ELSEVIER

Journal of Chromatography A, 849 (1999) 35–43

JOURNAL OF CHROMATOGRAPHY A

Validity of Darcy's law at low flow-rates in liquid chromatography

Tivadar Farkas[a,b,1], Guoming Zhong[a,b,2], Georges Guiochon[a,b,*]

[a]*Department of Chemistry, The University of Tennessee, Knoxville, TN 37996-1600, USA*
[b]*Division of Chemical and Analytical Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37803, USA*

Received 25 January 1999; received in revised form 31 March 1999; accepted 31 March 1999

Abstract

The applicability of Darcy's law at extremely low flow velocities has been questioned in the scientific literature. It was investigated using a simple chromatographic system. Ethylene glycol (viscosity, 19.9 cP at 20°C) was pumped through 10 to 25 cm long chromatographic columns packed with small porous spherical particles (size, 5 to 10 μm). The dependence of the linear velocity of this liquid on the inlet pressure was found to be linear in the range of Reynolds numbers (based on particle diameter) between $Re=1\cdot10^{-6}$ and $1\cdot10^{-4}$. These results contradict earlier reports by Fand et al. and more recent findings by Kececioglu and Jiang that suggest a limited applicability of Darcy's law to the range Re=0.3 to 0.7.

Keywords: Darcy's law; Flow-rate; Ethylene glycol

1. Introduction

Fluid dynamics plays an important role in chromatography because the linear velocity at which migrates the center of a band along a column is proportional to the fluid linear velocity. Countless reports have shown Darcy's law to be valid under the whole range of conventional experimental conditions and this law is universally accepted in the separation sciences [1,2]. Darcy's law relates the linear velocity of a fluid percolating through a porous medium and the pressure gradient along the direction of flow. In column chromatography, the packed bed is reasonably homogeneous and much longer than the column diameter. Therefore, the fluid direction is axial [2]. The integrated form of Darcy's law is

$$u = -\frac{k}{\eta}\cdot\frac{\Delta P}{L} \quad (1)$$

where u is the fluid velocity, k the permeability of the bed (proportional to the square of the average particle size), η the viscosity of the fluid, ΔP the inlet pressure (or head pressure in hydrodynamics), and L the column length. Although this law is essentially empirical, it was possible to derive it from the Navier–Stokes equation applied to a bed of particles [3]. However, Darcy's law has a limited range of validity. For example, Ergun [4] showed that, at high velocities, the relationship between flow velocity and inlet pressure is no longer linear because of inertial effects [5].

Dybbs and Edwards [6] reviewed a variety of experimental results relating to this phenomenon and

*Corresponding author. Tel.: +1-423-974-0733; fax: +1-423-974-2667.
E-mail address: guiochon@utk.edu (G. Guiochon)
[1]Present address: Phenomenex, Torrance, CA, USA.
[2]Present address: Praxair, Tonawanda, NY, USA.

0021-9673/99/$ – see front matter
PII: S0021-9673(99)00482-3

concluded that the following four different flow regimes can be identified, Darcy, inertial, Fochheimer and turbulent regimes, corresponding to higher and higher flow velocities. These flow regimes have been thoroughly investigated. However, there are no agreements regarding the demarcation between them, nor the nature of the parameter which best characterizes their boundaries, nor the critical values of any possible parameter at which the transitions occur. Fand et al. [7] considered for that the particle Reynolds number

$$\mathrm{Re} = \frac{u d_p \rho}{\eta} \quad (2)$$

where u is the superficial flow velocity, d_p the particle diameter, and ρ the fluid density. These authors set Reynolds number limits for the different flow regimes. After these authors, the upper limit of the Darcy regime and the transition with the inertial and Fochheimer regimes would be for Reynolds numbers between 1 and 10. They also stated that there was a third critical Reynolds number, Re_{DL}, below which Darcy's law did not apply and which separates the pre-Darcy from the Darcy regimes. More recently, Kececioglu and Jiang [8] considered that the characteristic length of the porous medium is not the particle diameter but is proportional to the square root of the permeability over the porosity of the bed. They suggested much lower values of Re for the transition (see later). Bear reviewed some previous works in which reference was made to the existence of a minimum pressure gradient below which there was very little or no flow [9]. All these results seem to suggest the existence of a fifth regime, the pre-Darcy flow regime.

