Journal of Chromatography, 461 (1989) 165–176
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1464

GENERALIZED TREATMENT OF SPATIAL AND TEMPORAL COLUMN PARAMETERS, APPLICABLE TO GAS, LIQUID AND SUPERCRITICAL FLUID CHROMATOGRAPHY

I. THEORY

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SUMMARY

Starting with Darcy's law, rearranged and expressed in terms of the local carrier *density* at a given temperature, general equations are derived for the spatial and temporal density distribution functions, average densities and column profiles of the mobile-phase fluid, and the observed (column-averaged) capacity factor(s) and column profiles of the solute component(s). These more direct, exact and tractable equations are applied to gas, liquid and supercritical fluid chromatography, and the results are discussed.

INTRODUCTION

In all chromatographic systems there is necessarily a pressure (or density) gradient of the mobile phase along the column. A fundamental problem, especially in packed-column supercritical fluid chromatography, where the mobile phase is both non-ideal and highly compressible, and column pressure drops may be substantial[1–7], is accurately relating an observed solute retention parameter (*e.g.*, the capacity factor, k') to the column inlet and outlet conditions and appropriate column-averaged quantities. Therefore, the ultimate goal of the present study is to provide a generalized solution to this basic problem by formulating sufficiently exact and numerically tractable integral equations, applicable to gas (GC), liquid (LC) and supercritical fluid (SFC) chromatography.

Starting with Darcy's law under isothermal conditions and neglecting what are normally minor temperature-gradient effects in analytical SFC[7], LC[8] and GC[9], general equations are derived for the spatial and temporal distribution functions in a column (packed or capillary), in terms of the local density, isothermal compressibility coefficient and viscosity of the mobile phase, where the last two properties depend on the local density as well. The spatial and temporal distribution functions, which essentially describe how the mobile-phase density varies with its position and residence time, respectively, in the column, are then applied to obtain general expressions for the spatial and temporal average densities, and the related column profiles, for prescribed inlet and outlet conditions. Similarly, starting with an expression for the solute capacity factor in terms of the local carrier density, the observed (or column-averaged) capacity factor is related to temporal averages involving the mobile-phase density. It is shown that the derived equations yield both new and familiar results for GC and LC. Their application to SFC, which will be covered in some detail in the seond part of this investigation[10], is also briefly considered. (Note that alternative approaches for SFC, treating some of the same aspects as the present study, are developed in refs. 3, 6 and, most noteworthy, 7.)

It should be emphasized that the isothermal distribution functions are ultimately expressed in terms of density, rather than pressure, where the former is the more convenient and natural state variable. There are three compelling reasons for this outcome. First, application of the condition of conservation of mass flow to Darcy's equation introduces a density factor which, in general, cannot be directly replaced by a term or terms involving pressure, using an equation of state that is both manageable and realistic (this is especially true for SFC). This would lead to cumbersome numerical evaluations and/or unnecessary (and, perhaps, invalid) approximations. Second, according to a recently developed, unified molecular theory of absorption[11,12] and adsorption[13,14] chromatography, solute retention (*e.g.*, k') is predicted to be a universal function of the reduced temperature and density (*not* pressure) of the mobile phase. Third, the isothermal viscosity of the mobile-phase fluid is a better behaved function of density and, according to theory, is more sensibly represented in terms of density[15].

THEORY

According to Darcy's law, at constant column temperature and for apparent Reynolds numbers within an acceptable upper limit[8], the linear velocity of the mobile phase, u, is related to the pressure gradient in the column, $\mathrm{d}P/\mathrm{d}x$, and the viscosity of the mobile phase, η, by

$$u = -(B/\eta)\,(\mathrm{d}P/\mathrm{d}x) \tag{1}$$

where B is the specific permeability coefficient of the column. In general, u, η and $\mathrm{d}P/\mathrm{d}x$ are local values, *i.e.*, they are all functions of x, the distance from the inlet of the column, at which $x = 0$ (and, at the outlet, $x = L$, the column length). Multiplying the numerator and denominator on the right-hand side of eqn. 1 by $\mathrm{d}\rho$, where ρ denotes the local mobile-phase density, and rearranging, one has

