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Evidence of a wall friction effect in the consolidation of beds of packing materials in chromatographic columns

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Abstract

Experimental observations demonstrate the intensity of the friction between the bed of a packed chromatographic column and its wall. The wall supports the bed but, in the process, causes the strong radial heterogeneity of the bed which has been previously reported and is now well documented. Friction against the wall is not entirely harmful, however. Without wall friction, the bed would contract with increasing head pressure. the bed in a typical analytical column would be a few mm longer in the absence of mobile phase flow than under standard operation conditions. Experiments demonstrate the existence of bed friction against the column wall in an axial compression column. They show that the friction coefficient depends on the nature of the solvent, the axial compression stress applied to the bed, and the bed length.

Keywords: Wall friction; Stationary phases, LC; Packing materials

1. Introduction

The packing procedures of chromatographic columns sound more like recipes than like the description of well-understood technical procedures [1]. The results obtained following expert recommendations [2–4] are often erratic and poorly reproducible from laboratory to laboratory, a sure indication that one or several critical parameters have not been identified properly and, therefore, remain(s) out of control. In view of the increasing importance of preparative chromatography as a major industrial separation process, this situation is most unsatisfactory. Considerable effort and large resources have to be invested in the development and/or purchase of sophisticated equipment. Still, serious difficulties are encountered when attempting reproducibly to pack efficient columns.

The existence of a wall-effect has been identified long ago [5,6]. It has always been confirmed by systematic investigations [7–9], although it was shown recently that the thickness of the wall effect is a function of the column diameter [9], not a constant number of particles, as suggested earlier [5]. This effect has been invoked more as a mantra [1] than as an explanation during the last 30 years. The physics of granulated materials has considerably evolved in the meantime [10]. It has been demonstrated that shaking or vibrating bulks of granulated materials may result in a grand scale circulation of the

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particles accompanied with a size segregation. This may explain certain of the results obtained with dry packing [5,6], which are different from those obtained with slurry packing or packing by autofiltration of a slurry. However, specialists agree that the presence of a rigid wall in contact with bulk granulated material is the main source of the heterogeneity of the packing density observed [10,11]. The only possibility there is to explain the long-distance effects of the wall reported in chromatographic columns, effects which are similar to others reported independently in various types of containers, is to be found in the friction between the bed and the wall. This explanation has already been suggested [12].

The goal of the present paper is to demonstrate that friction of the packed bed against the wall of chromatographic column is important and that it could explain many of the past observations. For this purpose, we use data derived from previous studies on columns packed with a dynamic axial compression skid [13–18] and prepared by the conventional slurry packing procedure [19]. A slight modification of the skid allowed the measurement of the friction stress between bed and column wall.

2. Theory

We first present some simple considerations of solid mechanics applied to a consolidated bed of packing material in a chromatographic column, assuming that there is no friction of the bed against the wall. Experimental results are not in agreement with the simple conclusions of this exercise. This contradiction shows that the assumption made is incorrect and that there is a certain degree of friction. In a second part of this section, we discuss the introduction of the friction coefficient in the balance of stresses, taking into account the fact that this coefficient is not constant along the column but depends on the radial stress of the packed bed against the wall.

2.1. Bed elasticity in the absence of friction

There are two different ways to consolidate a bed of packing material into a chromatographic column, by mechanical compression or by the effect of viscous friction. In the former case, axial, radial or annular compression, dynamic and static compression have been used. In this work, we consider only slurry packing (i.e., viscous friction) and what is called[1] dynamic axial compression in chromatography because these methods are easier to implement in our laboratory. Some of our conclusions are easy to extend to other forms of mechanical compression. Others need more care.

2.1.1. Stress in axial compression

If an elastic object, e.g., a bar, of length L and cross-sectional area A, having a modulus of elasticity E, is subject to an axial force F applied to its top section, the bar length is reduced [20] by

$$\Delta L = \frac{FL}{AE} \tag{1}$$

The same result would apply to a bed of packing material contained inside a chromatographic column and consolidated under an axial compressive stress or pressure $\sigma_z = F/A$, provided that the following assumptions are valid:

1. The bed is fully consolidated under a stress equal to or higher than σ_z,
2. The bed is homogeneous, isotropic, linear-elastic, and its density and Young modulus, E, are independent of the axial and radial positions [otherwise, $E(z,r)$ must be known and a differential equation substituted to Eq. (1)],
3. The bed is not supported, even in part, by its friction against the column wall.

This latter assumption is required by the balance of forces acting on the bed. Eq. (1) assumes that, whence the elastic strain has taken place and the bed has reached mechanical equilibrium, the force (and stress) inside the column bed is constant all along its length, so that the force F is entirely conveyed from the actual point of application (on the inlet frit or on the bed top) to the end frit. If there is friction at the wall, the axial force conveyed to the packing materi-

[1] This name has been given because the compression piston is free to move when the bed contracts, hence the stress applied is constant. It is inappropriate in engineering, however, because the inertial forces involved are negligible.

al is correspondingly reduced by the amount of force transferred to the column wall.

We know that this assumption of no friction along the column wall cannot be valid, at least when the column length is significant compared to the column diameter. We suspect that there is significant friction between the packing material and the wall [12]. This friction results in a shear stress τ acting along the column wall. The balance of forces in the column then becomes

$$F_i = F_o + R_f = F_o + \tau S = F_o + \tau\pi d_c L \quad (2)$$

with F_i and F_o being the force applied to the column inlet (corresponding to the axial compression stress σ_z), and the force conveyed by the bed to the exit frit, respectively. R_f is the wall friction, product of the shear stress, τ, and the wall surface area, $S = \pi d_c L$, with d_c column diameter and L column length. The difference between F_i and F_o is the force transmitted to the column walls by friction. Note that in Eq. (2) the shear stress τ is assumed to be constant along the column length. Most probably it is not so because it depends on the radial stress, σ_r, between the bed and the wall. Often, the shear stress τ is assumed to be proportional to the radial stress as $\tau = \mu\sigma_r$ where μ is the coefficient of friction. Since the radial stress varies along the column, decreasing from the column inlet to its outlet, the frictional term τS must be replaced by an integral. Eq. (1) is valid only if there is no friction between the packing material and the column.

Because E has been determined from the data obtained when compressing packing material in the 5 cm axial compression column [13–17] (i.e., under such experimental conditions that the wall friction is not negligible), the values obtained [18] are somewhat underestimated.

2.1.2. Stress in slurry packing

Consider now the slurry packing of analytical columns [4]. The stress applied to the column bed is no longer due to the mechanical compression of a piston but to the interaction of the bed with a stream of a viscous fluid pumped at constant flow-rate and percolating through the column. Again, we neglect the friction between the bed and the column wall for a moment. Because of the fluid flow, the stress is no longer strictly constant along the column. For the sake of convenience, we assume that the column is vertical and that the flow takes place in the upward direction. The stresses applied to the column bed due to fluid seepage result in the following equivalent boundary fluid forces [11]:

1. At column inlet, the pressure of the fluid entering the column acts over the column cross-section area, A, resulting in a boundary fluid force. The applied fluid pressure, p_{fluid}, results in a seepage force, $F_{fluid} = p_{fluid}A$, acting upward. In addition, there is a component of the boundary fluid force due to the hydrostatic pressure from the fluid in the column. This latter force is negligible compared to the seepage force at the fluid pressures typically used in liquid chromatography (at least 40 bars, to be compared with 20 to 50 cm of a liquid of density lesser than 1).
2. At the column outlet, since there is no fluid pressure applied to the column, the stress is practically equal to the atmospheric pressure (the pressure resistance of the detector and exit tubings is neglected, since this pressure is a small fraction of 1 bar). The corresponding boundary fluid force can be neglected.
3. Acting downward at the column centroid, is a force equal to the weight of the saturated packing material, $F_{packing} = \rho gLA$, where ρ is the saturated density of the packing material and g, the acceleration due to gravity. This force is also small relative to F_{fluid} and can be neglected.
4. The forces in the vertical direction (nearly equal to F_{fluid}) must be balanced by a downward force carried by the column. If there were no friction between the packing material and the column wall, the entire force F_{fluid} would act against the exit frit. Any portion of the applied fluid force resisted by wall friction would reduce the force on the exit frit. The existence of the exit frit force is well known. If there is nothing to hold the exit frit, it flies out of the column, followed by the packing material [21].

