D''$ . All details of the pore structure (dead ends, broad pore size distribution, constrictions, etc.) are believed to be taken into account properly by appropriate values for the two coefficients  $K''$  and  $D''$ .

The uniformity also implies that kinetics of the phase equilibrium is assumed to be infinitely fast.

Of course this set of assumptions is rather drastic. However they seem not to be unreasonable for e.g. reversed-phase chromatography (RPC) of small molecules, since such assumptions have been successfully applied [9]. For instance, kinetic effects are rarely observed in RPC of small molecules, and

combining the effect of pore structure in a correction factor (“tortuosity factor”, etc.) for the diffusion coefficient is common practice.

Furthermore, we exclude from the discussion mass transfer effect in the interstitial space. These effects are often not included in plate height equations. Also, they can be treated independently [10] and added later as contributions to the plate height. The same holds for slow kinetics.

Under this set of conditions “C-term” refers exclusively to the dispersion brought about by the slow equilibration within the particle, the equilibration involving internal flow and diffusion exclusively, with infinitely fast distribution.

The intraparticle flow it is assumed to be uniform in magnitude and to be in the longitudinal direction. That is basically incorrect, as has been shown [7,8,11]. However, we believe that this assumption may affect the numerical values occurring in some relations, but does not obscure the functional shape of these relations.

Intraparticle flow received renewed interest after electrically driven chromatography (“capillary electrochromatography”, CEC) was studied extensively. In many articles [12–17] the improved efficiency in CEC as compared to (packed) capillary LC (CLC) was attributed in the first place to the better flow uniformity in flow channels between the particles, as originally pointed out in seminal papers by Pretorius and Knox [18–20]. In the second place, and more important in the present context, it was indicated that in-particle flow could also be responsible for the improved plate heights. Such flow could easily exist when the double layer overlap within the pores of the particle [20,21] is still moderate. Originally this was postulated [22] especially for large solute molecules with slow diffusion within the particles. In the latter case the enhancement of mass transfer, the perfusion effect, becomes important at small internal flows.

The situation became even more complicated when it was found that internal flow could be as large as the flow in the flow channels [12,14,23]. This, in the first place would mean that the perfusion effect could more easily be important also for small molecules [24]. In the second place, as also discussed in Ref. [24], with such high internal flow-rates another effect on the plate height, in addition to the perfusion effect, comes into play: the smaller the

velocity difference between mobile zone (the interstices) and stationary zone (the particles), the less non-equilibrium is generated, and the less important the mass transfer between these two zones becomes. Ultimately, when the migration velocity in the particles equals the velocity outside the particles, there is no C-term contribution left (within the assumptions indicated above). In that extreme the system is, for the migration of the solute, uniform, and indistinguishable from an open tube. This second effect will be indicated in the sequel as “equilibrium effect” (for lack of a better expression). A theory on the plate height, when it is to be used for cases with high internal velocities, should include the equilibrium effect, whereas it should also be able to describe the above-mentioned perfusion effect.

In this contribution an attempt is made to develop such a theory, without resorting to full numerical simulation of the chromatographic transport process [11].

## 2. Methods and conventions

Frequent use will be made of double-primed symbols, borrowed from the work by Knox and Scott [9], such as  $K''$ ,  $k''$ ,  $D''$ , and  $\omega''$  (note that, unfortunately, in Ref. [24] the double primed  $k$  ( $k''$ ) had another meaning). These are used when the stationary zone [9] (including pore liquid within the adsorbent as well as adsorbent surface) is treated, as indicated, as a uniform phase. The mobile zone is the liquid between the particles, or outside the adsorbent layer, and does not include the pore liquid. In detail:  $K''$  is the mean concentration within the particle (counting its whole volume),  $q$ , over the concentration in the interstices,  $c$ ;  $k''$  is the mass in the particles over the mass in the interstices;  $D''$  is the mean diffusion coefficient in the particle, i.e. the ratio of the mass flux and the gradient in the mean concentration;  $\omega$  is the flow ratio, flow velocity in the particles over that in the interstices;  $\omega''$  is that ratio of migration rates in the particle and in the interstices.