$$\mathrm{d}x = -(B/\eta u)\,(\delta P/\delta \rho)_T \mathrm{d}\rho \tag{2}$$

where the partial derivative is introduced to affirm the isothermal condition. Eqn. 2 relates a differential spatial element to a differential density element and is used to describe how the carrier density varies with the distance along the column. It also follows that u, η and $(\delta P/\delta \rho)_T$ may be expressed as functions of ρ.

Conservation of mass flow requires that, through any cross-sectional area of the column,

$$u\rho = u_o \rho_o = \text{constant} \tag{3}$$

where the subscript o refers to the column outlet. Combining eqns. 2 and 3, one finds

$$dx = -(C/\eta)\rho\ (\delta P/\delta \rho)_T d\rho = -CD_x(\rho)d\rho \tag{4}$$

where $C = B/u_o\rho_o$, and where

$$D_x(\rho) = \eta^{-1}\rho\ (\delta P/\delta \rho)_T = (\eta\beta)^{-1} \tag{5}$$

is the unnormalized, spatial distribution function and $\beta = \rho^{-1}\ (\delta\rho/\delta P)_T$ is the isothermal compressibility coefficient of the carrier fluid.

The unnormalized, temporal distribution function, $D_t(\rho)$, which is used to describe how the mobile-phase density varies with its residence time in the column, is formulated by applying the usual definition of u as the time derivative of distance ($\dot{x}$):

$$u = \dot{x} = dx/dt \tag{6}$$

Eqns. 3–6 combine to give

$$dt = -ED_t(\rho)d\rho \tag{7}$$

which relates a differential temporal element to a differential density element, where $E = C/u_o\rho_o = B/(u_o\rho_o)^2$ and where

$$D_t(\rho) = \eta^{-1}\rho^2(\delta P/\delta \rho)_T = \rho(\eta\beta)^{-1} = \rho D_x(\rho) \tag{8}$$

Note that eqns. 4 (with 5) and 7 (with 8) have a common "core", *viz.*, $\eta^{-1}(\delta P/\delta\rho)_T$.

The mobile-phase density, averaged over the length of the column, *i.e.*, the spatial average density, $\langle\rho\rangle_x$, is simply

$$\langle\rho\rangle_x = \int_0^L \rho\ dx \Big/ \int_0^L dx \tag{9}$$

From eqns. 4 and 9,

$$\langle\rho\rangle_x = \int_{\rho_o}^{\rho_i} \rho D_x(\rho)\ d\rho \Big/ \int_{\rho_o}^{\rho_i} D_x(\rho)\ d\rho \tag{10}$$

where $D_x(\rho)$ is given by eqn. 5 and $\rho = \rho_i$ (inlet density) at $x = 0$ and $\rho = \rho_o$ (outlet density) at $x = L$.

The mobile-phase density averaged over the residence time in the column, *i.e.*, the temporal average density, $\langle\rho\rangle_t$, is simply

$$\langle\rho\rangle_t = \int_0^{t_u} \rho\ dt \Big/ \int_0^{t_u} dt \tag{11}$$

where t_u denotes the total residence time of typical mobile-phase molecules, or the migration time for truly unretained solute molecules (peak-maximum value). From eqns. 7 and 11,

$$\langle \rho \rangle_t = \int_{\rho_o}^{\rho_i} \rho D_t(\rho)\, \mathrm{d}\rho \Big/ \int_{\rho_o}^{\rho_i} D_t(\rho)\, \mathrm{d}\rho \tag{12}$$

where $D_t(\rho)$ is given by eqn. 8 and $\rho = \rho_i$ at $t = 0$ $(x = 0)$ and $\rho = \rho_o$ at $t = t_u$ $(x = L)$.

