COLUMN PRESSURE DROP IN CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY

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SUMMARY

Some relationships have been derived describing the pressure profile along a capillary column in supercritical fluid chromatography (SFC) in terms of experimental parameters. The calculated results for carbon dioxide as mobile phase suggest that, under usual operating conditions in capillary SFC, the pressure profile is nearly linear. The importance of the secondary effects detracting from applicability of the Hagen–Poiseuille equation is also discussed and shown to be negligible in most practical situations.

INTRODUCTION

In certain applications of capillary-column supercritical fluid chromatography (SFC) an accurate knowledge of the pressure drop across the column is necessary. For instance, when the diffusion coefficients of various solutes in dense fluids are measured with the chromatographic band-broadening technique[1–5] the pressure drop is required to assess the portion of band broadening that results from expansion of the mobile phase along the column. In analytical SFC, the pressure drop is needed when the effects are investigated of the experimental parameters on the column efficiency and resolving power[6]. Moreover, a theoretical interpretation of SFC retention data is greatly simplified if the pressure drop across the column can safely be neglected[7,8].

Theoretical studies of the column pressure drop in SFC have focussed on packed columns[9,10]. However, as pointed out by Schoenmakers *et al.*[9], the pressure drops across typical packed and capillary SFC columns may be comparable under the usual experimental conditions. In packed-column SFC the pressure drop may actually become an operating parameter since both the column inlet and outlet pressures can be measured and controlled. In capillary-column SFC, however, flame-based detectors are frequently used. With these detectors the column effluent must be decompressed prior to detection. A pressure sensor between the column and the detector would inevitably degrade the system's efficiency by causing a large extra-column contribution to band broadening. For these reasons, a brief theoretical analysis of the pressure profile along a capillary column appears worthwhile.

In the following sections, relationships are derived for the pressure profile along

the SFC capillary column in terms of experimental parameters. A few examples are shown of the calculated pressure drops in capillary-column SFC with carbon dioxide as the mobile phase. Finally, the significance of various effects detracting from the applicability of the Hagen–Poiseuille equation is also discussed.

THEORETICAL

Starting from the Hagen–Poiseuille equation, the mass flow-rate of the mobile phase through the column cross-section positioned at a distance z from the column inlet may be written as:

$$\dot{m} = -[\pi r^4 \rho/(8\eta)](\mathrm{d}P/\mathrm{d}z) \tag{1}$$

The meaning of the symbols is explained at the end of this article. The density and the dynamic viscosity of the mobile phase are those at the local pressure. The flow is assumed to be isothermal. The minus sign in eqn. 1 takes account of the fact that the pressure decreases in the direction of flow. Unlike the volumetric flow-rate or the mean linear flow velocity, the mass flow-rate in eqn. 1 is invariant with respect to temperature and pressure. This fact may be useful when there is no suitable substance to mark the dead retention time[11].

It follows from eqn. 1 that the local pressure, P, at a distance z from the column inlet satisfies the relationship:

$$\int_{P}^{P_i} v^{-1}\,\mathrm{d}P = 8\dot{m}z/(\pi r^4) \tag{2}$$

To evaluate the integral in eqn. 2, the pressure dependence of v^{-1} must be known. It should be noted that in SFC both η and ρ vary with pressure, whereas in gas chromatography the pressure dependence of η may be neglected[12]. Generally, v^{-1} may be expanded into a Taylor series with respect to pressure. As the pressure drop in capillary SFC is usually small compared to P_i, the series may be truncated after the second term:

$$v^{-1} = v_i^{-1} + (P - P_i)\kappa \tag{3}$$

Combination of eqns. 2 and 3 yields:

$$v_i^{-1}(P_i - P) - \kappa\,(P_i - P)^2/2 = 8\dot{m}z/(\pi r^4) \tag{4}$$

Eqn. 4 clearly shows the effect of κ upon the overall appearance of the pressure profile along the column. If $\kappa > 0$, the dependence of P on z is convex in the upward direction, i.e., the pressure at half the column length is greater than the arithmetic mean of the inlet and outlet pressures. This is the case in gas chromatography. If $\kappa < 0$, the dependence is concave, and when $\kappa = 0$ a linear pressure profile results. Eqn. 4 may be solved to give:

$$P = P_i - \kappa^{-1}v_i^{-1} + \kappa^{-1}[v_i^{-2} - 16\kappa\dot{m}z/(\pi r^4)]^{\frac{1}{2}} \tag{5}$$

Finally, the mean column pressure may be obtained by averaging eqn. 5 over the column length, L:

$$\bar{P} = P_i - \kappa^{-1}v_i^{-1} + \frac{\pi r^4}{24\kappa^2\dot{m}L}\left[v_i^{-3} - \left(v_i^{-2} - \frac{16\kappa\dot{m}L}{\pi r^4}\right)^{3/2}\right] \tag{6}$$

The column-outlet pressure, P_0, may be calculated by substituting L for z in eqn. 5. Although eqns. 5 and 6 fail for strictly linear pressure profiles ($\kappa = 0$), an application of the l'Hôpital rule shows that they converge to their correct counterparts in the limit of $\kappa \to 0$ [$P = P_i - 8\dot{m}Lv_i/(\pi r^4)$ and $\bar{P} = P_i - 4\dot{m}Lv_i/(\pi r^4)$, respectively].