The conversions of double primed parameters into regular ones or vice versa is straightforward; e.g. for an LSC or RPC system:

$$k' = (-\varepsilon_{in} + \varepsilon_{out} k'') / (\varepsilon_{in} + \varepsilon_{out})$$

$$D'' = \gamma_{sz} D_m / (1 + k_1)$$

where  $\gamma_{sz}$  is the tortuosity of the pore space in the adsorbent,  $k_1$  is the internal retention factor, ratio of masses in the adsorbent surface and in the adsorbent pore liquid,  $\varepsilon_{out}$  is the volume fraction of the interstices between the particles,  $\varepsilon_{in}$  is the volume fraction of the pores within the particles, and  $\omega'' = \omega / (1 + k_1)$ .

Conversions that complicate equations will be avoided as much as possible.

Symbolic as well as numerical calculations were carried on a PC with Pentium processor with 32 Mb RAM, using Mathematica version 4.0 (Wolfram Research, Champaign, IL, USA).

## 3. Results

In Ref. [24] the perfusion effect was taken from the work of Rodrigues [6]. In that work the enhanced mass transfer brought about by internal flow was treated by using an enhancement factor,  $\phi$ , applied to the diffusion coefficient, equal to:

$$\phi(\nu_1) = \frac{\nu_1}{18} \cdot \frac{1}{\text{Coth}(\nu_1/6) - 6/\nu_1} \quad (1)$$

where  $\phi$  is the enhancement factor, ratio of the mass transfer rates in the presence and in the absence of internal flow,  $\nu_1$  is the reduced internal velocity, equal to  $u_i d_p / D''$ ,  $d_p$  is the particle size and  $D''$  is the diffusion coefficient within the particle.

Eq. (1) has not been derived rigorously by Rodrigues, but it is accepted as a reasonable approximation.

The equilibrium effect was treated in Ref. [24] by considering a modified mass balance equation for the mobile zone, i.e. with the longitudinal coordinate,  $z$ , as the independent variable:

$$\varepsilon_{out} \frac{\partial c}{\partial t} + \varepsilon_{in} \frac{\partial q}{\partial t} = -\varepsilon_{out} u_{out} \frac{\partial c}{\partial z} - \varepsilon_{in} u_{in} \frac{\partial q}{\partial z} \quad (2)$$

where  $c$  is the solute concentration,  $t$  is time,  $u_{out}$  is the interstitial velocity,  $u_{in}$  is the internal migration velocity, equal to  $\nu_{in} / (1 + k_1)$ ,  $\nu_{in}$  is the internal fluid velocity, and  $k_1$  is the internal retention factor, mass

adsorbed over mass in liquid phase in the pores within the particles.

This equation was solved in Ref. [24] in the Laplace domain, with  $c \rightleftharpoons \bar{c}$  and  $q \rightleftharpoons \bar{q}$ , taking the relation between  $\bar{c}$  and  $\bar{q}$  as being the same as when there is no internal flow, i.e. neglecting the perfusion effect. The argument there was that the perfusion effect can be taken into account later, i.e. by substituting a value for  $D''$  in agreement with Eq. (1). In this way, after uncoupling of the perfusive and equilibrium effect, the result for the mass transfer contribution to the plate height,  $H_c$ , was:

$$H_c = \frac{d_p^2 \varepsilon_{in} \varepsilon_{out} (1 + k_1) (1 + k_1 - \omega) u_0}{30 D_m (\varepsilon_{in} + \varepsilon_{out}) \gamma_{sz} (1 + k')^2 (\varepsilon_{out} + \varepsilon_{in} \omega) \phi(v_i)} \quad (3)$$

where  $\omega$  is the flow ratio,  $v_{in}/v_{out}$ ,  $d_p$  is the particle diameter,  $u_0$  is the migration velocity of the unrestrained,  $\gamma_{sz}$  is the tortuosity factor for diffusion within the particle and  $k'$  is the retention factor.

Eq. (3) reduces to the classical equation for liquid solid chromatography [cf. Giddings [10], p. 158, Eq. (4.5.26)] for  $\omega \rightarrow 0$ . It also is satisfactory in that it predicts a zero value for  $H$  when the migration rates in both zones are the same, i.e. when  $\omega = 1 + k_1$ . As shown in Ref. [24], it gives a reasonable agreement with experimental results, that indeed showed very small values for  $H$  when the retention factor (and with that  $k_1$ ) approached zero, under conditions where high internal flow was present.

However, there are two, probably related, problems with Eq. (2) and its derivation. The first is that it predicts negative values for  $H_c$  for cases where  $\omega > (1 + k_1)$ . Negative plate heights would constitute a marvellous tool in separation science, but it follows from first principles that these are impossible. We suppose at this stage that the occurrence of the factor  $(1 + k_1 - \omega)$  in Eq. (3) is incorrect and brought about by the artificial uncoupling of the perfusive and equilibrium effects. This can be clarified as follows.