To determine numerical values for the integral limits in eqns. 10 and 12, ρ_o and ρ_i, at the column operating temperature, T, and the respective pressures, P_o and P_i, one needs reliable equation-of-state information for the mobile-phase fluid being studied (gas, liquid or supercritical fluid). Evaluation of these integral equations (as well as subsequent relationships) also requires a knowledge of $\eta(\rho)$ at T (*e.g.*, by fitting tabulated viscosity data[15]) and $\beta(\rho)$ at T (again, from equation-of-state data), over the density range ρ_o to ρ_i.

Before considering a retained solute component, let us first derive other useful equations for averaged mobile-phase or unretained-solute quantities. In general, it follows from eqns. 10 and 12 that the average value of the nth power of the carrier density, $\langle \rho^n \rangle_j$, where $j = x$ or t, is given by

$$\langle \rho^n \rangle_j = \int_{\rho_o}^{\rho_i} \rho^n D_j(\rho)\, \mathrm{d}\rho \Big/ \int_{\rho_o}^{\rho_i} D_j(\rho)\, \mathrm{d}\rho \tag{13}$$

where $n = 1, 2, 3, 4, \ldots$. Also, the average linear velocity of the mobile phase, $\langle u \rangle$, is obtained from

$$\langle u \rangle = L/t_u = \int_0^L \mathrm{d}x \Big/ \int_0^{t_u} \mathrm{d}t \tag{14}$$

Using eqns. 4, 7–10 (with $E = C/u_o\rho_o$) and 14, one finds

$$\langle u \rangle = L/t_u = u_o\rho_o/\langle \rho \rangle_x \tag{15}$$

where $\langle \rho \rangle_x$ is given by eqn. 10. Multiplying eqn. 15 by the effective cross-sectional area of the column, A_{eff} (assumed to be constant throughout the column), where $LA_{\mathrm{eff}} = V_v$ is the void volume of the column, and rearranging, one obtains

$$V_v\langle \rho \rangle_x = (u_o\rho_o A_{\mathrm{eff}})t_u = \dot{m}t_u = G_u \tag{16}$$

where, with units of ml for V_v, g/ml for $\langle \rho \rangle_x$ and minutes for t_u, $\dot{m} = u_o\rho_o A_{\mathrm{eff}}$ is then the observed mass flow-rate of the mobile phase in units of grams per minute. Furthermore, $V_v\langle \rho \rangle_x$ or $\dot{m}t_u$ represents the total mass of mobile-phase fluid required to sweep typical carrier molecules or unretained solute molecules from the inlet to the outlet of the column. This "void mass" is designated as G_u. Eqn. 16 suggests two possible methods for determining G_u: (a) measurement of V_v and computation of $\langle \rho \rangle_x$; (b) measurement of $\dot{m}$ and t_u.

Turning now to a retained solute component (subscript s) and comparing its linear velocity with that of the mobile phase or an unretained solute component (subscript u) one has

$$u = \dot{x} = \mathrm{d}x/\mathrm{d}t = \mathrm{d}x/\mathrm{d}t_u \tag{17}$$

$$u_s = \dot{x}_s = \mathrm{d}x/\mathrm{d}t_s = u/(1 + k') \tag{18}$$

where k' is the local capacity factor of the solute, *i.e.*, the value at column position x, corresponding to a local density ρ. Therefore, from eqns. 3–5, 7, 8, 17 and 18, one obtains the following equations for the observed (peak-maximum) retention times, t_u and t_s, and the observed or temporal-averaged capacity factor, $\langle k' \rangle_t$

$$t_u = \int_0^L (1/u)\, \mathrm{d}x = E \int_{\rho_o}^{\rho_i} D_t(\rho)\, \mathrm{d}\rho \tag{19}$$

$$t_s = \int_0^L [(1 + k')/u]\, \mathrm{d}x = E \int_{\rho_o}^{\rho_i} (1 + k')\, D_t(\rho)\, \mathrm{d}\rho \tag{20}$$

$$\langle k' \rangle_t = (t_s - t_u)/t_u = \int_{\rho_o}^{\rho_i} k' D_t(\rho)\, \mathrm{d}\rho \Big/ \int_{\rho_o}^{\rho_i} D_t(\rho)\, \mathrm{d}\rho \tag{21}$$