It follows from the above consideration that the pressure dependence of v^{-1} plays a key rôle in determining the pressure profile along the column. Unfortunately, no explicit equation can be given to express v^{-1} as a function of pressure throughout the temperature and pressure range pertinent to SFC. This is because, over such a broad range of fluid states, neither density nor dynamic viscosity can be related to temperature and pressure by a single explicit expression with an accuracy sufficient for the present purpose. For this reason, the assessment of the pressure dependence of v^{-1} should be based upon the experimental data for a given fluid, at least when η is concerned.

As an example, Fig. 1 shows v^{-1} as a function of pressure for carbon dioxide at three different temperatures. The dynamic viscosity values used were those recommended by Stephan and Lucas[13]. Their tabulated data were smoothed graphically with the Reichenberg correlation[14] serving as an approximate guide. The densities were calculated from the corresponding-states correlation of Lee and Kesler[15]. The isotherms shown in Fig. 1 were drawn through the data points calculated at a pressure step of 5 bar. At any particular pressure, the respective value of κ to be used in eqns. 5 and 6 was approximated by the slope of the straight line drawn to the nearest neighbouring point on the lower-pressure side. The 315-K isotherm in Fig. 1 displays an enhancement of v^{-1} at pressures somewhat above the critical. The enhancement probably becomes more apparent as the critical temperature is approached; however, a verification of this conjecture seems to be precluded by the uncertainties regarding the dynamic viscosity of carbon doxide in the critical region[13]. The uncertainty of the data plotted in Fig. 1 may be estimated to be $\pm 8\%$; this figure comes from the combined uncertainties of η and ρ, ± 5 and $\pm 3\%$, respectively.

For certain ranges of temperature and pressure, higher-order terms of the Taylor series should be included in eqn. 3 to account for the curvature of the isotherm showing v^{-1} as a function of pressure (cf., the 315-K isotherm in Fig. 1 at pressures close to 100 bar). In such an instance, higher powers of the difference ($P_i - P$) would appear in eqn. 4, and eqn. 4 would have to be solved numerically to yield the pressure profile along the column. For such a procedure, however, the respective higher-order derivatives of v^{-1} with respect to pressure would be required. At present, the derivatives cannot be evaluated because of limited precision of the viscosity data.

It is apparent from Fig. 1 that κ may acquire both positive and negative values
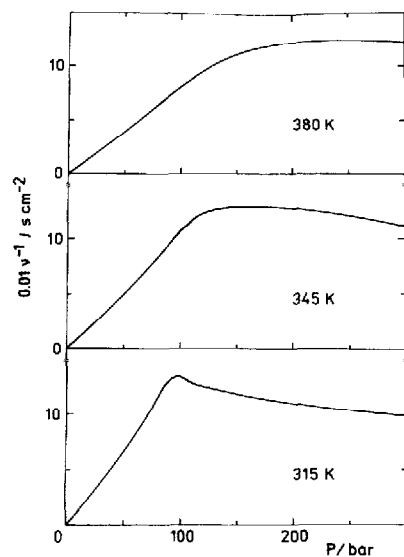
Fig. 1. Reciprocal kinematic viscosity of carbon dioxide as a function of pressure and temperature.

within the temperature and pressure ranges pertinent to SFC. Hence, in principle, both positive and negative departures from a linear pressure profile may occur in capillary-column SFC with carbon dioxide as the mobile phase, although the deviations are very small (see below). This situation differs markedly from that in low-pressure gas chromatography where only positive deviations from linear pressure profiles are possible.

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RESULTS AND DISCUSSION

In Table I a few examples are listed of the calculated pressure drops for three capillary columns within the temperature and pressure ranges pertinent to SFC with carbon dioxide as the mobile phase. It follows from the $\Delta \bar{P}$ entries in Table I that, under operating conditions typical of isothermal SFC with carbon dioxide as the mobile phase, the pressure profile along a capillary column may be considered to be linear.