Liquid chromatography is carried out under experimental conditions corresponding to values of the Reynolds number which are much lower than 1. The fluid used is selected among common solvents, which have viscosities between 0.4 (organic solvents) and 2 (water–methanol mixtures) cP, exceptionally more for some buffered solutions [2]. The average size of the particles used is between 1 and 50 to 80 μm, depending on the intended application. The mobile phase velocity is usually selected in order to achieve values of the particle Peclet number, ud_p/D_m, of the order of 5 to 20, with D_m, the molar diffusivity of the solute at infinite dilution in the solvent. For chromatographic systems, the diffusivity is most usually between $2\cdot10^{-6}$ and $2\cdot10^{-5}$ cm^2/s. These numbers combine to give typical values of the Reynolds number in chromatography which are between 0.001 and 0.1. Only in exceptional cases have chromatographic experiments been conducted in a packed bed at Reynolds number higher than 0.1. Thus, it would be of the utmost importance for chromatographers to know about a pre-Darcy flow regime and about the transition between pre-Darcy and Darcy regime, if indeed such phenomena, which have never been observed in the separation sciences [1,2], do exist. Unfortunately, the pre-Darcy regime has triggered less interest than other flow regimes, probably because extremely low flow velocities have little practical applicability in hydrodynamics or engineering.

Fand et al. [7] quote a lower limit for the Darcy (often also called viscous) flow regime of $\mathrm{Re}<10^{-5}$, well below the range in which any chromatographic experiments have ever been conducted. This statement is not based on their data since all their measurements were carried out at Reynolds number in excess of 1 (Ref. [6], Figs. 2 to 4). On the contrary, Kececioglu and Jiang [8] found more recently that Darcy's law has very little applicability and that the pre-Darcy flow regime is valid for a much broader range of Reynolds numbers. They reported that the flow of water through a bed of randomly packed glass beads with a particle diameter of 3 mm followed Darcy's law only in the range $0.3<\mathrm{Re}<0.7$. They also found that the limits for Darcy flow depend on the particle diameter of the beads (e.g., for 6 mm beads the corresponding interval would be $0.6<\mathrm{Re}<1.0$). If confirmed, this result means that the entire realm of chromatographic separations would take place within the pre-Darcy regime. This suggestion is too important an issue for chromatographers to ignore.

Obviously, chromatographic techniques make it very easy to investigate accurately the validity of Darcy's law at very low values of Re since standard features are the use of (1) small, quasi-spherical particles of silica, packed into relatively long columns; (2) pumps allowing the percolation of these columns with a wide variety of solvents at a constant flow-rate and a high inlet pressure; and (3) detectors

allowing an accurate measurement of the flow velocity (with repeatability of 0.3% or better [10]). Furthermore, chromatographers have striven for many years to pack dense, homogeneous beds because this is a necessary condition to maximize the efficiency of the separations performed. The degree of homogeneity of the column beds was investigated recently [11]. While chromatographic beds are not completely homogeneous, they are probably much more so than beds obtained by pouring porous glass beads into a container ''at random'' and applying mere ''systematic tapping'' [8]. In typical columns, the width of the radial distribution of the local linear velocities of the solvent at the outlet of the column is less than 5% of the cross-section average velocity [11].