It also follows from eqns. 16 and 21 that the net retention mass, $\langle G_n \rangle$, defined by

$$\langle G_n \rangle = G_s - G_u = \dot{m}(t_s - t_u) \tag{22}$$

where G_s is the mass of mobile phase at T required to sweep the retained solute component from the inlet to the outlet of the column, is related to $\langle k' \rangle_t$ by

$$\langle G_n \rangle = \dot{m}(t_s - t_u) = \dot{m} t_u \langle k' \rangle_t = V_v \langle \rho \rangle_x \langle k' \rangle_t = \langle \rho \rangle_x \langle V_n \rangle \tag{23}$$

where $\langle V_n \rangle = V_v \langle k' \rangle_t$ is the observed net retention volume. Eqn. 23 should prove to be particularly useful in SFC.

The local capacity factor in fluid-absorption chromatography[11,12] is predicted to have the general form

$$k' = k'_e \exp(a\rho + b\rho^2) \tag{24}$$

where $a < 0, b > 0$ and $k' \rightarrow k'_e$ as $\rho \rightarrow 0$. Inserting eqn. 24 into eqn. 21, one obtains

$$\langle k' \rangle_t = k'_e \langle \exp(a\rho + b\rho^2) \rangle_t \tag{25}$$

It is important to note that $\langle k'\rangle_t$ is proportional to the temporal average of the exponential in eqn. 25, which, in general, cannot be rigorously replaced by an exponential involving temporal averages of powers of the density. However, if $(\rho_i - \rho_o)/\rho_o$ is sufficiently small with respect to unity, a reasonable approximation is possible. Rewriting eqn. 24 as

$$k' = k'_e \exp[a\langle\rho\rangle_t + b\langle\rho^2\rangle_t] \cdot \exp[a(\rho - \langle\rho\rangle_t) + b(\rho^2 - \langle\rho^2\rangle_t)] \tag{26}$$

expanding the second exponential in eqn. 26 as a power series in ρ, and applying eqns. 13 (with $j = t$) and 21, one obtains

$$\begin{aligned}\langle k'\rangle_t = {} & k'_e (\exp[a\langle\rho\rangle_t + b\langle\rho^2\rangle_t]) \, [1 + a^2(\langle\rho^2\rangle_t - \langle\rho\rangle_t^2)/2 + \\ & ab(\langle\rho^3\rangle_t - \langle\rho\rangle_t\langle\rho^2\rangle_t) + b^2(\langle\rho^4\rangle_t - \langle\rho^2\rangle_t^2)/2 + \ldots] \approx \\ & k'_e \exp[a\langle\rho\rangle_t + b\langle\rho^2\rangle_t]\end{aligned} \tag{27}$$

It can be shown that if $a\rho + b\rho^2 < 0$, then $\langle\exp(a\rho + b\rho^2)\rangle \geqslant \exp(a\langle\rho\rangle_t + b\langle\rho^2\rangle_t)$, thus establishing an upper limit on this approximation.