The considerations of the preceding section assumed that the flow is isothermal, and that the hydrodynamic behaviour of a capillary SFC column conforms strictly to the Hagen–Poiseuille equation. In practice, however, there are several effects that may detract from the validity of these assumptions for a real capillary column, viz., (i) departures from the isothermal flow regime, (ii) departures from the laminar flow regime, (iii) column-end effects and (iv) distortion of the parabolic velocity profile within the column by coiling-induced secondary flow. Below, the significance is discussed of each of these effects in capillary-column SFC with carbon dioxide as the mobile phase. The treatment is far from being exact. Rather, the simple numerical examples given below are intended to illustrate the *maximum* impact of the particular effect.

TABLE I

CALCULATED PRESSURE DROPS AND THERMAL EFFECTS IN SEVERAL CAPILLARY SFC COLUMNS WITH CARBON DIOXIDE AS THE MOBILE PHASE

$T(K)$	$P_i(bar)$	$\bar{u}_i(cm/s)$	$\Delta P(bar)$	$10^3 \Delta \bar{P}(bar)$	$\dot{q}_d/\dot{m}(J/g)$	$\dot{q}_e/\dot{m}(J/g)$
Column 20 m × 50 μm I.D.						
315	75	2	1.11	1.9	0.48	−2.94
		5	2.81	12.3	1.20	−7.45
	150	2	3.32	−1.7	0.43	−0.95
		5	8.27	−9.9	1.08	−2.36
345	75	2	1.03	1.2	0.65	−1.16
		5	2.59	8.0	1.63	−2.92
	150	2	1.90	0	0.40	−1.84
		5	4.76	0.2	0.99	−4.61
	240	2	2.99	−1.0	0.42	−0.67
		5	7.45	−5.5	1.05	−1.68
380	75	2	1.07	1.3	0.84	−0.78
		5	2.69	8.6	2.11	−1.96
	150	2	1.43	0.8	0.46	−1.11
		5	3.58	3.9	1.15	−2.79
	240	2	2.19	0	0.41	−0.84
		5	5.47	0	1.03	−2.09
Column 10 m × 25 μm I.D.						
315	150	2	6.63	−6.4	0.86	−1.89
		5	16.43	−38.7	2.16	−4.70
380	75	2	2.15	5.4	1.68	−1.57
		5	5.50	36.6	4.21	−4.01
Column 1 m × 10 μm I.D.						
315	150	2	4.15	−2.5	0.54	−1.19
		5	10.32	−15.3	1.35	−2.95
380	75	2	1.33	2.1	1.05	−0.97
		5	3.38	13.7	2.63	−2.47

(i) Thermal effects

When a fluid moves down a capillary tube two effects tend to change the temperature of the fluid. The first is the dissipation of the mechanical energy due to the viscosity of the fluid. To a first approximation, the heat formed by viscous dissipation per unit time under laminar flow conditions may be expressed by:

$$\dot{q}_d = 8v_i L \bar{u}_i \dot{m}/r^2 \qquad (7)$$

In the sixth column of Table I, several values are listed of the ratio $\dot{q}_d/\dot{m}$ in capillary-column SFC with carbon dioxide as the mobile phase. The second thermal effect is the temperature change due to expansion of the fluid along the column. In the extreme case of a thermally insulated column, the expansion would be isenthalpic, and the rate of the internal energy change due to expansion could be approximated as:

$$\dot{q}_e = -\mu C_p \Delta P \dot{m}/M \qquad (8)$$

The minus sign is to indicate that the fluid cools down when μ is positive, which is the case in supercritical fluids. The values of the ratio $\dot{q}_e/\dot{m}$ are shown in the seventh column of Table I. The values of the product μC_p were derived from the Lee and Kesler correlation[15]. An inspection of the $\dot{q}_d$ and $\dot{q}_e$ entries in Table I reveals that the two thermal effects tend to offset each other but that the cooling due to expansion prevails in most cases. Accordingly, in capillary-column SFC with carbon dioxide as the mobile phase, heat has to be supplied to the column to keep it at a constant temperature. It may be shown that, for a given fluid at a given temperature and pressure, the ratio $\dot{q}_e/\dot{q}_d$ is nearly independent of the column geometry and the mean linear flow velocity, at least under laminar flow conditions. However, the absoute amounts of heat involved are minute since very small mass flow-rates are used in capillary-column SFC (typically, 10^{-6} to 10^{-4} g/s for carbon dioxide as the mobile phase). Hence, in capillary-column SFC with carbon dioxide as the mobile phase, thermal effects appear to be insignificant.

(ii) Departures from the laminar flow regime
    The Reynolds number for the flow in a capillary SFC column may be written as:

$$Re = ru_{max}v^{-1} \tag{9}$$

Setting $r = 100 \ \mu m$, $u_{max} = 10$ cm/s and $v^{-1} = 1500$ s/cm^2 (*cf.*, Fig. 1), the maximum value of the Reynolds number in capillary-column SFC with carbon dioxide as the mobile phase is 150. This is still well below the critical value (Re $\approx$ 2200) at which the onset of turbulence starts. Hence, the departures from laminar flow appear to be negligible in capillary-column SFC. In packed-column SFC the effects of turbulence are more significant[16].