In theory, the porosities of stable packed beds of particles range from 0.26 upward, with the closest packed arrangement of spheres having a porosity $\epsilon = 0.26$ [12]. In practice, it is exceptional to encounter beds with interparticle porosities lower than 0.30. Chromatographic columns are packed by pumping a light slurry of the packing material into a column closed at the exit end by a frit. The bed is consolidated by the hydrostatic pressure and the viscous friction stress associated with the high flow-rate percolation of a suitable solvent, pumped through the column under high pressure. The beds obtained are compact, with interparticle porosities in the range 0.35–0.45 [13]. Guan and Guiochon [14] measured the interparticle porosity of the column, packed with 10 μm particles, that was later used in this study and found a value of $\epsilon = 0.399$. Note that the total porosity of chromatographic columns is higher, since the particles used are porous. Common values of the total bed porosity are in the range $\epsilon_T = 0.6–0.75$.

The aim of this report is to present the results obtained in a study of the relationship between linear flow velocity and column inlet pressure, using conventional chromatographic techniques simply adapted for operation at unusually low Reynolds numbers.

2. Experimental

The instrument used was a Hewlett-Packard (Palo Alto, CA, USA) liquid chromatograph Model 1050, equipped with a built-in pressure gauge, a solvent delivery system and a data station. The HPLC pump operates at constant flow-rate, under the control of a microcomputer, with programs supplied by the manufacturer. The specification is a relative standard deviation of the retention times (all proportional to the flow-rate) less than 0.3% at flow-rates lower than 0.1 ml/min. We checked the flow-rate at each setting of the pump used in our experiments (between 0.006 and 0.5 ml/min) by collecting the effluent in a glass container over a measured period of time and weighing it. Since the collection time was long (between 0.1 and 40 h), the weight measurement and the subsequent flow-rate calculation was accurate, but only the average value of the flow-rate over the collection time could be obtained. This method is standard for the calibration of flow-rates in our laboratory. Its accuracy is limited by the evaporation losses. These are minimized by collecting the column effluent in a container with a narrow opening, closed with a loose cotton plug. In the case of ethylene glycol which has a very low vapor pressure at room temperature (1 mmHg at 53°C; 1 mmHg = 133.322 Pa), they are entirely negligible. The long term stability of the pump has been established by similar collection experiments carried out at higher flow-rates during a number of independent chromatographic experiments. The relative standard deviation of all the flow-rate measurements is less than 1%.

The flow-rate measurements gave values less than 1% larger than those set on the pump. As for most HPLC pumps, the one used for this study corrects the set flow-rate to allow for the compressibility of the solvent (for ethylene glycol, $\chi_0 = 0.37 \cdot 10^{-4}$ bar^{-1}). Because the inlet pressure is lower than 200 bar, the influence of the pressure dependence of the compressibility and the viscosity of the solvent on the actual flow-rate are small and can be neglected [15]. The inlet pressure readings were made long after the flow-rate settled (e.g., approximately 1 h for the low settings of the flow-rate) and at least twice during collection of the solvent. The relative standard deviation of the three readings made for each measurement was always less than 3%.

Finally, a correction was made to the pressure readings by subtracting the pressure drop caused by the resistance to flow due to the instrument itself. There are two contributions to this resistance. First,

the tubings, the valves (especially the sampling valve, necessary for conventional chromatographic analyses), and the detector cause some obstruction to the flow of the fluid. The extent of this correction was derived from previous recordings of the pressure drop displayed by the gauge when no column was connected to the instrument. Probably because our liquid chromatograph was designed to operate preferably at flow-rates in the range of 0.5 to 5 ml/min, this contribution was found to be negligible in the experiments reported here (note that in our measurements the injector valve was by-passed and the detector was not connected to the column outlet).

The other source of systematic errors is the pressure drop caused by the column end-fittings especially the two frits which are necessary to keep the packing stable during column operation. The nominal pore size of these frits was 2 μm, but the actual pore diameter is most probably smaller than that, since the fines that come with 3 μm packing materials never clog these frits. In order to make sure that the measured pressure drop was caused only by the porous bed, a separate series of measurements was performed by mounting on the instrument a blank column made by attaching the frits and end-fittings from a previously investigated column to a piece of empty tubing. The results of the measurements of the pressure drop caused by the instrument tubings and column end-fittings are plotted in Fig. 1.