Finally, let us obtain the salient equations for generating the various column profiles. The local mobile-phase density, ρ, at a fractional distance x/L from the column inlet is, from eqn. 4,

$$x/L = \int_0^x \mathrm{d}x \Big/ \int_0^L \mathrm{d}x = \int_\rho^{\rho_i} D_x(\rho)\,\mathrm{d}\rho \Big/ \int_{\rho_o}^{\rho_i} D_x(\rho)\,\mathrm{d}\rho \tag{28}$$

As ρ is inversely proportional to u, eqn. 28 may also be used to construct u/u_o *vs.* x/L profiles. The local density, ρ, when the carrier or an unretained solute has spent the fractional time τ_u/t_u on the column is, from eqns. 7 and 17,

$$\tau_u/t_u = \int_0^{\tau_u} \mathrm{d}t \Big/ \int_0^{t_u} \mathrm{d}t = \int_\rho^{\rho_i} D_t(\rho)\,\mathrm{d}\rho \Big/ \int_{\rho_o}^{\rho_i} D_t(\rho)\,\mathrm{d}\rho \tag{29}$$

which, with eqn. 28, also permits the construction of τ_u/t_u *vs.* x/L profiles. The local mobile-phase density, ρ, corresponding to the fractional solute migration time τ_s/t_s on the column is, from eqns. 7 and 18,

$$\tau_s/t_s = \int_0^{\tau_s} \mathrm{d}t_s \Big/ \int_0^{t_s} \mathrm{d}t_s = \int_\rho^{\rho_i} (1 + k')D_t(\rho)\,\mathrm{d}\rho \Big/ \int_{\rho_0}^{\rho_i} (1 + k')D_t(\rho)\,\mathrm{d}\rho \tag{30}$$

which, with eqn. 28, may also be used to construct τ_s/t_s *vs.* x/L profiles.

APPLICATIONS AND DISCUSSION

Let us begin by examining gas–liquid chromatography (GLC) with, in general, a non-ideal mobile phase. The equation of state for a non-ideal carrier gas under fairly high, but not extreme, inlet-pressure conditions ($P_i < 10$ atm), is well represented by[16]

$$(PM_c/RT) = \rho[1 + (B_{cc}\rho/M_c)] \approx \rho[1 + (B_{cc}P/RT)] \tag{31}$$

where R is the gas constant, T is the column temperature, and M_c and B_{cc} denote the molar mass and second virial coefficient, respectively, of the neat carrier gas. From eqn. 31,

$$\rho(\delta P/\delta\rho)_T = (RT/M_c)\,\rho\,[1 + (2B_{cc}\rho/M_c)] \tag{32}$$

From published viscosity data[15] and, according to theory[9], the viscosity of the carrier gas within the stated pressure limit is well represented by

$$\eta^{-1} = \eta_e^{-1}\,[1 + \alpha_c\rho] \tag{33}$$

where $\alpha_c < 0$ is a constant (for a given carrier gas and temperature) and $\eta \rightarrow \eta_e$ as $\rho \rightarrow 0$. Through second power in density, eqns. 5, 32 and 33 yield

$$D_x(\rho) = I\rho\,(1 + A_c\rho) \tag{34}$$

where $I = \eta_e^{-1}\,(RT/M_c)$ = constant, and

$$A_c = (2B_{cc}/M_c) + \alpha_c \tag{35}$$

From eqns. 10 and 34, the spatial average density, $\langle\rho\rangle_x$, for a non-ideal carrier gas is then

$$\langle\rho\rangle_x/\rho_o = J_2^3(\rho)\cdot[1 + \Delta_x] \tag{36}$$

where

$$J_n^m(\rho) = (n/m)\,[(\Gamma^m - 1)/(\Gamma^n - 1)] \tag{37}$$

$$1 + \Delta_x = [1 + A_c\rho_o J_3^4(\rho)]/[1 + A_c\rho_o J_2^3(\rho)] \tag{38}$$

and where $\Gamma = \rho_i/\rho_o$, and $\Delta_x \ll 1$ is a small correction term (see below). Applying eqns. 35–38 to carbon dioxide at 310 K, where $\alpha_c = -0.786$ ml/g[15], $B_{cc} = -114$ ml/mol[17] and, hence, $A_c = -5.967$ ml/g, and letting $P_i = 5$ atm and $P_o = 1$ atm (from eqn. 31, $\rho_i = 8.850 \cdot 10^{-3}$ g/ml, $\rho_o = 1.738 \cdot 10^{-3}$ g/ml and, hence, $\Gamma = 5.092$), one calculates