(iii) Column-end effects
    In the derivation of the Hagen–Poiseuille equation the parabolic velocity profile is supposed to be developed throughout the length of the capillary. At the inlet of any real capillary column, however, there is a transient region within which the fluid is accelerated and the velocity pattern developed. At the outlet end of the column the opposite occurs. According to the treatment quoted by Dushman and Lafferty[17] for an incompressible fluid, the column pressure drop corrected for the end effects may be written as:

$$\Delta P = 8\eta L\bar{u}_i/r^2 + 1.14\rho\bar{u}_i^2 \tag{10}$$

Assuming that $\rho = 0.8$ g/cm^3 and $\bar{u}_i = 5$ cm/s, the second term on the right-hand side of eqn. 10 amounts to $2.3 \cdot 10^{-5}$ bar, which is negligible compared to ΔP in Table I.

(iv) Effect of column coiling
    The Hagen–Poiseuille equation applies to a straight tube. Since a capillary column must obviously be coiled, the impact of coiling on the applicability of the equation should be assessed. In a coiled column, centrifugal forces cause the streamline of maximum velocity to be pushed out in the direction of increasing distance from the coil centre. Thus, a double helical secondary flow pattern is developed in the column,

TABLE II

EFFECT OF COLUMN COILING IN CAPILLARY SFC WITH CARBON DIOXIDE AS THE MOBILE PHASE

$u_{max} = 10$ cm/s, $v^{-1} = 1500$ s/cm^2, $R = 7.5$ cm.

r (μm)	λ	δ	α	β
25	3000	$1.7 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	1
100	750	$1.9 \cdot 10^{-2}$	$2.8 \cdot 10^{-3}$	0.9996
160	469	$8.0 \cdot 10^{-2}$	$7.1 \cdot 10^{-3}$	0.9943

and, consequently, the parabolic velocity profile is distorted. Under the flow conditions typical of capillary-column SFC, the velocity profile in the coiled column may be described by the expressions of Dean and Topakoglu[18,19]. These complex expressions will not be repeated here. Instead, the resulting typical values of several quantities characterizing the secondary flow in capillary-column SFC are listed in Table II. It is seen that, under the usual conditions in capillary-column SFC with carbon dioxide as the mobile phase, the effect of coiling upon the applicability of the Hagen–Poiseuille equation is not significant. However, this conclusion no longer applies when the radius ratio, λ, is minimized intentionally to produce a gain in column efficiency[20].

CONCLUSION

The model developed in this work makes it possible to calculate the pressure profile along a capillary column in SFC. It appears that, under operating conditions typical of isothermal SFC with carbon dioxide as the mobile phase, the deviations of the pressure profile from linearity are negligible. Simple calculations suggest that, under the same conditions, possible secondary effects (i)–(iv) do not introduce a significant error into the column pressure drop calculated from the Hagen–Poiseuille equation.

SYMBOLS

C_p Isobaric molar heat capacity of the mobile phase at the column-oven temperature and the column-inlet pressure

L Column length

$\dot{m}$ Mass flow-rate of the mobile phase through the column

M Molar mass of the mobile phase

P Pressure

P_i Column-inlet pressure

P_0 Column-outlet pressure

ΔP Pressure drop across the column, $P_i - P_0$

$\bar{P}$ Mean pressure in the column

$\Delta\bar{P}$ Deviation of the mean pressure in the column from the arithmetic mean of the inlet and outlet pressures, $\bar{P} - (P_i + P_0)/2$

$\dot{q}_d$ Rate of heat formation due to viscous dissipation of the mechanical energy of the mobile phase in the column

$\dot{q}_e$ Rate of the internal energy change due to expansion of the mobile phase along the column

r Column radius

R Radius of the column coil

Re   Reynolds number

u_{max} Maximum linear velocity of the mobile phase at a given column cross-section

$\bar{u}_i$ Mean cross-sectional linear velocity of the mobile phase at the column inlet

z Distance from the column inlet

α Ratio of the maximum radial velocity to the maximum axial velocity of the mobile phase in the column

β Ratio of the mass flow-rate through the coiled column to the mass flow-rate through the corresponding straight column with the same pressure drop

δ Maximum relative deviation of the axial velocity from that corresponding to the parabolic velocity profile

η Dynamic viscosity of the mobile phase

κ Pressure derivative of v^{-1} at the column-oven temperature and the column-inlet pressure

λ Aspect ratio, R/r

μ Joule-Thomson coefficient of the mobile phase at the column-oven temperature and the column-inlet pressure

v Kinematic viscosity of the mobile phase

v_i Kinematic viscosity of the mobile phase at the column inlet

ρ Density of the mobile phase

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