The balance of these different forces requires that in the absence of wall friction, the stress applied to the outlet frit by the packing material be equal to p_{fluid}, because both the column weight and the hydrostatic pressure of the fluid are negligible in comparison to the applied inlet pressure during the packing of the column. Inside the column, the

seepage force is applied by the moving fluid to the packing material by frictional drag. This seepage force can be expressed in terms of the force per unit volume of packing material, j, [11] as

$$j = \frac{\text{seepage force}}{\text{volume}} = \frac{p_{\text{fluid}}A}{LA} = \frac{p_{\text{fluid}}}{L} \quad (3)$$

which decreases linearly from the column inlet to its outlet.

2.1.3. Comparison between viscous shear stress and mechanical stress

If we consider an intermediate section of the column and write the balance of stress in this section, we find that the axial stress is constant in the case of a mechanical axial compression (mechanical stress) but increases linearly from column inlet to outlet in the case of hydraulic consolidation. However, there is no stress of hydraulic origin in the case of pure mechanical compression while the stress caused by the flow increases linearly with increasing column length in the latter case. Thus, in both cases, the total stress is constant. If we neglect the friction against the wall, the total stress applied to the column bed by the two consolidation processes is equivalent in the absence of flow through the axial compression column.

Under conventional operation conditions, the bed of an axial compression column is subject to the superimposition of a mechanical axial stress and a hydraulic seepage stress. The mechanical stress applied is $(\sigma_z - p_{\text{fluid}})$ if the applied fluid pressure is p_{fluid}. In the absence of wall friction, the actual stress in the packing material remains constant and equal to σ_z if $\sigma_z > p_{\text{fluid}}$. If the mechanical stress applied to the piston is lower than the inlet pressure of the column, the fluid stream entering the column tends to push the piston back. A ratchet in the piston actuating system avoids this movement in normal operation. The piston becomes then equivalent to the flange of a conventional column.

2.1.4. Application, calculation of the actual bed length

The compressibility of 5 cm I.D. columns packed by mechanical axial compression of slurries made with different packing materials for chromatography was measured by Sarker and coworkers [15–17]. From the data reported, Stanley et al. [18] determined that the modulus of elasticity of these columns was approximately 450 MN/m^2. Under an axial compressive stress of 100 atm (1 atm = 101 325 Pa), Eq. (1) suggests that this modulus corresponds to a relative decrease in the column length of

$$\frac{\Delta L}{L} = \frac{\sigma}{E} = \frac{1 \cdot 10^4 \text{ kN/m}^2}{450 \cdot 10^3 \text{ kN/m}^2} = 0.022 \text{ m per meter of column} \quad (4)$$

or 2.2 mm for a 10 cm long column and 3.3 mm for a 15 cm long column. In the case of a column percolated by a stream of mobile phase with an inlet pressure of 100 atm, the reduction of column length would be only half as large, because the actual seepage stress increases linearly from 0 to 100 atm[2] along the column. The reduction in length of the bed of a typical 15 cm long analytical column would still be 1.6 mm. This value is much larger than any bed shrinking effect yet reported. It is well-known in chromatography that a void volume equivalent to 1% of the column length causes an important if not a catastrophic loss of column efficiency.

From data by Abbott [22], such a void volume would result in the column having an efficiency reduced to less than a third of its nominal value. Most analysts are aware of the connection between a large drop in the efficiency of the column used and the formation of a void at its inlet. They know how to remedy such efficiency losses by taking off the inlet frit and filling the void with fresh packing material. In the absence of wall friction, when the inlet pressure is applied and the mobile phase stream begins to percolate through the column, the bed would contract reversibly. It would expand back when the flow is stopped. When the column is open, the bed would fill it exactly. It would be difficult to diagnose the actual source of efficiency loss and nearly impossible to remedy it. Column beds would have to be locked under a compression stress corre-

[2] This calculation assumes that the external porosity of the bed, hence the column permeability, remains constant in spite of the important change in the local values of the mechanical stress. Although the actual numerical result may change slightly, it is doubtful that the logical conclusion of the present exercise would be altered if a more exact calculation were to be made.

sponding to the maximum allowed inlet pressure of the mobile phase. This operation could be done only on the manufacturer's premises and would require expensive machinery and a costly column design. Thus, from this point of view, the wall friction is beneficial.

The contradiction between our daily observations and the predictions from engineering mechanics, that the effective length of the column bed should vary so significantly upon changes in the inlet pressure in the absence of wall friction, demonstrates that this assumption is in error. Wall friction does exit. This friction is the only force which may explain the relative stability (once it has been consolidated) of the bed length under major changes in external stress, a stability which is better than predicted. Note that it is only when the bed has been consolidated under a stress exceeding that used in regular practice that the bed can be considered as behaving elastically under stress. For reasons explained elsewhere in this paper, this very assumption is valid only over short periods of time: consolidation is never completely achieved.

2.2. Bed elasticity in the presence of friction

We now assume that the friction between the bed and the column wall is no longer negligible. Train [23] has measured the distribution of the local stress (most likely, the sum of the principal stresses) in a mechanically compressed bed and showed that it exhibits wide, systematic variations. The values reported are much lower in the third of the cylindrical bed at the end opposite the piston than at the end of the bed where the stress is applied, close to this piston. Away from the applied stress, σ_z, the radial distribution of the stress is nearly uniform. In the third of the bed close to the piston, the stress is higher in a wedge-shaped region near the edge of the piston than in the central portion of the piston. Close to the piston, the stress may locally deviate from σ_z to a large extent, especially close to the wall where it exceeds σ_z significantly. The stress measured along the wall varies considerably from the piston to the opposite end of the bed.

Therefore, since the measured stress varies along the length of the column, it is likely that the radial stress will vary as well and it is not possible to assume that the shear stress is constant. The shear stress, $\tau(z)$, is a function of the radial stress applied by the bed against the wall. Because the column has a cylindrical symmetry, we will assume that the stresses are independent of the azimuthal angle. The force due to the frictional resistance between the wall and the packing material sliding along the wall is given by

$$R_f = \pi d_c \int_0^L \tau(z) dz \tag{5}$$

Combination of Eqs. (2) and (5) gives

$$F_i = F_o + R_f$$

$$F_o = \frac{\pi d_c^2 p_{fluid}}{4} - \pi d_c \int_0^L \tau(z) dz \tag{6}$$

The measurement of F_o for columns of different lengths could allow the determination of the friction coefficient and its dependence on the column length.

3. Experimental

3.1. Equipment

Experiments were carried out using an LC-50 dynamic axial compression column system (Prochrom, Champigneulles, France) previously described [13,15]. The packing material is compressed by a piston moving inside a 5 cm I.D. cylinder and actuated by a hydraulic jack. The maximum compression pressure allowed with this system is approximately 100 kg/cm^2. A dual piston pump, Dynamax SD-1 (Rainin, Woburn, MA, USA), was used for solvent delivery (maximum flow-rate, 800 ml/min, maximum pressure, 1500 p.s.i.; 1 p.s.i. = 6894.76 Pa). The detector was a SpectraFocus from Thermoseparation Products (Riviera Beach, FL, USA). The UV absorbance was recorded at 254 nm. Samples were injected with a six-port switching valve from Valco (Houston, TX, USA), actuated by a manual electrical switch.