$$\langle\rho\rangle_x/\rho_o = 3.4916 \tag{39}$$

where $J_2^3(\rho) = 3.5039$ and $\Delta_x = -0.0036$. Therefore, the correction term is trivially small and $\langle\rho\rangle_x/\rho_o$ under the chosen conditions is very well approximated by $J_2^3(\rho)$. (For more common GC carrier gases, such as helium, hydrogen and nitrogen, which have much smaller B_{cc} values[17] and, hence, A_c values, the correction term would be one order of magnitude smaller.)

It is of practical interest, for the accurate determination of net retention volumes, to compare $\langle\rho\rangle_x/\rho_o$ from eqn. 39 with the value which one would obtain by assuming ideal-gas behavior:

$$\langle\rho\rangle_x/\rho_o = \langle P\rangle_x/P_o = J_2^3(P) \qquad (40)$$

where

$$J_2^3(P) = (2/3)\,[(P_i/P_o)^3 - 1]/[(P_i/P_o)^2 - 1] \qquad (41)$$

is the reciprocal of the well known Martin–James compressibility factor, $J_3^2(P)$. With $P_i/P_o = 5$, eqns. 40 and 41 give

$$\langle P\rangle_x/P_o = 3.4444 \qquad (42)$$

If the volumetric flow-rate of the carrier gas is determined at $T = 310$ K and $P_o =$ 1 atm, and is denoted by $\dot{V}(T, P_o)$, then the more exact treatment gives the following result for the net retention volume, $\langle V_n\rangle$, at T and $\langle P\rangle_x$

$$\langle V_n\rangle = (t_s - t_u)\,\dot{V}(T, \langle P\rangle_x) = (t_s - t_u)\,(\rho_o/\langle\rho\rangle_x)\,\dot{V}(T, P_o) \qquad (43)$$

while the ideal-gas assumption would give

$$\langle V_n\rangle = (t_s - t_u)\,(P_o/\langle P\rangle_x)\,\dot{V}(T, P_o) \qquad (44)$$

where $\dot{V} = \dot{m}/\rho$. From eqns. 39 and42–44 it is seen that, with carbon dioxide as the carrier gas and under these experimental conditions, the ideal-gas assumption would lead to an error of +1.37% in the determination of $\langle V_n\rangle$. Fortunately, with the more commonly used carrier gases, the error would be one order of magnitude smaller[16].

Turning to the temporal average density and proceeding as before, eqns. 8, 12 and 34 give

$$D_t(\rho) = I\rho^2(I + A_c\rho) \qquad (45)$$

$$\langle\rho\rangle_t/\rho_o = J_3^4(\rho)\cdot[1 + \Delta_t] \qquad (46)$$

where

$$1 + \Delta_t = [1 + A_c\rho_o J_4^5(\rho)]/[1 + A_c\rho_o J_3^4(\rho)] \qquad (47)$$

and where A_c and $J_n^m(\rho)$ are given by eqns. 35 and 37, respectively. For carbon dioxide and under the same experimental conditions, one calculates values of $\Delta_t = -0.0025$ (again, a trivial correction), $\langle\rho\rangle_t/\rho_o = 3.8328$ and $\langle P\rangle_t/P_o = J_3^4(P) = 3.7742$, where the former average is 1.55% higher than the latter. Also, provided the inlet pressure is not extreme ($P_i < 10$ atm.), GC column profiles based on density distributions should be within a few percent of those based on pressure distributions.