The mass balance within the particle without flow can be written as:

$$\frac{\partial q}{\partial t} = D'' \left( \frac{\partial^2 q}{\partial r^2} + \frac{1}{r} \frac{\partial q}{\partial r} \right) \quad (4)$$

and this was indeed the equation solved in Refs. [5,24] by the Laplace method, with boundary condition:

$$q(d_p/2) = K''c(z) \quad (5A)$$

and

$$q'(0) = 0 \quad (5B)$$

leading to a time constant for the equilibration of the particle with its surrounding mobile phase equal to:

$$\tau = 1/60 \frac{d_p^2}{D''} \quad (6)$$

which is independent of the flow ratio,  $\omega$ . However, one would expect  $\tau$  to approach zero when  $u_{in}$  approaches  $u_{out}$  (see above).

With  $u_{in} < > 0$  it is in the first place important to replace Eq. (4) by:

$$\frac{\partial q}{\partial t} + u_{in} \frac{\partial q}{\partial z} = D'' \left( \frac{\partial^2 q}{\partial r^2} + \frac{1}{r} \frac{\partial q}{\partial r} \right) \quad (7)$$

as indicated earlier [5], losing the spherical symmetry in the system. However, we are now also inclined to believe that in that case the boundary conditions for Eq. (7) have to be changed, such that the longitudinal gradient in  $c$ ,  $\partial c/\partial z$ , is taken into account.

Although as yet we have found no way to solve Eq. (7) with these boundary conditions in terms of the Laplace transform for finding the moments of the elution curve, Eq. (7) as it is reveals the important point: the RHS of both Eqs. (4) and (7) gives the curvature in the  $c$ -dependence on  $r$ . It is exactly this curvature that describes the non-equilibrium: it holds generally that with no curvature the whole particle is in equilibrium with the surrounding mobile phase and there is no mass transfer term. The values of  $\partial q/\partial t$  and  $\partial q/\partial z$  are opposite in sign. Thus, omitting the second term in Eq. (6) must lead to too low values for curvature and time constant. This is taken care of in Rodrigues' treatment by inserting  $\partial q/\partial z$ , leading to the expression Eq. (1). In addition, however, using the proper boundary condition has an effect in the same direction. When neglecting the longitudinal gradient, and taking  $q(d_{pi}/2) = K''c(d_{pi}/2)$ , the mean value of  $\partial q/\partial z$  is by definition zero, whereas in reality the longitudinal gradient in  $c$  is

accompanied by a matching longitudinal gradient in the particle concentration  $q$ . Thus, when one does take the gradient into account in the boundary condition, the curvature in  $q$  becomes even smaller. Eventually, when the migration velocities inside and outside the particle are equal, one can conjecture that the whole LHS of Eq. (7) vanishes. Indeed, in first order it holds  $\partial q/\partial t = -u_{\text{migration}} \partial q/\partial z$ , and for  $u_{\text{migration}} = u_{\text{in}}$  the LHS vanishes. The time course of  $q$  then mirrors the  $c$ -time course, irrespective of the rate of mass transfer (and also the Laplace transforms have the same shape).

### 3.1. The open tubular analog

In view of the difficult mathematics arising from Eq. (7), we looked for easier-to-handle systems that could have the same characteristics. One of them is the open tubular column, with a moving stationary liquid phase at the wall (OTML). Interestingly enough, such a system has been studied experimentally [25]. For such a system the perfusion effect is absent, as the migration vector in the stationary layer is perpendicular to the direction of mass transfer. However, the equilibrium effect should be there.

The plate height for the OTML using a liquid–liquid system (LL) is easily derived in terms of double-primed variables (i.e. directly applicable to LLC). When we use a moving coordinate in the  $z$ -direction with a velocity equal to that of the “stationary” layer,  $u_{\text{in}}$ , the classical theory can be applied. The plate height in the moving system,  $H^m$ , is:

$$H^m = \frac{2d_f^2}{3D''} \frac{k''}{(1+k'')^2} (u_{\text{out}} - u_{\text{in}}) \quad (8)$$

where  $k''$  is the retention factor for an LL system, ratio of the masses of solute in the stationary zone and the mobile zone. Eq. (7) predicts a position variance,  $\sigma_z^2$ , after a time  $t$ , of  $H^{m*} z_{\text{travelled}}^m$ , or  $H^m t (u_{\text{out}} - u_{\text{in}}) / (1 + k'')$ :

$$\sigma_z^2 = \frac{2d_f^2}{3D''} \frac{k''}{(1+k'')^3} (u_{\text{out}} - u_{\text{in}})^2 t \quad (9)$$

