

Unified Molecular Theory of Chromatography and Its Application to Supercritical Fluid Mobile Phases. 1. Fluid-Liquid (Absorption) Chromatography

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A statistical thermodynamic treatment based on a lattice-fluid model is used to describe the equilibrium between a mobile fluid phase and a stationary liquid phase in chromatographic systems. General equations, applicable to gas, liquid, and supercritical fluid mobile phases, are obtained for the equilibrium composition of the stationary phase and for solute retention in fluid-liquid chromatography. These equations yield familiar retention expressions for ideal and moderately nonideal gas-liquid chromatography (GC), for traditional liquid-liquid chromatography (LC), and for reversed-phase liquid chromatography with chemically bonded stationary phases. It is shown that replacing the "poor" solvent by the "good" solvent in LC with a binary mobile phase through increasing the volume fraction of the latter is formally equivalent to replacing empty space by molecules in supercritical fluid-liquid chromatography (SFC) with a single-component mobile phase through increasing the density (occupied volume fraction) of the SF carrier. The solute capacity factor, k , in SFC is well represented by $\ln k = \ln k^0 + F(T_R, \rho_R)$, where T_R and ρ_R are the reduced temperature and reduced density of the mobile phase, $F(T_R, \rho_R)$ (eq 82) is the mobile-phase contribution which is a quadratic function of ρ_R and a linear function of T_R^{-1} and solute carbon number (homologous solute series), and k^0 , the stationary-phase contribution, is the capacity factor as $\rho_R \rightarrow 0$, corresponding to ideal GC. This SFC retention equation is successfully applied to the interpretation and prediction of experimental data.

Introduction

The initial impetus for this work was the clear need for a simple and useful molecular theory of solute retention in supercritical fluid chromatography—one that was properly based on statistical thermodynamics and wherein solute retention behavior could be explicitly related to the reduced variables of the mobile phase and other accessible pure-component physical properties and/or molecular parameters. In the process of developing and testing a theory based on a lattice-fluid model came the recognition of certain interrelationships and formal similarities among the equations describing supercritical fluid chromatography (SFC) and several previously derived expressions (based on kindred models) for gas and liquid chromatography (GC and LC, respectively).

The end result of this realization is a unified theory of chromatography, encompassing all three types of mobile phases, the first part of which (absorbent stationary phases) is presented here. (In part 2 we treat adsorbent stationary phases and concurrent absorption and adsorption phenomena.) Familiar GC and LC expressions and the desired equations for SFC evolve from our universal equations. Moreover, new physical insights and other information directly applicable in the practice of chromatography are provided. For example, the resulting equations indicate how ideal and moderately nonideal GC bear on SFC, and point to certain exploitable analogies between LC and SFC.

Given the more advanced state of theory and theoretical treatments of experimental data in GC and LC, SFC is ultimately emphasized. The status of SFC practice is well described in at least 10 review articles since 1978,¹⁻¹⁰ which summarize (a) the history (including the various pioneering studies), development, and current state of the method; (b) physical principles and

thermodynamic aspects; (c) actual and potential applications in analytical and physical chemistry; (d) its advantages and drawbacks relative to GC and LC; (e) its projected niche in the realm of chromatography and hyphenated techniques (e.g., SFC-MS and SFC-FTIR); (f) the instrumentation; (g) existing and potential supercritical fluid mobile phases and their critical and salient physical properties; (h) common stationary phases and the relative merits of capillary vs. packed columns. Also, many aspects of the physical and thermodynamic basis of SFC may be found in three excellent earlier reviews¹¹⁻¹³ on "high-pressure gas chromatography". Therefore, we shall focus on the SFC background and findings of the most direct relevance to the present paper.

It is reasonable to expect that the "solvating power" of the supercritical fluid (SF) mobile phase should depend on the average distance between molecules and on the thermal energy, suggesting that density (ρ) and temperature (T) should be the key SF variables governing solute retention in SFC. Indeed, during the past few years it has become evident that density (rather than pressure, P) and temperature are the most sensible independent variables for describing and analyzing the effect of the SF mobile phase on solute retention. It has been observed,^{3,14} for example, that the dependence of $\ln k$ (solute capacity factor) on P at fixed T is rather complicated, often giving rise to S-shaped curves, whereas plots of $\ln k$ vs. ρ at fixed T appear to be quite generally describable by simple quadratic functions.^{3,5} This is also seen¹⁵⁻¹⁹ in plots of $\ln k$ vs. T^{-1} , which are virtually linear when constructed at fixed ρ , but are usually complicated and resist simple thermodynamic treatment^{16,17} when constructed and analyzed under constant P conditions. The relative simplicity of density representations is also evident in solubility enhancement by supercritical fluid extraction.⁸ Thus, physical arguments and experimental