A pressure transducer (Omega, Stamford, CT, USA; model PX603-2KG5V) was used to measure the column back pressure. A displacement sensor

(Reagan Controls, Charlotte, NC, USA; model PAA1555) was used to measure changes of the column length smaller than 1 cm. The accuracy of this sensor is 0.01 mm. Larger changes are measured with a ruler, from the displacement of an index on the piston, with an accuracy of 1 mm. The electrical signals of the displacement sensor, the pressure transducer, and the UV detector were collected with a data acquisition module from Waters (Milford, MA, USA) and recorded in a microcomputer for data analysis.

3.2. Packing materials

The packing material used in this work was a C_{18} bonded silica, Zorbax (BTR Separations, Wilmington, DE, USA). The average particle size is 10 μm.

3.3. Procedures

3.3.1. Column packing and consolidation

The dynamic axial compression column was packed following the procedure previously described in detail [13]. The dry weight of material (240 g, except when the bed length is varied) was measured. The particles were mixed with isopropanol (except when otherwise indicated) and turned into a thick slurry which was left settling for a few hours. Afterward, the top portion or supernatant was removed to eliminate the fine particles and the dust, if any. The slurry volume was approximately 800 ml at the end of this procedure. The slurry was then poured into the empty, precleaned column. Column compression began immediately, and the compression pressure was raised rapidly to the final value at which consolidation was desired (17, 33 and 41 atm in this work). During the consolidation phase following the application of the compression stress, the length of the bed was recorded. After letting the bed stabilize for a few hours, the compression stress was released abruptly and the length of the bed recorded again during stabilization.

In the range of flow-rates used during column packing, the behavior of the slurry of packing material used never seemed to deviate from Newtonian behavior. However, no attention was paid to the flow of slurry which takes place during a very short time and we did not investigate this issue. The slurry is poured into the column. The time needed to close the column and start pumping is short and insufficient for sedimentation to proceed to any significant degree. Compression of the bed takes place without any migration of the top of the slurry. The rear of the slurry migrates by 10 to 30 cm, but, during this operation, the liquid flow-rate varies and its variations are difficult to interpret, let alone to measure. An independent study of the flow characteristics of the slurry could give useful information regarding the possible interactions between the particles of the packing material.

During standard operation of the column, the mobile phase enters through the frit placed in the compression piston and exits through the frits in the top flange of the column. In this mode, the two types of compression stress applied to the bed add up. The mechanical stress resulting from the stress applied to the piston is highest close to the piston and decreases toward the top frit, as results from Train's data [23]. On the other hand, the mechanical stress resulting from the head pressure of the column and the mobile phase stream tends to be higher toward the end of the column, i.e., the top frit.

3.3.2. Bed slippage with flow

After the column has been consolidated for a day, the flow was interrupted. The stress applied by the hydraulic jack to the piston, hence the bed, was released and the piston let free to slide down. The flow was then resumed progressively, but in the opposite direction, the mobile phase entering through the top frit and moving downward, to the piston. The head pressure was raised stepwise, up to ca. 80 atm (corresponding to a flow-rate of approximately 700 ml/min). During this operation, the length of the bed was measured with the position sensor, as during the consolidation of the column bed.

3.3.3. Friction measurement

A tubular extension, allowing the positioning of the exit frit 30 mm below the top of the column, was fastened in the place of the standard exit flange. After consolidation of the bed under a mechanical stress of ca. 40 bars, this extension is taken away and replaced by a plug. This plug is made of a 49 mm O.D., 25 mm long stainless steel cylinder to which are bolted two 50 mm O.D., 2 mm thick PTFE disks.

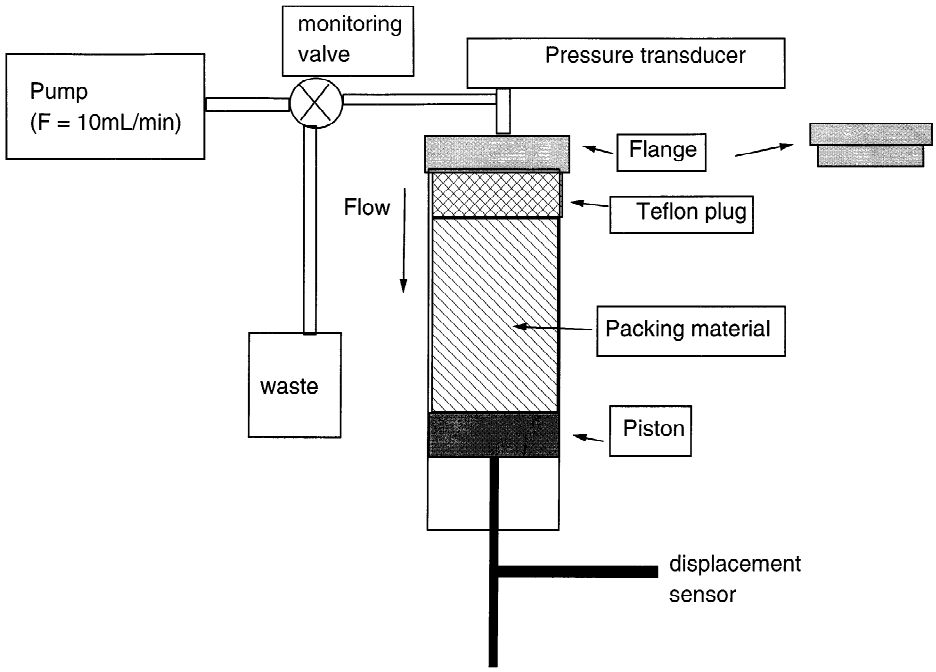

Fig. 1. Schematics of the set-up used to pack beds and to measure the shear force of the bed against the wall.

The purpose of this device is to allow pushing back the column bed under a known mechanical stress obtained by pumping a fluid through the column inlet, on top of the plug, while avoiding the seepage (i.e., flow) of this fluid through the bed. The design limits the friction of the plug while allowing its smooth axial movement. The purpose of the extension is to allow easy positioning of the plug without having to move the consolidated bed, hence, without disturbing the packed bed nor causing orientation of the particles upon their sliding along the wall. After the standard top flange is bolted, methanol is pumped from an LC pump (Waters 6000A) into the top of the column above the plug, through an adjustable valve. Fig. 1 shows a schematic of this set-up. The pressure above the plug is recorded as well as the position of the axial compression piston, now free to slide back.

4. Results and discussion

4.1. Consolidation of the column bed

Typical plots of the bed length versus time, following the rapid application of the axial compression stress to the piston, are reported in Fig. 2 for two compression pressures, 17 and 41 bar. In both cases, the bed consolidates rapidly at first, then more slowly. Still, a slow decrease in column length continues to take place during the whole experiment. Long time records of the column length give the impression that consolidation is a quasipermanent process and is never terminated. This is consistent with one-dimensional consolidation theory in soil mechanics [11] and with long term observations made in the settling of building foundations [24]. Similar observations have been reported previously [14,16–18].