Three different chromatographic columns were used for this study: a 100×4.6 mm column packed with 10 μm particles (Zorbax, Rockland Technologies, now Hewlett-Packard, Newport, DE, USA); a 150×4.6 and a 250×4.6 mm column, both packed with 5 μm particles (Vydac, Hesperia, CA, USA and Phenomenex, Torrance, CA, USA, respectively). Later in this work, these columns are labeled I, II and III, respectively. All packing materials were conventional C_{18}-modified porous spherical silicas for chromatography (having average pore sizes of 150 Å, 300 Å and 150 Å, respectively). The 100 mm long column was packed in our laboratory. It was

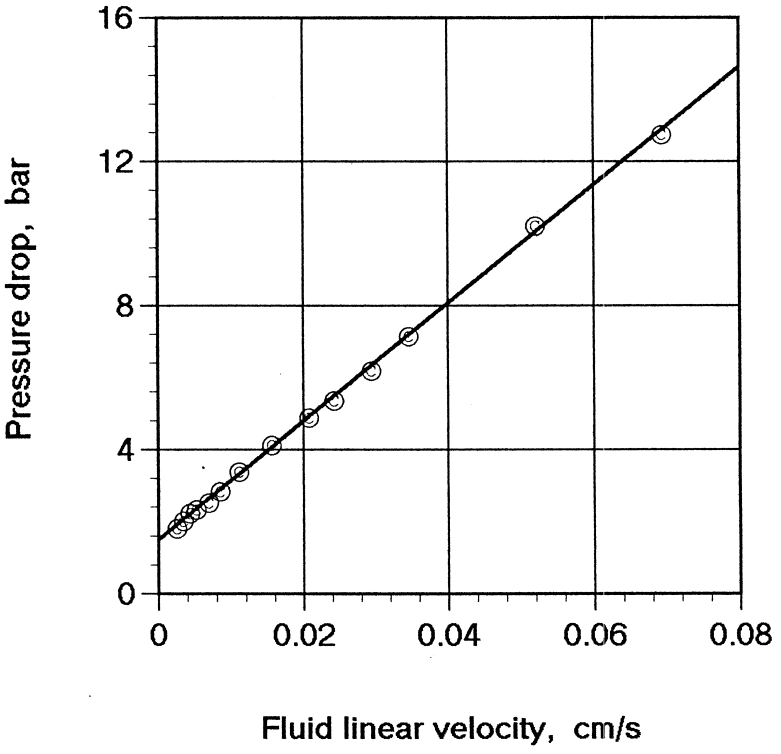

Fig. 1. Plot of the inlet pressure of a blank (i.e., empty) column versus the linear velocity of ethylene glycol.

studied previously and a detailed report on its characteristics and performance is available elsewhere [14]. The Vydac and Phenomenex columns were new commercial columns. The total porosity, ϵ_T, for each column was determined by recording the transit time, t_0, of an unretained marker (uracil in a methanol–water solution) at a flow-rate of 1 ml/min and by dividing this value by the total volume of the column tubing. The values of the total porosity of the three columns investigated in this study were $\epsilon_T = 0.593$, 0.611 and 0.602, respectively.

Ethylene glycol (purchased from J.T. Baker, Phillipsburg, NJ, USA) was used as the mobile phase. It has a density $\rho = 1.109$ g/ml and a viscosity $\eta = 19.9$ cP at 20°C.

3. Results and discussion

Preliminary experiments showed that mixtures of ethylene glycol and water exhibited too low a viscosity for our purpose. The Reynolds numbers achieved were not low enough. The columns had to be operated under low flow-rates and the inlet pressures required to achieve these flow-rates were extremely low, practically impossible to measure with any accuracy using the pressure gauge of the chromatograph. We needed to reach lower Reynolds numbers while using relatively high inlet pressures for their accurate measurement. Eliminating the mobile phase velocity between Eqs. (1) and (2) gives a relationship between the parameters of the experiment and the Reynolds number achieved

$$\mathrm{Re} = kd_p \cdot \frac{\Delta P}{L} \cdot \frac{\rho}{\eta^2} \tag{3}$$

Eq. (3) shows that high viscosity fluids and long columns, packed with relatively small particles, are required in order to combine inlet pressures which are high enough to be measured accurately and low linear velocities compatible with low values of Re.