Concluding the discussion of GC by considering a retained solute component, the local k' through the first power in density is[11,12]

$$k' = k'_e \exp[(2B_{cs} - \bar{V}_s^\infty)\rho/M_c] \tag{48}$$

where B_{cs} is the carrier gas–solute interaction second virial coefficient and $\bar{V}_s^\infty$ is the infinite-dilution partial molar volume of the solute in the stationary liquid. Expanding the exponential in eqn. 48 as a power series in ρ, applying eqns. 13 and 21 and taking the logarithm of the result, one obtains, through the first power in density,

$$\ln \langle k' \rangle_t = \ln k'_e + [(2B_{cs} - \bar{V}_s^\infty)\rho_o/\mathrm{M}_c]\,[\langle \rho \rangle_t/\rho_o] \tag{49}$$

where $\langle \rho \rangle_t/\rho_o \approx J_3^4(\rho)$. Replacing ρ_o/M_c by P_o/RT (with negligible error) and approximating $\langle \rho \rangle_t/\rho_o$ by $\langle P \rangle_t/P_o = J_3^4(P)$ (with up to a few percent error; see above), one finds

$$\ln \langle k' \rangle_t \approx \ln k'_e + [(2B_{cs} - \bar{V}_s^\infty)P_o/RT] \cdot J_3^4(P) \tag{50}$$

which is a more approximate, but familiar, result[9].

Using the present density formalism, treatment of averages in liquid chromatography is even more straightforward. Analysis of equation-of-state information[8] and viscosity data[15] for dense fluids indicates that $D_x(\rho)$ follows the form

$$D_x(\rho) = c\rho^r \tag{51}$$

where c is a constant and $r > 0$ may be as large as 4. Accordingly, from eqns. 8, 10, 12 and 37,

$$\langle \rho \rangle_x/\rho_o = J_{r+1}^{r+2}(\rho) \tag{52}$$

$$\langle \rho \rangle_t/\rho_o = J_{r+2}^{r+3}(\rho) \tag{53}$$

Further, as it is unlikely that, under normal LC operating conditions, the outlet and inlet densities will differ by more than 5% ($1.00 < \rho_i/\rho_o \leqslant 1.05$), it follows that

$$\langle \rho \rangle_x \approx \langle \rho \rangle_t \approx (\rho_i + \rho_o)/2 \tag{54}$$

with a maximum error of about 0.1%. Also, if the local k' can be described by eqn. 24, then, from eqn. 27,

$$\ln \langle k' \rangle_t \approx \ln k'_e + a\langle \rho \rangle_j + b\langle \rho \rangle_j^2 \tag{55}$$

where $j = x$ or t, $\langle \rho^2 \rangle_j \approx \langle \rho \rangle_j^2$ and $\langle \rho \rangle_j \approx (\rho_i + \rho_o)/2$, the arithmetic-mean value. Note that, for liquids, ρ_i and ρ_o may be calculated, with acceptable accuracy, using the Tait equation of state[8] and knowledge of P_i and P_o at T.

SFC, on the other hand, is by no means as straightforward. The mobile phase is very non-ideal (in contrast to GC) and highly compressible (in contrast to LC). As a result, $D_x(\rho)$ and $D_t(\rho)$ are more complex analytical functions of ρ. Although the second part of this investigation[10] treats applications to SFC in great detail, the utility of the present approach in SFC will, nevertheless, be illustrated here.

The Jacobsen–Stewart modification of the Benedict–Webb–Rubin (BWR) equation of state yields exceptionally reliable *PVT* data, over very wide ranges of pressure and temperature, for low-molar-mass, non-polar fluids[18,19]. Using this BWR equation of state and tabulated viscosity data[15], the "core" of $D_x(\rho)$ and $D_t(\rho)$, $\eta^{-1} \cdot (\delta P/\delta\rho)_T$, can be readily and accurately generated as an analytical function of ρ, at the desired temperature, for carbon dioxide and light hydrocarbons[10,19]. For carbon dioxide an excellent fit to η^{-1} $(\delta P/\delta\rho)_T$ is obtained with a seventh-order polynomial in ρ[10]:

$$\eta^{-1} (\delta P/\delta\rho)_T = \sum_{l=0}^{7} c_l \rho^l \tag{56}$$

It follows from eqns. 5 and 8 that

$$D_x(\rho) = \sum_{l=0}^{7} c_l \rho^{l+1} \tag{57}$$

$$D_t(\rho) = \sum_{l=0}^{7} c_l \rho^{l+2} \tag{58}$$

from which the various mobile-phase averages and column profiles may be calculated, once the c_l values have been determined.