4.2. Relaxation of stress in the bed

Plots of the length of the bed versus time, after rapid release of the compression stress, are reported in Fig. 3 for three values of the compression stress, 17, 33, and 41 bar. The relaxation of the stress is rapid. The bed expends by a length which is approximately two thirds of the length by which it contracted when the stress was applied initially (see

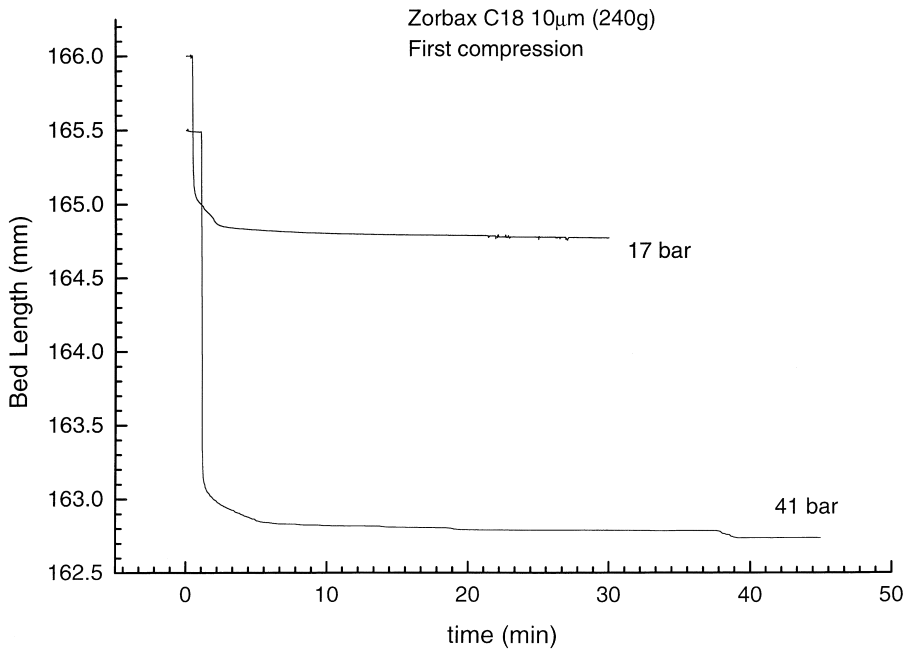

Fig. 2. Consolidation of the column bed. Decrease in bed length as a function of time at two consolidation pressures. Zorbax C_{18} silica, 240 g.

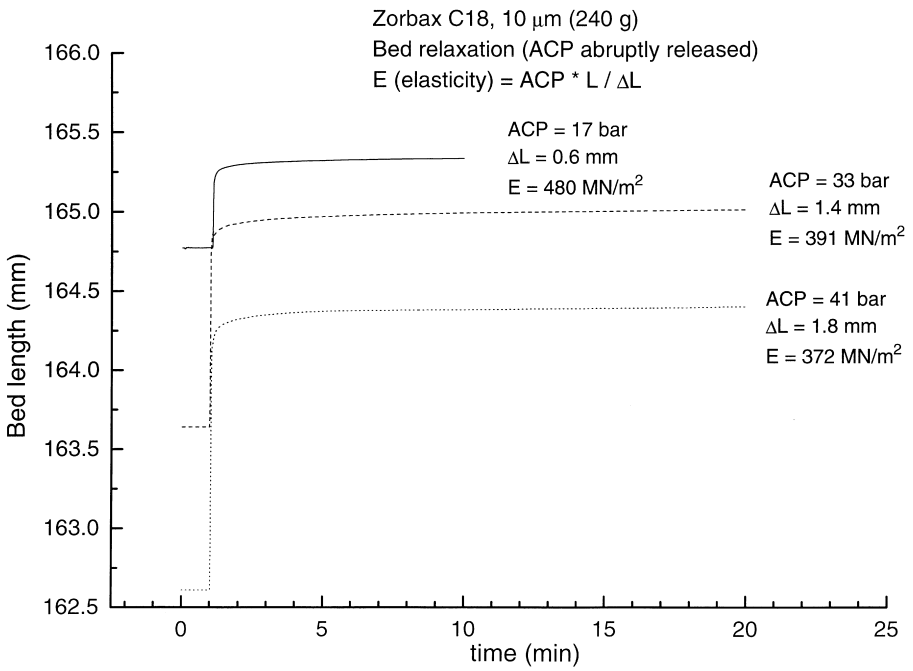

Fig. 3. Consolidation of the column bed. Increase in bed length upon rapid stress relaxation in the bed as a function of time, at three consolidation pressures. Measurement of the elasticity of the bed. Zorbax C_{18} silica, 240 g.

Fig. 2). Many similar experiments performed over the years in our laboratory, on beds of the same packing material or of other such materials, mechanically similar, carried out for this study and for others, led to the same conclusion. Over short periods of time, if the compression stress was applied a second time and removed, and for stress excursions below the consolidation pressure, the bed appears to behave elastically. However, this is observed on the background of an unceasing consolidation, as explained in the previous section.

From the axial recovery under stress relaxation, the modulus of short term elasticity is calculated (Eq. (1)). The length L_o is defined as the bed length after the first consolidation has taken place under the set compression stress for several hours and this stress has been relaxed. The values obtained are given in Fig. 3. Their average is 414 MN/m^2 with a relative standard deviation of 14%. The modulus seems, however, to decrease with increasing consolidation stress. In a previous study, Stanley et al. [18] reported a value of 465 MN/m for another sample of Zorbax C_{18}. The relative difference between these two values (12%) is not significant.

4.3. Bed length with flow reversal

After consolidation of the column bed under axial compression, the mechanical stress was released and the piston left free to move backward. The direction of the flow was reversed and the mobile phase pumped into the column through the top frit. The head pressure of the liquid was raised progressively, stepwise. The duration of each successive step was a few minutes. A plot of the head pressure versus time during this experiment is given in Fig. 4. This figure shows also a plot of the bed length versus time. The column length increased slightly and equilibrated rapidly after each successive step in the head pressure profile. Then, it remained stable. Although the bed expanded slightly, it could not move because the extent of back movement of the piston in neutral position is limited by design.

The same experiment was carried out with the

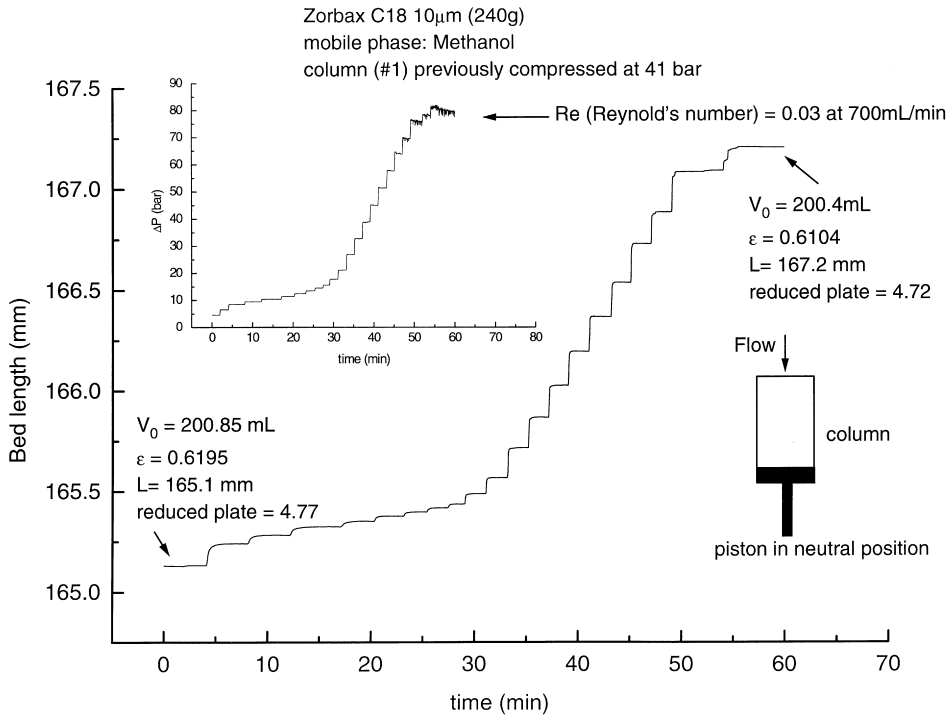

Fig. 4. Seepage of mobile phase through the bed. Plots of the inlet pressure and the bed length versus time. Piston in neutral position.