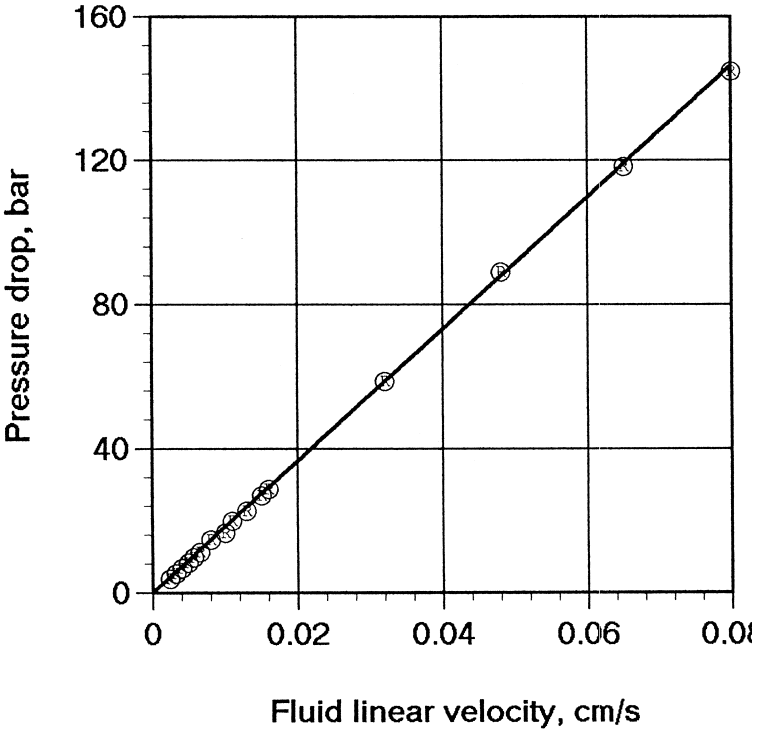

Fig. 2. Plot of the column inlet pressure versus the linear velocity of ethylene glycol percolating through a 100×4.6 mm chromatographic column packed with 10 μm C_{18} bonded porous spherical particles (average pore size 150 Å).

The use of pure ethylene glycol proved to be satisfactory for our purpose.

Fig. 2 shows a plot of the inlet pressure measured for the 100×4.6 mm column packed with 10 μm particles versus the linear velocity of pure ethylene glycol pumped at volumetric flow-rates between 0.015 and 0.5 ml/min. The corresponding values of the fluid velocity and the Reynolds number were between 0.0024 and 0.08 cm/s and between $8 \cdot 10^{-6}$ and $3 \cdot 10^{-4}$, respectively. The experimental data fitted well to a linear dependence of the linear velocity of the fluid on the inlet pressure of the column, over nearly two orders of magnitude of Reynolds numbers. A fit of the data points corresponding to the lowest six values of Re to a straight line (Fig. 3) gave values of the coefficients which are not significantly different from those obtained when fitting the whole set of data points to a straight line (see Table 1). This proves that there is no significant deviation from Darcy's law in the range of linear velocities investigated in this experiment.

The second column was investigated under similar conditions and behaved similarly. Compared to the first column, the second one was packed with 5 μm spherical particles (instead of 10 μm particles) and was 50% longer. Fig. 4 shows the plot of the inlet pressure versus the flow-rate for this second column. The range of linear velocities explored with this column overlaps the lower end of the range explored with the first column and the Re values were between $4 \cdot 10^{-6}$ and $4 \cdot 10^{-5}$. The plot shows again that the inlet pressure increased linearly with increasing linear velocity of the fluid.

The permeability of the column was only approximately three-times lower than that of the first

Table 1
Fit of the experimental data to Darcy equation (Eq. (1)).