This variance corresponds in the fixed coordinate system to a plate height,  $H = \sigma_z^2 / z_{\text{travelled}}$ , or  $\sigma_z^2 / (u_m t)$ :

$$H = \frac{2d_f^2}{3D''} \frac{k''}{(1+k'')^2} (u_{\text{out}} - u_{\text{in}})^2 / u_m \quad (10)$$

with  $u_m$  being the migration velocity. It holds

$$u_m = \frac{u_{\text{out}} + k'' u_{\text{in}}}{1 + k''} \quad (11)$$

so that, after substituting  $\omega u_{\text{out}}$  for  $u_{\text{in}}$  and some rearrangement:

$$H = \frac{2d_f^2}{3D''} \frac{k''}{(1+k'')^2} \frac{(-1 + \omega'')^2}{(1+k''\omega'')} u_{\text{out}} \quad (12)$$

This equation is satisfactory in that it does not predict negative  $H$ , while it does predict zero  $H$  for  $\omega'' = 1$ . It cannot be compared directly to Eq. (3), as it is in double-primed terms, suitable for liquid–liquid chromatography, with no stagnant mobile phase in the pores. Also for practical applications and optimization studies,  $u_{\text{out}}$  should be rearranged into  $u_0$ , the migration velocity of an unretained marker. Both conversions to a LSC form are straightforward, but are not given here in order not to interrupt the argument.

We have no doubts that Eq. (12), after such conversion, could be used also for OT cases where the stationary phase at the wall does not move itself, but rather a migration with velocity  $u_{\text{in}}$ , occurs in this zone. It would therefore be tempting to use a modified Eq. (12), with  $d_f$  replaced by  $d_p$ , and at the same time replacing  $2/3$  by  $1/30$ , for the packed column case we are interested in.

Of course, this approach would not be satisfactory, as the perfusion effect would not be taken into account. Also, using the result for the contiguous zone that the wall coated layer constitutes to the non-contiguous zone of many particles fixed in position appears a bit precarious. Therefore we postpone this to after a later section.

### 3.2. Slab-formed stationary zone

A geometry which can be handled mathematically is that of a slab of stationary zone, closed at the faces (flat or cylindrical) parallel to the  $z$ -direction, and open for diffusion and flow at the upstream and downstream faces. This model has been used earlier by Rodrigues et al. [5], be it without taking the

longitudinal concentration gradient into account for the boundary condition. The system is a bit difficult conceptually, as in a not-too-complicated treatment one should assume the mobile phase to be uniform laterally, and that it has the same velocity throughout, which is difficult to imagine in Fig. 1 and would violate i.a. the continuity equation for the liquid. However, the same difficulties arise in any known treatment of mass transfer in and around a sphere, as in packed columns, and we believe that the model yields some useful insight.

Finding the plate height for this system was carried out via the Laplace domain as follows. The differential mass balance was written as:

$$s \bar{q} + u_{\text{in}} \frac{\partial \bar{q}}{\partial z} = D'' \frac{\partial^2 \bar{q}}{\partial z^2} \quad (13)$$

As boundary conditions we used:

$$\bar{q}(d_s/2) = K'' (\bar{c}(z) + d_s/2 \bar{c}'(z)) \quad (14A)$$

and

$$\bar{q}(-d_s/2) = K'' (\bar{c}(z) - d_s/2 \bar{c}'(z)) \quad (14B)$$

thus assuming that a linear approximation of  $\bar{c}(z)$  is sufficient, but more accurate than taking  $K'' \bar{c}(z)$  for both boundaries [5]. The solution found for  $\bar{q}(z)$  is a complicated function with exponentials or hyperbolic

functions, containing  $\nu_1$ , which is  $u_{\text{in}} d_s/D''$ ,  $K''$ ,  $\bar{c}(z)$  and  $\bar{c}'(z)$ .

The function  $\bar{c}(z)$  was symbolically integrated over  $z$  from  $-d_s/2$  to  $d_s/2$  in order to find the mean value in the slab, which then contained  $\bar{c}(z)$  as well as  $\bar{c}'(z)$ .