piston in the rearward position. Then the piston is free to move backward, although it does not do so under its own weight. Fig. 5a shows the pressure profiles during an experiment in which methanol was pumped into the column bed through the top flange (direction opposite to the one used under standard operating conditions). The piston begins to move backward for an inlet pressure of approximately 5.5 bar. The rear displacement was approximately 4 mm, corresponding to an increase of the external porosity of 2.5%. The stress due to the back pressure of the liquid acting on the piston itself was low, the hydraulic resistance of the exit tubing being small. The sliding of the bed is caused by the seepage stress no longer being balanced by the wall friction. Fig. 5b shows the results of a similar experiment in which the direction of the methanol is reversed, the liquid entering through the piston. The stress applied to the piston is the head pressure of the column. The piston now starts sliding for a lower value of the applied pressure, approximately 3 bar. The extent of the back migration of the piston is 3 mm. However, there are no reasons to think that the piston is stuck to the top of the bed and that the bed itself has expanded, causing an increase of the external porosity. More probably, a void filled with the solvent has formed between the piston and the bed, while the piston was receding, slowly deforming the leakproof fittings on its side. Similar experiments carried out with an empty column (no packing material) and a fixed piston showed a high permeability of the system (pressure drop less than 2 bar at 100 ml/min).

A plot of the bed length versus the head pressure of methanol is given in Fig. 6a. The bed length increases linearly with increasing head pressure up to about 3 and 5.5 bar, depending on the direction of solvent flow. As seen in Figs. 4 and 5a, the length reported in Fig. 6a for each value of the head pressure is achieved rather rapidly and remains constant thereafter. This phenomenon could not take place if there was not a strong friction of the bed against the column wall. Finally, Fig. 6b shows plots of the flow-rate versus the head pressure of the solvent. The permeability of the bed is much higher (i.e., the flow-rate at a given head pressure larger) when the flow is in the downward direction and the bed is truly expanded. The result obtained with an upward flow direction confirmed the interpretation of the data in Fig. 5b given above.

4.4. Determination of the friction shear stress of the bed against the column wall

The PTFE plug manufactured in the departmental workshop was first placed inside the empty column barrel, against the piston (Fig. 1). The mobile phase was then pumped into the column under slowly increasing pressure and the plug position was recorded. The result is shown in Fig. 7. The plug remains static until a pressure of ca. 14 bar is reached. Then it starts moving at a nearly constant velocity corresponding to the pump flow-rate, as shown in Fig. 8 by a comparison of the records of the pressure upstream the plug and the displacement of the piston (note that the displacement record stops after 7.5 mm, the sensor range being limited [25]). In the same time, the pressure drops rapidly from the value corresponding to static friction to that corresponding to dynamic friction. This is the classical result observed in the determination of shear stress. The results obtained are reproducible as illustrated in Fig. 8 and Table 1a.

The same experiment was repeated on beds similar to those used in the experiments discussed earlier in this work (Figs. 2–4), after the consolidation of these beds had taken place under 20 or 41 bar. Some typical records are reported in Fig. 9 on beds obtained with 240 g of Zorbax consolidated under 20 bar (length, ca. 165 mm). The pressure upstream the plug was raised stepwise. When the friction becomes insufficient to keep the bed in place, it starts moving and the pressure above the plug drops significantly (Fig. 9). The bed continues slipping along the metal cylinder, at a constant velocity, until the experiment is stopped. The variation with time of the pressure upstream the plug provides the determination of the stress corresponding to static friction. The values obtained under various sets of experimental conditions are summarized in Table 1b. It is worth noting that these values are well reproducible (relative standard deviation 2 to 5%).

4.5. Factors influencing the friction shear stress of the column bed against its wall

Preliminary experiments have shown that the shear stress required for moving the consolidated bed depends considerably on two factors, the nature of the fluid impregnating the bed and the degree of

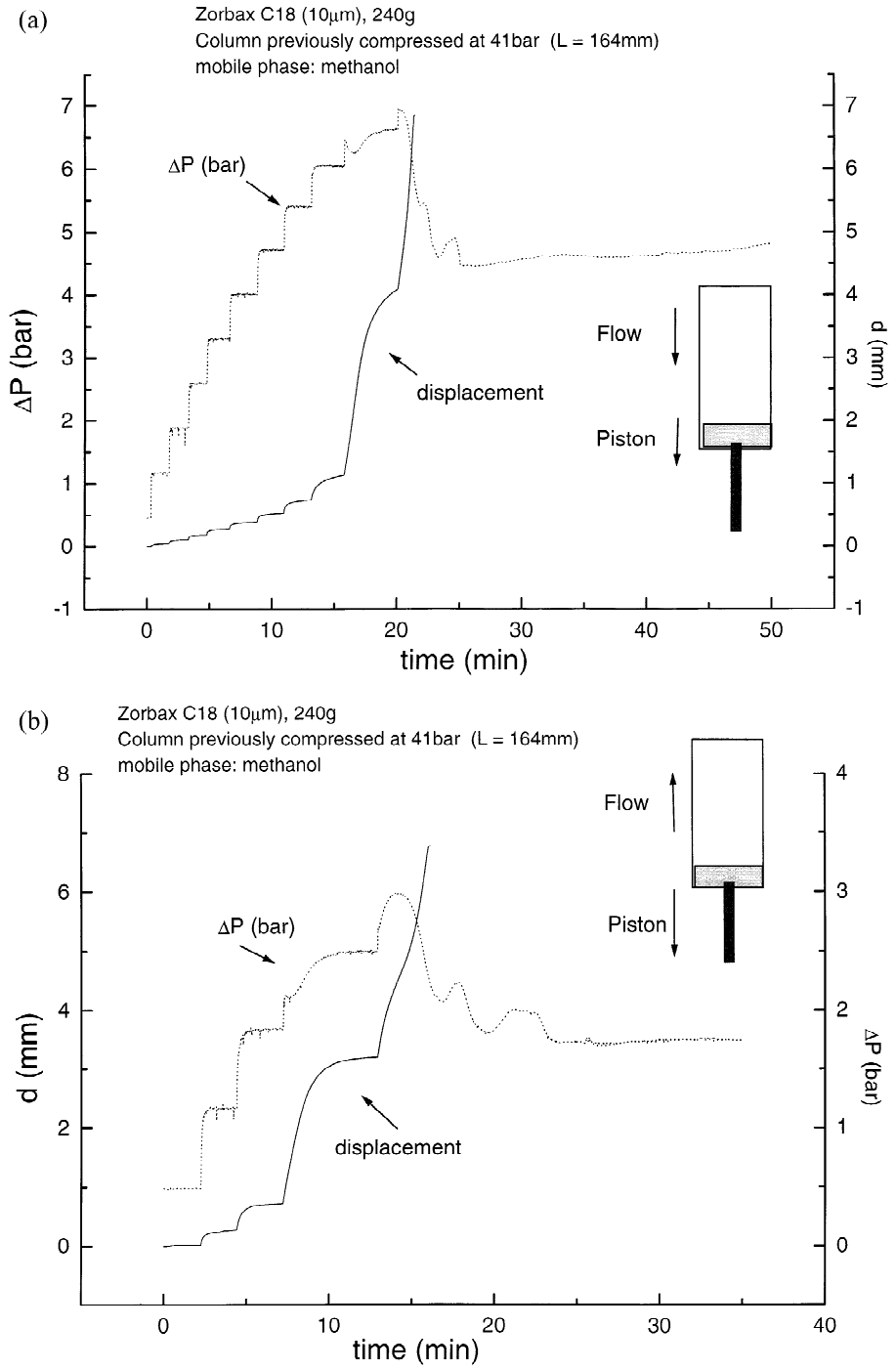

Fig. 5. Seepage through the bed. Column length and inlet pressure versus time. Same experiment as in Fig. 3. Piston in rearward position. (a) Flow velocity downward. At 7 mm, the position sensor becomes saturated. (b) Flow velocity upward.