Curve	Column	Slope	Intercept	ϕ	r^2
Fig. 1	None	164	1.51		0.997
Fig. 2	I	1829	0.08	865	1.000
Fig. 3	I	1796	0.18	849	0.999
Fig. 4	II	6300	0.27	593	0.998
Fig. 5	III	17 982	0.34	940	0.999

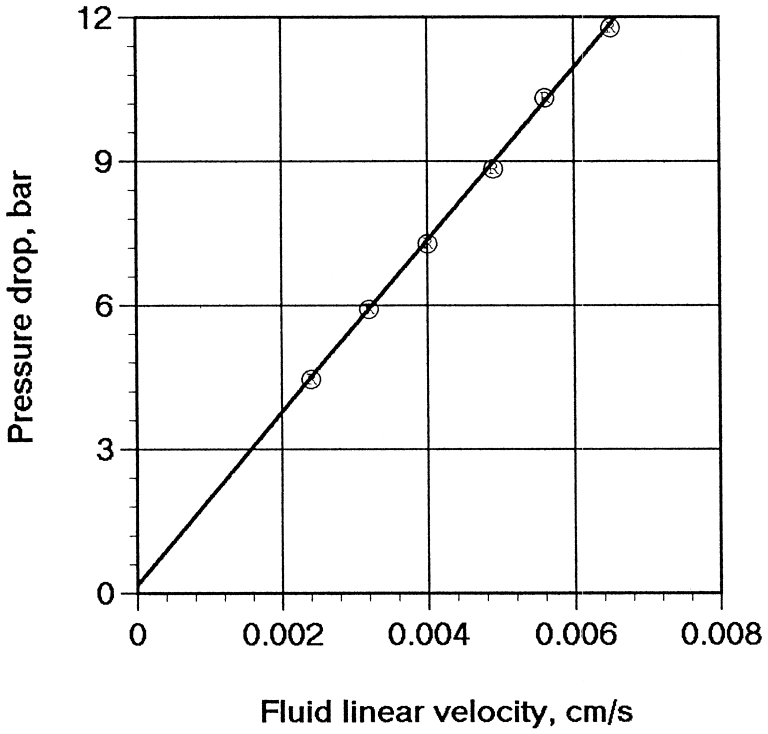

Fig. 3. Plot of low pressure data in Fig. 2.

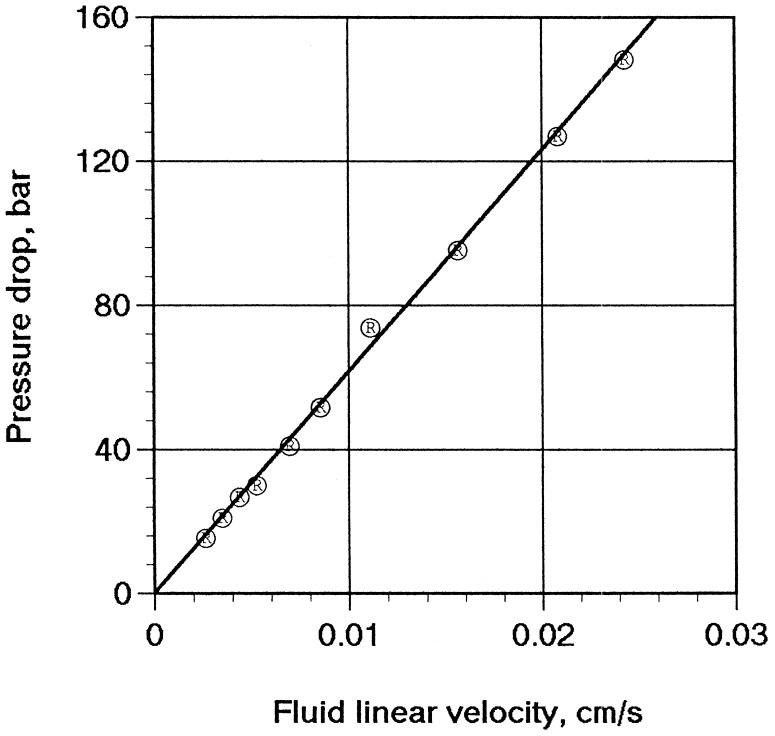

Fig. 4. Plot of the column inlet pressure versus the linear velocity of ethylene glycol percolating through a 150×4.6 mm chromatographic column packed with 5 μm C_{18} bonded porous spherical particles (average pore size 300 Å).