Next an equation equivalent to Eq. (7) for the mobile zone was used. As this contains  $d\bar{q}/dz$  and  $\bar{q}(z)$  contains  $d\bar{c}/dz$ , the equation was second order in  $z$ . The solution could be found. Time moments were found using the method of van der Laan [26] from the Laplace transform  $\bar{c}(z)$  and these were converted into a plate height. The result is:

$$H = \frac{d_s^2}{6D''} \frac{k''}{(1+k'')^2} \frac{(-1+\omega'')^2}{(1+k''\omega'')} \frac{1}{\phi'(\nu_1)} u_{\text{out}} \quad (15)$$

where  $\phi'(P)$  is

$$\phi'(\nu_1) = \frac{\nu_1}{6} \cdot \frac{1}{\text{Coth}(\nu_1/2) - 2/\nu_1} \quad (16)$$

$\phi'(\nu_1)$  a mass transfer enhancement factor, analogous to the ones introduced by Rodrigues et al. for a slab and a sphere [5].

Eq. (15) surprisingly is the same as Eq. (12) for the OT analog, except for the numerical factor, which is four times smaller, and the presence of the factor  $\phi'(\nu_1)$ . We found this surprising, as the stationary zone migration in the OT case proceeds through a contiguous zone, while here the migration in a slab (and sphere) stationary zone is interrupted each time the solute reaches the end of the particle.

Accepting this behaviour as correct, the first difference between the slab case and the OT case is simply a result of the differing geometry and the boundary conditions: for the slab, with no internal flow the symmetry around the middle of the slab imposes  $d\bar{q}/dz=0$ , the same as the boundary condition for the coated layer at the outer wall.

The second difference is more important. The additional factor strongly resembles the factor Eq. (1) found for spheres by Rodrigues et al. Eq. (16) holds for a slab closed at the longitudinal walls. Both expressions, (1) and (16), approach unity when  $\nu_1$  goes to zero, so that the classical C-term equations are recovered. In (1) the argument of the Cosh is  $\nu_1/6$ , whereas this is  $\nu_1/2$  in Eq. (16). Rodrigues' expression for a sphere gives a much slower increase

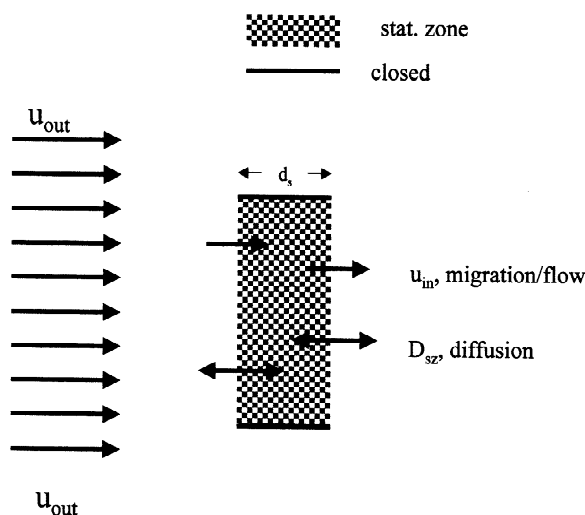


Fig. 1. Stationary zone in the form of a slab, with uniform flow in mobile zone.

with  $v_1$ . The reasoning to explain this can be found in Ref. [5]. Briefly, the time constants of equilibration by convection/migration on the one hand and by diffusion on the other hand are compared. In a sphere, diffusion is much faster than in the model slab, because of the larger open area and the shorter mean distance. Quantitative calculation yields the factor 1/3 needed to arrive at  $v_1/6$  as the argument in Eq. (1).

### 3.3. A final expression

We tentatively propose as the most appropriate expression for the C-term one based on Eq. (15), with  $1/6 d_s^2/D''$  replaced by  $1/30 d_p^2$  and the slab enhancement factor  $\phi'(v_1)$  by Rodrigues' expression [6] for  $\phi(v_1)$  for the sphere:

$$H = \frac{d_p^2}{30 D} \frac{k''}{(1+k'')^2} \frac{(-1+\omega'')^2}{(1+k''\omega'')} \frac{1}{\phi(v_1)} u_{\text{out}} \quad (17)$$

with  $\phi(v_1)$  as in Eq. (1).

This equation would combine reasonable behaviour at  $\omega'' \rightarrow 1$ , whereas the perfusion effect is taken into account properly, i.e. in agreement with Eq. (1). Note that the expression is simply a product of an equation such as Eq. (11) (replacing  $2/3 d_f^2$  by  $1/30 d_p^2$ ) and  $1/\phi(v_1)$ , so that we conclude that separation of equilibrium and perfusion effect seems to be possible after all.