- (1) Klesper, E. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 738.
- (2) Klesper, E.; Hartmann, W. *Eur. Polym. J.* **1978**, *14*, 77.
- (3) van Wasen, U.; Swaid, I.; Schneider, G. M. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 575.
- (4) Novotny, M.; Springston, S. R.; Peadar, P. A.; Fjeldsted, J. C.; Lee, M. L. *Anal. Chem.* **1981**, *53*, 407A. Fjeldsted, J. C.; Lee, M. L. *Anal. Chem.* **1984**, *56*, 619A.
- (5) Peadar, P. A.; Lee, M. L. *J. Liq. Chromatogr.* **1982**, *5* (Suppl. 2), 179.
- (6) Gere, D. R. *Science* **1983**, *222*, 253.
- (7) Novotny, M.; Springston, S. R. *J. Chromatogr.* **1983**, *279*, 417.
- (8) Schneider, G. M. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 841.
- (9) White, C. M.; Houck, R. K. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1986**, *9*, 4.
- (10) Chester, T. L. *J. Chromatogr. Sci.* **1986**, *24*, 226.

- (11) Sie, S. T.; Rijnders, G. W. A. *Anal. Chim. Acta* **1967**, *38*, 31.
- (12) Giddings, J. C.; Myers, M. N.; McLaren, L.; Keller, R. A. *Science* **1968**, *162*, 67.
- (13) Vigdergauz, M. S.; Semkin, V. I. *Russ. Chem. Rev.* **1971**, *40*, 533.
- (14) van Wasen, U.; Schneider, G. M. *Chromatographia* **1975**, *8*, 274.
- (15) Lauer, H. H.; McManigill, D.; Board, R. D. *Anal. Chem.* **1983**, *55*, 1370.
- (16) Chester, T. L.; Innis, D. P. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1985**, *8*, 561.
- (17) Yonker, C. R.; Wright, B. W.; Petersen, R. C.; Smith, R. D. *J. Phys. Chem.* **1985**, *89*, 5526.
- (18) Yonker, C. R.; Smith, R. D. *J. Chromatogr.* **1986**, *351*, 211.
- (19) Provided that no phase boundary is crossed, $\ln k$ vs. T^{-1} at fixed ρ gives a continuous straight line from the SF region through the critical isotherm and into the liquid region.¹⁵

observations clearly indicate that, although pressure is a more convenient variable to control and measure in SFC practice, density is the key variable. This realization has led to recent emphasis on density-gradient programming over pressure-gradient programming.^{5,20-22} As we shall see, this emphasis is well placed. Our SFC retention equation will confirm that SF density and temperature are the natural variables.

It has been remarked that "much remains to be learned about the physicochemical phenomena related to SFC separations".⁴ In fact, the relatively slow development of SFC has been partly attributed to the lack of a sufficiently quantitative theory of solute retention.³ It has been noted³ that, for the range of densities and pressures normally encountered in SFC experiments (typically up to at least twice the critical density and several times the critical pressure of the SF, especially with packed columns), a description based neither on excess properties (as is possible in LC²³) nor on virial coefficients (as is done in GC^{11,13}) is fully adequate. Although no one has yet proposed a molecular theory, there have been attempts to develop macroscopic thermodynamic models to address certain aspects of SFC. The most noteworthy effort was by Schoenmakers²⁴ who based his approach on the semiempirical Lee-Kessler equation of state and the solubility-parameter concept. Although the treatment met with some success in describing the effect of the SF mobile phase on solute retention, absolute retention is not addressed and rather complex algebraic equations have to be solved (by computer) to implement the treatment. Others^{3,14,16,17} have applied classical thermodynamics to examine pressure and/or temperature effects on retention. With respect to earlier work, Giddings et al.^{1,5,12,13,25} used a modified solubility-parameter approach to assess solute retention characteristics and propose a scale of "solvent strength" or "solvating power" for various SF mobile phases which is still useful for screening purposes. In short, there remains a need for a tractable molecular theory which is applicable over the normal operating range of temperatures and densities and which permits a more explicit and quantitative description of solute retention behavior in SFC.

General Theory

Here we utilize a mean-field lattice model to derive the relevant equations to describe the equilibrium distribution of solute between a fluid mobile phase and an adsorbent stationary phase (treated as a bulk liquid), and, hence, solute retention in fluid-liquid chromatography. In view of the lack of a simple and useful molecular theory, supercritical fluid mobile phases are ultimately emphasized. However, the global equations obtained will be seen to apply equally to gas (ideal and moderately nonideal) and liquid mobile phases, thus marking the first unified theory of chromatographic retention.