column, not six times as expected from the change in length and particle size. The nominal particle sizes given by manufacturers of silica adsorbents used in chromatography are often approximate averages which cannot be used for accurate calculations of column permeabilities. For this reason, we measured the particle size distribution by laser-beam scattering, using a Mastersizer instrument (Malvern Instruments, Southborough, MA, USA). The average particle diameters found for the three materials used in this study were 9.7, 5.3 and 5.1 μm, respectively. These differences do not explain the permeability of column II, which was not as low as expected for its average particle size. This is probably explained by a different degree of bed consolidation achieved during the preparation of this column, difference which would translate into a higher interparticle porosity and a higher permeability. Differences of this type and of that order of magnitude are common in chromatography. Still, the lower permeability of this column made possible to perform measurements at low values of the linear velocity without reaching into the low limit of accurate response of the pressure gauge (ca. 5 bar or less).

The third column used was 250 mm long and was packed with particles having a nominal average size of 5 μm. The data obtained are plotted in Fig. 5. The relationship between the linear velocity and the inlet pressure is also linear for this column. The range of Re investigated extends now from $1.7 \cdot 10^{-6}$ to $3 \cdot 10^{-5}$. The permeability of this last column is three-times lower than that of the second column and nine times lower than that of the first one. The difference between the permeability of the first and the third column can be explained by their differences in average particle size and length.

For this last column the intercept for $u = 0$ was 0.34 bar. This value is most probably due to an offset of the pressure gauge as well as to experimental errors. However, it could conceivably be explained also by the existence of a threshold pressure gradient below which there would be no flow [9]. In this case,

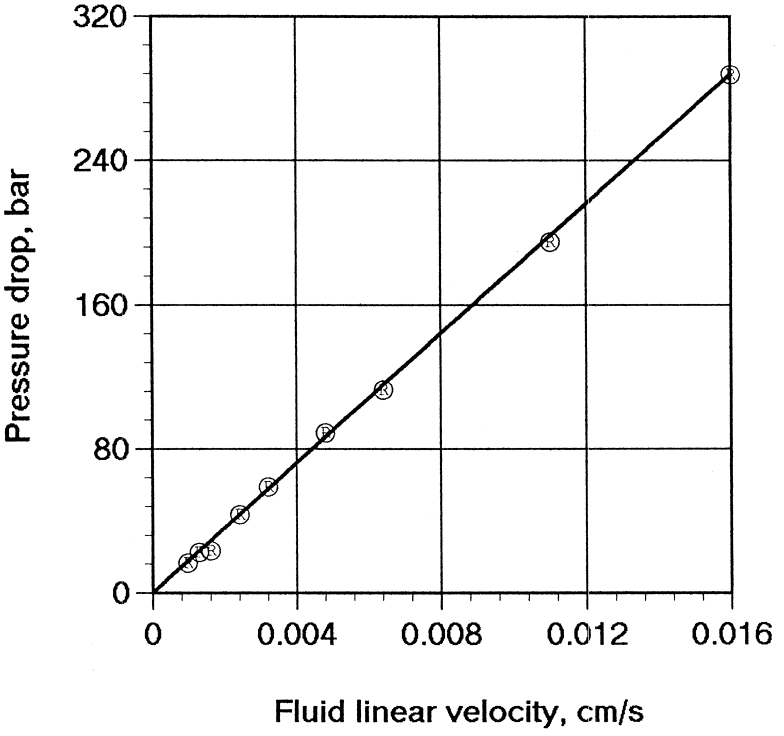

Fig. 5. Plot of the column inlet pressure versus the linear velocity of ethylene glycol percolating through a 250×4.6 mm chromatographic column packed with 5 μm C_{18} bonded porous spherical particles (average pore size 150 Å).