Table I gives some numerical results for an SFC (packed) column, with carbon dioxide as the mobile phase at 320 K, having an inlet pressure of P_i = 120 bar and an outlet pressure of P_o = 100 bar, with respective densities of ρ_i = 0.6331 and ρ_o =

TABLE I

NUMERICAL RESULTS FOR SFC COLUMN PROFILES WITH CARBON DIOXIDE AT 320 K

Column inlet: P_i = 120 bar; ρ_i = 0.6331 g/ml. Column outlet: P_o = 100 bar; ρ_o = 0.4497 g/ml.

ρ/ρ_o	x/L	τ_u/t_u	u/u_o
1.408	0.000	0.000	0.710
1.367	0.165	0.185	0.732
1.326	0.308	0.340	0.754
1.285	0.432	0.470	0.778
1.245	0.541	0.581	0.803
1.204	0.636	0.675	0.831
1.163	0.722	0.757	0.860
1.122	0.799	0.828	0.891
1.082	0.870	0.891	0.925
1.041	0.937	0.948	0.961
1.000	1.000	1.000	1.000

0.4497 g/ml. Listed in the first column are local densities, given as ρ/ρ_o, in ten equally spaced decrements from ρ_i to ρ_o (note that these ρ values can be easily converted to P values using the extended BWR equation of state[10]). For the purpose of examining mobile-phase profiles, the values in the second (fractional distance, from eqn. 28), third (fractional residence time, from eqn. 29) and fourth (relative velocity, from eqn. 3) columns are computed. Note also that the arithmetic mean of ρ/ρ_o is 1.204, whereas $\langle\rho\rangle_x/\rho_o = 1.241$ (from eqn. 10) and $\langle\rho\rangle_t/\rho_o = 1.252$ (from eqn. 12). The result for the temporal average density, for example, reveals that the mobile phase is spending relatively more time in the high-density, inlet region of the column, where it is moving with a relatively slower velocity.

From Table I it is seen that the arithmetic-mean density is reached when typical mobile-phase molecules have passed through 63.6% of the column length and have spent 67.5% of their residence time in the column. Therefore, the initial (inlet) rate of change of ρ/ρ_o with x/L or τ_u/t_u is smaller than the final (outlet) rate. At both the spatial and temporal midpoints ($x/L = 0.5$ and $\tau_u/t_u = 0.5$) the local density is greater than the arithmetic-mean density. It is also apparent that a typical carrier molecule requires over half of its total residence time to reach the positional midpoint of the column.

Fairly exact and detailed calculations and analyses, such as those outlined above, for both the mobile phase and retained solutes[10], are therefore possible for SFC. At this stage, the procedure is limited to carbon dioxide or a light hydrocarbon as the neat mobile phase. Also, the theory, in its present form, is not applicable to density-programmed SFC.

CONCLUSIONS

The equations derived here permit a more tractable and exact approach to obtaining and analyzing average densities and column profiles of gas, liquid and supercritical fluid mobile phases. They also provide a more direct means of relating observed solute retention quantities to temporal density averages ($\langle\rho^n\rangle_t$), which is of practical importance in packed-column SFC[10,20].

ACKNOWLEDGEMENTS

This material is based on work supported by the National Science Foundation under Grant CHE-8305045. The author is also grateful to R. E. Boehm, T. J. Bruno, A. Hussam, D. P. Poe and R. L. Riester for helpful discussions.

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