The general model is a natural extension of the Flory-Huggins approach,²⁶ with the added and important (especially in treating the mobile phase) feature that expansion and compression effects are explicitly included. This type of model has been variously referred to as a compressible-lattice, lattice-gas, lattice-fluid, or Ising-fluid model. It has been successfully applied to describe nematic liquid-crystalline systems,²⁷⁻³⁰ pure fluids,^{31,32} fluid

mixtures (including supercritical ones),^{32,33} polymer solutions,³⁴ and the solubility of solids in supercritical fluids.³⁵ A related model has been recently employed to treat solute retention in reversed-phase liquid chromatography (RPLC) with chemically bonded stationary phases (CBSP).³⁶

Let us consider a three-dimensional lattice having a nearest-neighbor coordination number of z and containing M cells or sites, each having a volume v_0 ; the total volume of the system is then $V = Mv_0$. Randomly distributed on this lattice are N_0 "holes" or vacancies, each occupying a single site, N_a solute molecules, each occupying r_a sites, and, in general, N_b , N_c , and N_d other molecules, each occupying r_b , r_c , and r_d sites, respectively, where $M = N_0 + r_a N_a + r_b N_b + r_c N_c + r_d N_d$. We shall later identify component b as the mobile phase (carrier), component d as the stationary liquid phase and, depending on the particular chromatographic mode, component c may be the second component of the mobile phase or stationary phase. Although a variety of molecular structures may be considered within the general framework of the model,²⁷⁻³⁰ for present purposes the molecules are assumed to be completely flexible chains, each having r_i singly (terminal) or doubly (internal) connected segments ($i = a, b, c, d$) which occupy the r_i lattice sites along the restricted random walk described in ref 26.

For sufficiently large z , one obtains²⁶ the following expression for the dimensionless configurational entropy of the mixture, S/k_B

$$-S/k_B = \sum_{i=a}^d (N_i \ln N_i - N_i) - \sum_{i=a}^d N_i (r_i - 1) \ln \{(z-1)/M\} + (M - \sum_{i=a}^d r_i N_i) \ln (M - \sum_{i=a}^d r_i N_i) - (M - \sum_{i=a}^d r_i N_i) - M \ln M + M \quad (1)$$

where $M = N_0 + \sum_{i=a}^d r_i N_i$ and k_B is the Boltzmann constant. If the (attractive) interaction energy between immediately adjacent (but unconnected) molecular segments i and j is denoted by ϵ_{ij} , the dimensionless total interaction energy in the mixture, $E/k_B T$, is²⁶

$$E/k_B T = (z/2k_B T M) \sum_{i,j=a}^d r_i N_i r_j N_j \epsilon_{ij} \quad (2)$$

where T is the temperature in kelvin and $\epsilon_{ij} < 0$. If we denote the cell partition function per segment of molecule i by q_i and include the contribution

$$A_q/k_B T = -\sum_{i=a}^d r_i N_i \ln q_i \quad (3)$$

the entire dimensionless Helmholtz free energy of the mixture, $A/k_B T$, consistent with the Bragg-Williams approximation, is simply given by the sum of eq 1, 2, and 3:

$$A/k_B T = A_q/k_B T + E/k_B T - S/k_B \quad (4)$$

The dimensionless pressure-to-temperature ratio, Φ , is determined by²⁸⁻³⁰

$$\Phi = Pv_0/k_B T = -[\partial(A/k_B T)/\partial M]_{T,N} \quad (5)$$

where P is the pressure and $N = \sum_{i=a}^d N_i$ is the total number of molecules. From eq 1-5 we obtain one form of the equation of state of the mixture

$$\Phi = -\ln(1 - \sum_{i=a}^d \theta_i) - \sum_{i=a}^d \theta_i (1 - r_i^{-1}) + (z/2k_B T) \sum_{i,j=a}^d \theta_i \theta_j \epsilon_{ij} \quad (6)$$

(30) Dowell, F.; Martire, D. E. *J. Chem. Phys.* **1978**, *68*, 1088, 1094; **1978**, *69*, 2332, 4012.

(31) Sanchez, I.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352 and references therein.

(32) Kleintjens, L. A. *Fluid Phase Equilib.* **1983**, *10*, 183 and references therein.

(33) Lacombe, R. H.; Sanchez, I. *J. Phys. Chem.* **1976**, *80*, 2568.

(34) Sanchez, I.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.

(35) Vezzetti, D. *J. Chem. Phys.* **1982**, *77*, 1512; **1984**, *80*, 866.