the corresponding Reynolds number would be of the order of $1 \cdot 10^{-8}$. This is the maximum possible estimate of the end of a pre-Darcy flow regime. The magnitude of such a hypothetical threshold could be related to the surface tension between the solid surface and the fluid percolating through it, i.e., to how well the liquid wets the solid surface. However, measurements of the column inlet pressure were always made after steady-state flow was achieved, which makes highly unlikely that the wettability of the solid phase by the fluid had an effect in our experiments. Furthermore, the organic solvent used here – ethylene glycol – is known to wet well the chemically bonded octadecyl silica used as the solid phase.

4. Conclusions

The inlet pressure required to percolate ethylene glycol through three different chromatographic columns increased linearly with increasing linear flow velocity between $1 \cdot 10^{-3}$ and $8 \cdot 10^{-2}$ cm/s. The values measured were corrected for the hydraulic resistances of both the chromatograph and the end-fittings and frits of the columns. The pressure drop was proportional to the velocity of the fluid in the whole range of Reynold numbers investigated, from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-4}$. This demonstrates that Darcy's law is valid in this range for the system studied. The use of Darcy law in chromatography appears to be entirely justified.

This result does not agree with the conclusions of Fand et al. [7], who did not perform measurements in a range of flow velocity which could support their statement. It contradicts also the more recent results of Kececioglu and Jiang [8] who claimed that they found Darcy's law to be applicable in a very limited range of flow velocity. We believe that their results are due to the use of an excessively loose bed of coarse beads. A pre-Darcy flow regime could not be observed in our experiments. Further experiments are

required to determine the upper limit of such a possible effect. The use of glycerol as the mobile fluid (viscosity 1400 cP at 20°C) would make possible operating the columns used in this work at Reynolds numbers of $5 \cdot 10^{-9}$. However, the measurement of the flow-rate would be extremely long and tedious.

Acknowledgements

This work was supported in part by Grant DE-FG05-88-ER13869 of the US Department of Energy and by the cooperative agreement between the University of Tennessee and the Oak Ridge National Laboratory.

References

[1] J.C. Giddings, Unified Separation Science, Wiley, New York, 1991.
[2] G. Guiochon, S.G. Shirazi, A.M. Katti, Fundamentals of Nonlinear and Preparative Chromatography, Academic Press, Boston, MA, 1994.
[3] H.I. Ene, C. R. Acad. Sci. (Paris) 312 (1991) 1269.
[4] S. Ergun, Chem. Eng. Prog. 48 (1952) 89.
[5] R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, Wiley, New York, 1960.
[6] A. Dybbs, R.V. Edwards, in: J. Bear, M.Y. Corapcioglu (Eds.), Fundamentals of Transport Phenomena in Porous Media, NATO ASI Series, Vol. 82, 1984, p. 199.
[7] R.M. Fand, B.Y.K. Kim, A.C.C. Lam, R.T. Phan, J. Fluids Eng. 109 (1987) 268.
[8] I. Kececioglu, Y. Jiang, J. Fluids Eng. 116 (1994) 164.
[9] J. Bear, in: Dynamics of Fluids in Porous Media, Elsevier, New York, 1972, p. 127.
[10] M. Kele, G. Guiochon, J. Chromatogr. A 830 (1999) 41.
[11] T. Farkas, G. Guiochon, Anal. Chem. 69 (1997) 4592.
[12] A.E. Scheidegger, The Physics of Flow Through Porous Media, McMillan, New York, 1974.
[13] B.J. Stanley, C.R. Foster, G. Guiochon, J. Chromatogr. A 761 (1997) 41.
[14] H. Guan, G. Guiochon, J. Chromatogr. A 731 (1996) 27.
[15] M. Martin, G. Blu, G. Guiochon, J. Chromatogr. Sci. 11 (1973) 641.