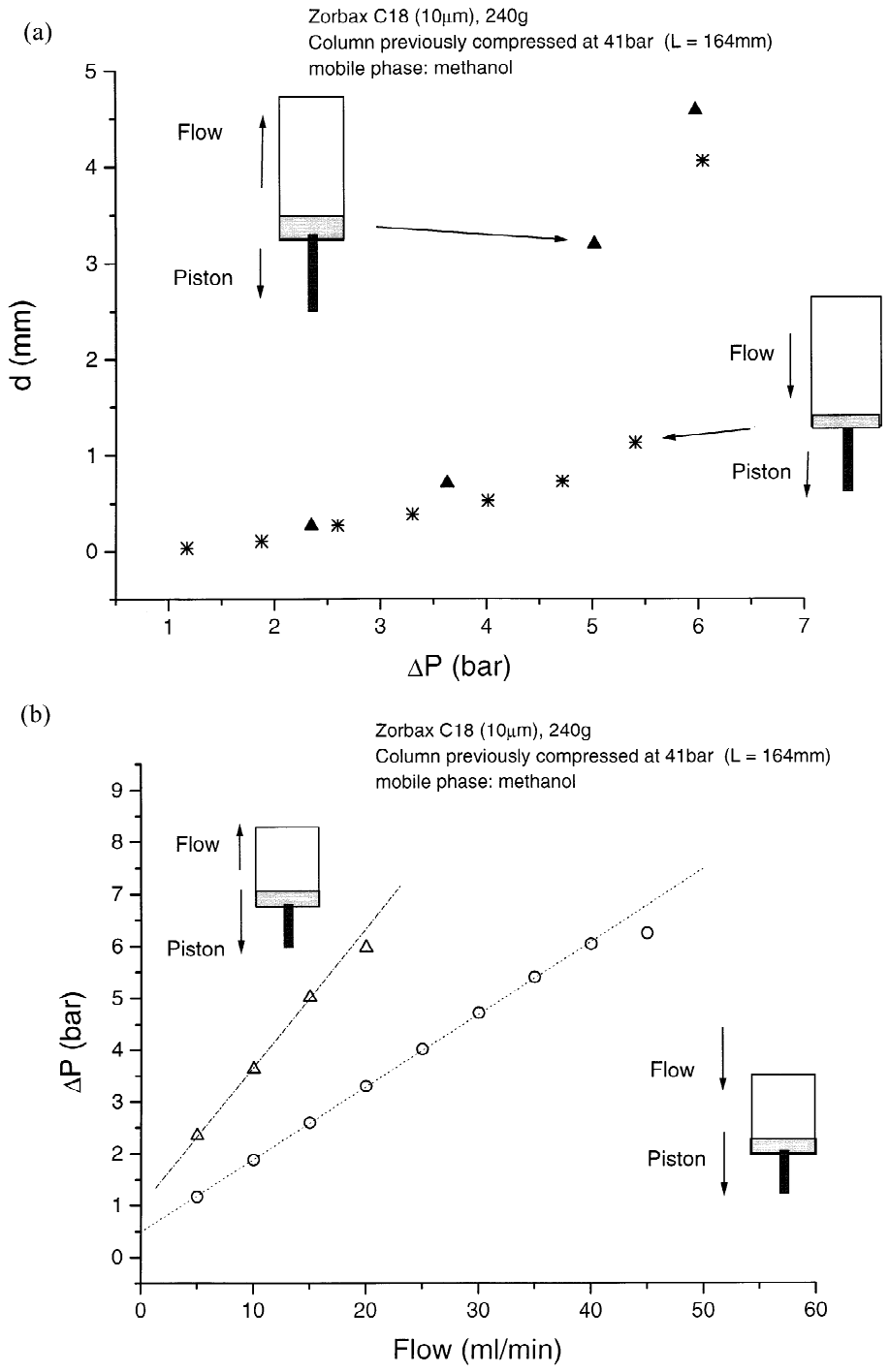

Fig. 6. Seepage through the bed. Influence of the solvent head pressure on the column bed. (a) Piston position versus head pressure. (b) Head pressure versus flow-rate during the experiment in Fig. 5(a and b).

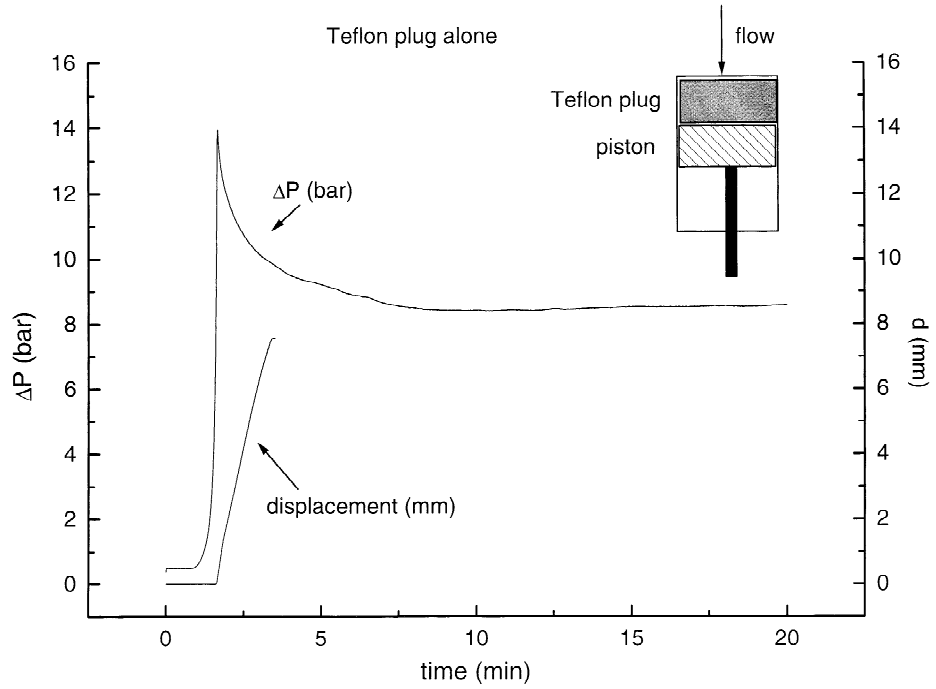

Fig. 7. Friction of the bed against the column wall. Blank run. Plots of the fluid pressure against the plug (Fig. 1) and of the apparent bed length versus time.