The form of Eq. (17) is only directly suitable for LL systems. For LSC systems, it is better brought in the same form as Eq. (3), expressing  $k''$  in  $k'$ ,  $D''$  as  $\gamma_{sz} D_m/(1+k_1)$ ,  $\omega$  in  $u_{\text{in}}$ ,  $u_{\text{out}}$  and  $k_1$ . The result is

$$H_c = \frac{d_p^2}{30 \gamma_{sz} D_m} \frac{\varepsilon_{\text{in}}}{(\varepsilon_{\text{in}} + \varepsilon_{\text{out}})} \frac{(1+k_1-\omega)^2}{(1+k')^2(1+\varepsilon_{\text{in}}/\varepsilon_{\text{out}}\omega)^2} \frac{1}{\phi(v_1)} u_0 \quad (18)$$

When Eq. (19) is compared with the one valid [10] in the absence of pore flow, i.e. Eq. (3) with  $\omega=0$ , a difference by a factor:

$$\frac{(1+k_1-\omega)^2}{(1+\varepsilon_{\text{in}}/\varepsilon_{\text{out}}\omega)^2(1+k_1)^2} \frac{1}{\phi(v_1)} \quad (19)$$

is noted.

The two parts of Eq. (19) correspond to the

equilibrium and the perfusion effect respectively. Which of the two is more important for the decrease in plate height depends strongly on the diffusion coefficient and on the retention factor. The larger the retention, the less important is the equilibrium effect. The importance of the perfusion effect,  $1/\phi(v_1)$  depends exclusively on the absolute value of  $v_1$ , which, at least for LSC with diffusion in the liquid pore liquid exclusively (no surface diffusion [9,27]), is independent of the retention factor.

## 4. Discussion

Although we have no formal proof, we believe that a reasonable expression for the effect of pore flow on the C-term has been derived. For practical purposes it may not differ much from that presented in Ref. [24]; however, it is free, as far as we can see, from an internal inconsistency. It also predicts the right behaviour in extreme cases. For instance, when the pore flow is opposite in sign but equal to the interstitial flow, the equation predicts, for the unrestrained, infinite values for  $H_c$ . This is correct, as under such conditions the peak does not move, it only spreads out, and the ratio of variance and travelled distance becomes infinite. Another extreme is when  $\omega$  is equal to  $(1+k_1)$ , in which case the mass transfer term is zero. In this situation the solute migrates as fast in the interstices as in the adsorbent zone. In fact, separation takes place in the adsorbent, with the transport in the interstices being an unnecessary complication. The separation in the adsorbent is equivalent to the separation in a monolith.

This extreme is of course artificial; it is doubtful if one could ever approach this situation for a retained component in practice. It is therefore more useful to consider the consequences that Eqs. (18) and (19) would bring about for cases where  $\omega$  approaches 1, a situation we have seen quite regularly in our institute. With  $k'=3$ , and  $\varepsilon_{\text{in}}=\varepsilon_{\text{out}}=0.4$ , the improvement in the plate height as given by the first part of Eq. (19) can amount to roughly a factor of 4 when  $\omega$  approaches 1. For a small molecule, a velocity of 4 mm/s, and a particle size of 5  $\mu\text{m}$ , the second part can give another factor 1.5

An important limitation of the present proposal should be mentioned. It has been shown by study of

C-terms in standard HPLC, that in reversed-phase systems appreciable surface diffusion occurs [9,27]. This means that the equations used above to find the value for  $\nu_1$  cannot be used without modification, as it was assumed that diffusion within the particles occurs exclusively in the pore liquid, with the result that  $\nu_1$  is independent of the retention. This would require, for RP systems as commonly used in CEC, further investigation. However, the importance of the effect remains of the same order.

The proposal given may be useful for the interpretation of experimentally observed plate heights. However, for optimizing separations there may be a caveat, similar those encountered in, for example, capillary electrophoresis and micellar electrokinetic chromatography: improved plate height does not necessarily lead to better resolution for a peak pair with given properties, e.g. relative retention or mobility. A non-selective faster migration, such as electro-osmotic flow, may improve the plate height, but contributes nothing to the resolution. Similarly, in the case of intra-particle flow, it is not easy to see if the resolution improves in the same proportion as does the square root of the plate height. Further studies of this are required.

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