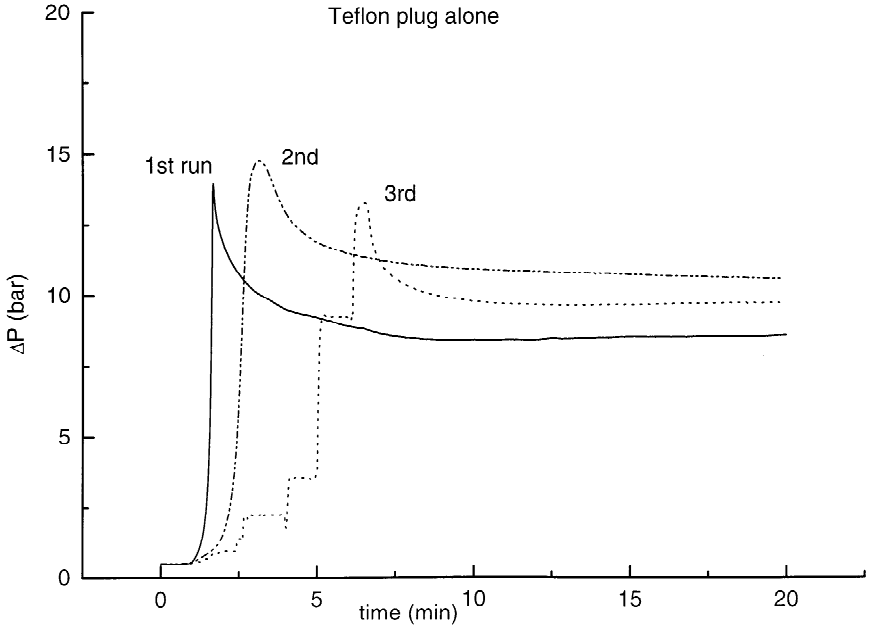

Fig. 8. Friction of the bed against the column wall. Reproducibility of the shear stress threshold required to move the plug: the three curves are repetition of the same experiment.

Table 1
Measurement of the shear stress between a bed of packing material and the column wall

(a) Blank experiment (plug alone)		
Experiment	Stress (bar)	
1	14.76	
2	13.94	
3	13.27	
Average	13.99	
RSD (%)	5.3	
(b) Long bed packed in methanol (240 g)[a]		
Experiment	Total stress (bar)	Stress on the bed
1	43.2	29.2
2	45.0	31.0
3	43.9	29.9
Average	44.0	30.0
RSD (%)	2.1	3.0
(c) Short bed (50 g)	Stress on the bed (bar)	
Methanol	1.5	
Water	70.9	
Dry packed	44.2	

[a] In acetone, the total stress is 81.4 and the stress on the bed 67.4 bar.

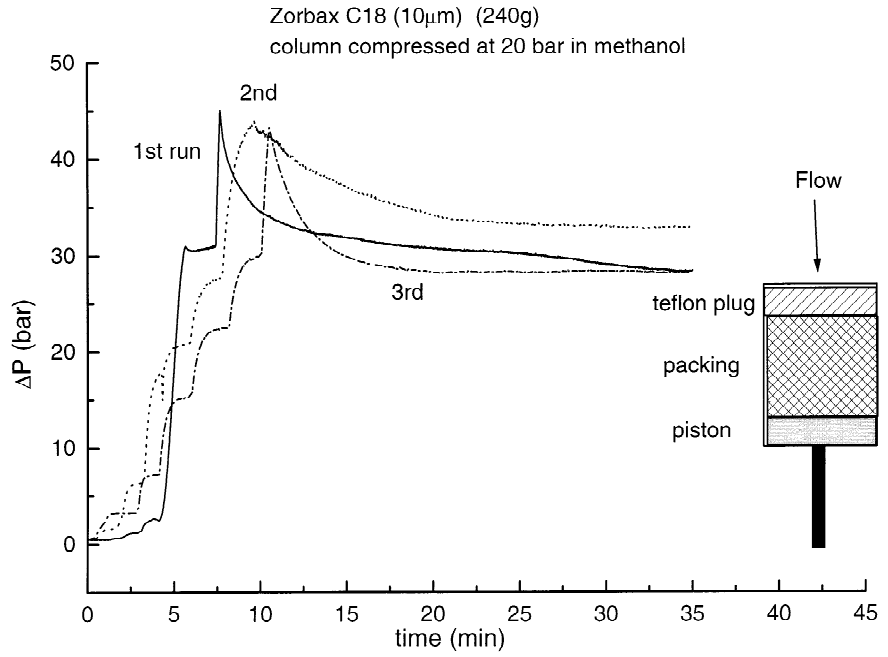

Fig. 9. Friction of the bed against the column wall. Friction of a bed of 240 g of Zorbax C_{18} (10 μm) preconsolidated under 20 bar. Plot of the fluid pressure against the plug (Fig. 1) versus time. Reproducibility of the shear stress threshold required to move the bed (Zorbax C_{18} silica, 240 g, consolidated under 20 atm).

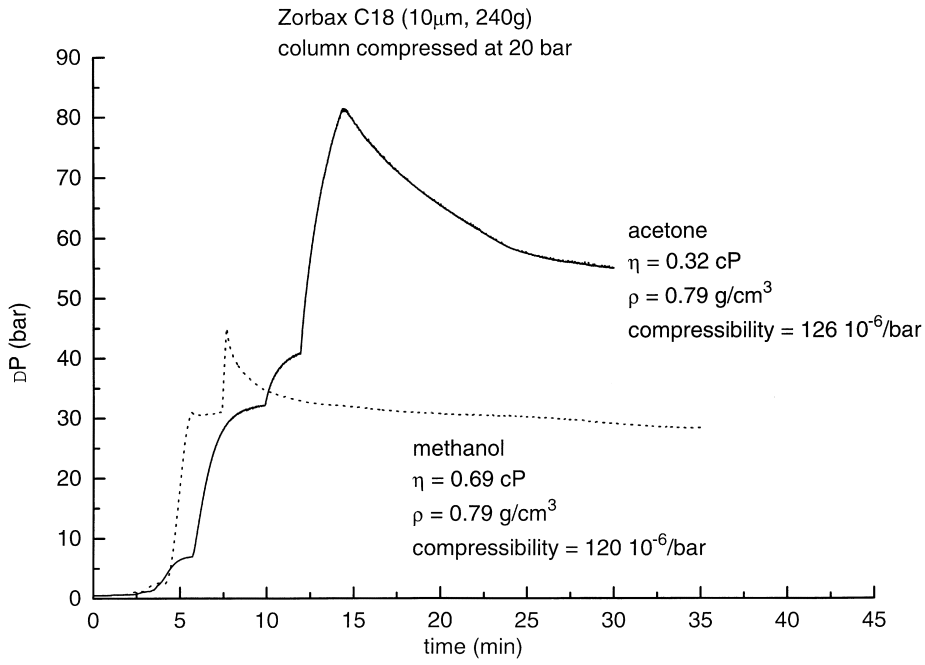

Fig. 10. Friction of the bed against the column wall. Influence of the slurry solvent used. Dotted line, bed consolidated in methanol. Solid line: bed consolidated in acetone (Zorbax C_{18} silica, 240 g, consolidated under 20 atm).

particle breakage experienced by the packing material in the column. Figs. 10 and 11 illustrate the effect of the first of these factors. The stress is relatively small with methanol, larger with acetone (Fig. 10). With dry particles, the measurement could not be made on a bed of the size (240 g, ca. 165 mm long) used with the organic solvents. The plug would not move, even under a stress of 150 bar applied to the plug. Higher pressures would exceed the safety limit of the column. A shorter bed (50 g, ca. 31 mm long) was used. It was preconsolidated under 27 bar, hence denser that the longer bed [26]. The threshold shear stress could be measured with dry particles but the value found is very large, 30-times higher than methanol under the same conditions (Table 1c). A still higher value was observed for a bed impregnated with water. This result will not surprise those practitioners who have wondered why it is so difficult to unpack the bed of an reversed-phase LC column which was used with pure water while this is so easy to do if the column was used with pure methanol. Note that the blank (i.e., the stress required to move the plug) was measured before or after each experiment reported here, as described in Fig. 9. Although it is reproducible over a short period of time (Table 1a), it increased from 14 to 19 atm between the experiments reported in Figs. 7–10 and those in Fig. 11. Part of this change was due to the replacement of the fittings of the piston head, which had become leaky, by new ones.

The progressive increase of the friction shear stress was also due to the operating procedure. In order to limit the amount of packing material used in these experiments (Figs. 9–11), the packing material from a previous bed was reused a second time. However, we had to avoid the progressive adjustment caused by the running in of the lateral surface of the bed in contact with the column wall and the metal surface of the wall. This would have lead to erroneous friction data. So, between successive friction shear stress measurements, the bed was stirred into a slurry in enough fresh solvent before being consolidated again. If a change in solvent was required, the new solvent was percolated through the consolidated bed until elimination of the previous solvent from the internal porosity of the particles.

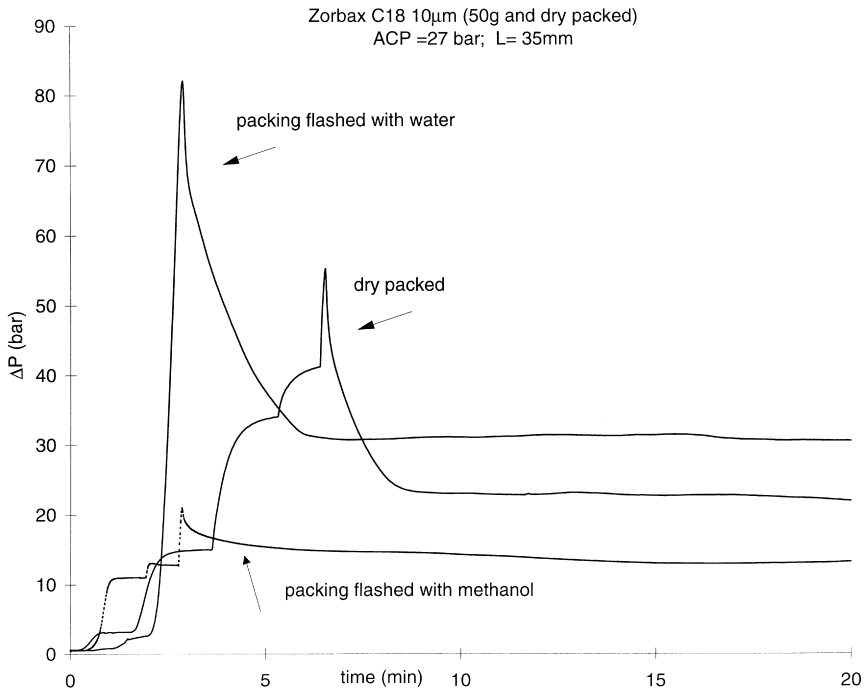

Fig. 11. Friction of the bed against the column wall. Influence of the slurry solvent used. Curve 1: bed consolidated in methanol. Curve 2: bed consolidated in water. Curve 3: bed consolidated in air (dry packing). Zorbax C_{18} silica, 50 g, consolidated under 27 atm.

This procedure, however, causes particle breakage (mostly when the bed begins to slip along the column wall) and the fine, broken particles accumulate. The accumulation of fine particles causes a progressive increase of the friction coefficient. This phenomenon is exemplified by a comparison between the experimental results described above. The stress required to move a bed packed with a methanol slurry is 20-times less with the short bed (Fig. 11) than with the long one (Figs. 9 and 10). The explanation is that the results shown in Fig. 11 were obtained not only with a new piston head fitting but with a new sample of packing material.

4.6. Estimate of the friction coefficient of the bed against the column wall

Finally, we investigated the influence of the bed length on the friction shear stress. The experiments described above were repeated on beds of different lengths prepared from methanol slurries of the packing material. Each measurement was carried out with a fresh portion of packing material. A plot of the shear threshold versus the column length is given in Fig. 12. The shear stress threshold increases faster than the bed length. When the bed length increases, the threshold increases. However, the reaction of the plug against the immobile bed causes an increase of the radial stress of the bed against the wall, thus increasing the friction.

5. Conclusion

This work demonstrates the influence of friction between the bed of packing material and the column wall on the properties of the bed and, particularly on its homogeneity. Without friction, the bed could probably be highly homogeneous. Hence, the column efficiency would be much higher, possibly twice or more. However, it would be much more difficult to pack and operate these excellent columns which would have to be kept or at least operated under mechanical compression. Because of this friction at

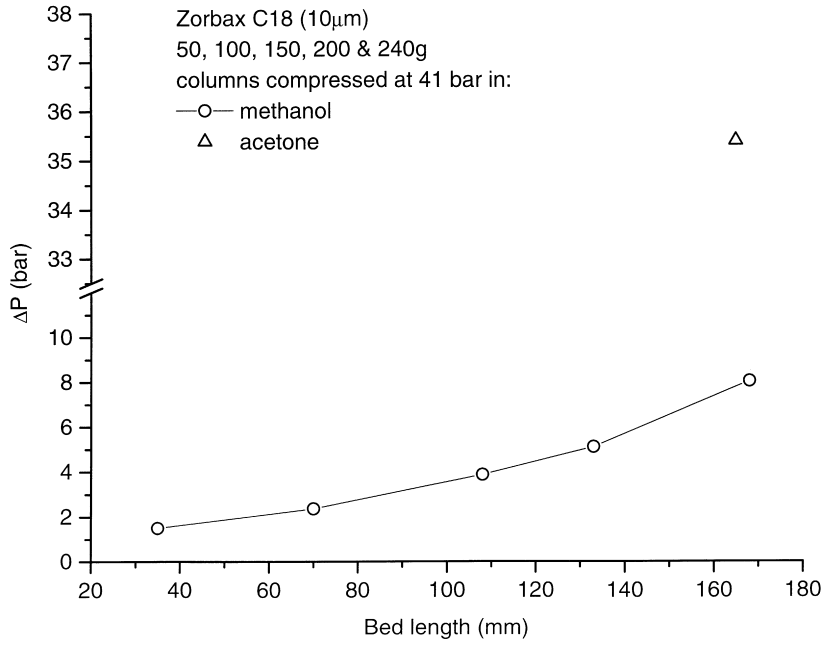

Fig. 12. Friction of the bed against the column wall. Influence of the bed length. Zorbax C_{18} silica, consolidated under 41 atm.

the column wall, the beds are mechanically stable, at least within a range of experimental conditions which appears to be satisfactory in practice. However, the friction at the walls causes a heterogeneous distribution of the stress and strain throughout the bed. As a consequence, the porosity and permeability distributions in the column are not homogeneous either. The resulting lack of homogeneity of the bed causes band spreading.

These results raise new questions. Is there an optimum friction coefficient? What controls the friction coefficient between the packed bed and the wall? What controls the friction between particles? What is the distribution of stress and strains in a bed and is it possible to modify it, to increase the homogeneity of the bed? At this stage, we know from solid mechanics that the coefficient of friction between the packing material and the column wall depends on the roughness of the wall. The upper limit of the coefficient of friction would occur with a rough surface, having asperities on the order of the diameter of the packing material. Under these conditions, some of the particles would be immobilized between asperities against the wall surface. This would force slip or failure to take place within the packing material itself, about one or two particle diameters away from the wall. The corresponding coefficient of friction would then be nearly equal to $tg\phi$, where ϕ is the friction angle of the packing material, about 30 for Kromasil NP 10 and 36 to 40 for Zorbax Pro 10 Sil [26], giving maximum values of the friction coefficient of 0.58 and 0.73 to 0.84, respectively. The lower limit of the coefficient of friction would be zero for a completely frictionless surface. For a highly polished surface, such as the wall of the column used in this work, the coefficient of friction could be measured in the laboratory. Preliminary data suggests values of the order of 0.38 for Zorbax [27]. Contrary to the observations reported here, the principles of soil mechanics suggest that the coefficient of fiction would be independent of the fluid used in the packing process, but dependent upon the density or porosity of the packing material which in turn was affected by the fluid properties. Certainly, the interactions between particles of C_{18}-bonded silica, which are hydrophobic, are much stronger in water than in an organic solvent. These issues are under current investigation.

Acknowledgements

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