(36) Martire, D. E.; Boehm, R. E. *J. Phys. Chem.* **1983**, *87*, 1045 and references therein.

(20) Bowman, L. M., Jr.; Myers, M. N.; Giddings, J. C. *Sep. Sci. Technol.* **1982**, *17*, 271.

(21) Fieldsted, J. C.; Jackson, W. P.; Peadar, P. A.; Lee, M. L. *J. Chromatogr. Sci.* **1983**, *21*, 222.

(22) Fields, S. M.; Lee, M. L. *J. Chromatogr.* **1985**, *349*, 305.

(23) Locke, D. C.; Martire, D. E. *Anal. Chem.* **1967**, *39*, 921. Martire, D. E.; Locke, D. C. *Anal. Chem.* **1971**, *43*, 68.

(24) Schoenmakers, P. J. *J. Chromatogr.* **1984**, *315*, 1.

(25) Giddings, J. C.; Myers, M. N.; King, J. W. *J. Chromatogr. Sci.* **1969**, *7*, 276.

(26) Hill, T. H. *An Introduction to Statistical Thermodynamics*; Addison-Wesley: Reading, MA, 1960; Chapters 20 and 21.

(27) Alben, R. *Mol. Cryst. Liq. Cryst.* **1971**, *13*, 193; *J. Chem. Phys.* **1973**, *59*, 4299.

(28) Peterson, H. T.; Martire, D. E.; Cotter, M. A. *J. Chem. Phys.* **1974**, *61*, 3547.

(29) Ågren, G.; Martire, D. E. *J. Chem. Phys.* **1974**, *61*, 3959; *J. Phys. (Paris)* **1975**, *36*, C1-141.

where $\theta_i = N_i r_i / M$ is the fraction of the total volume or total number of sites occupied by molecules of component i (and similarly for component j). Note that $\theta_0 + \sum_{i=a}^d \theta_i = 1$, where θ_0 refers to the volume fraction of unoccupied lattice sites or holes. If we designate the stationary and mobile phases by the subscripts s and m , respectively, eq 6 becomes, in general

$$\Phi_x = -\ln \left(1 - \sum_{i=a}^d \theta_{i(x)} \right) - \sum_{i=a}^d \theta_{i(x)} (1 - r_i^{-1}) + (z/2k_B T) \sum_{i,j=a}^d \theta_{i(x)} \theta_{j(x)} \epsilon_{ij} \quad (7)$$

where $x = s$ or m and where, at equilibrium

$$\Phi_s = \Phi_m \quad (8)$$

The dimensionless chemical potential of the h -th component, $\mu_h/k_B T$, is determined from

$$\mu_h/k_B T = [\partial(A/k_B T)/\partial N_h]_{T,M,N_{-h}} \quad (9)$$

where N_{-h} denotes the number of molecules of components other than the h -th one. From eq 1-4 and 9

$$\mu_{h(x)}/k_B T = (zr_h/k_B T) \sum_{i=a}^d \theta_{i(x)} \epsilon_{ih} + \ln (\theta_{h(x)}/r_h) - r_h \ln \left(1 - \sum_{i=a}^d \theta_{i(x)} \right) - (r_h - 1) \ln (z - 1) - r_h \ln q_{h(x)} \quad (10)$$

where $h = a, b, c$, or d and, again, $x = s$ or m . The equilibrium condition at the operational temperature and pressure (hence, at the operational Φ value) is given by

$$\mu_{h(s)}/k_B T = \mu_{h(m)}/k_B T \quad (11)$$

Applying eq 10 and 11 to the solute component ($h = a$), we obtain

$$\ln [\theta_{a(s)}/\theta_{a(m)}] = r_a [\ln (1 - \sum_{i=a}^d \theta_{i(s)}) - \ln (1 - \sum_{i=a}^d \theta_{i(m)})] - (zr_a/k_B T) [\sum_{i=a}^d (\theta_{i(s)} - \theta_{i(m)}) \epsilon_{ai}] + r_a \ln (q_{a(s)}/q_{a(m)}) \quad (12)$$

The chromatographic distribution constant or partition coefficient, K , is defined as the ratio of the equilibrium concentration of solute in the stationary phase, $c_{a(s)}$, to that in the mobile phase, $c_{a(m)}$, in the limit of infinite dilution of the solute ($N_a \rightarrow 0$ or $\theta_a \rightarrow 0$). Clearly, this ratio is also equal to the ratio of the respective θ_a 's, i.e.

$$K = \lim_{N_a \rightarrow 0} (c_{a(s)}/c_{a(m)}) = \lim_{N_a \rightarrow 0} (\theta_{a(s)}/\theta_{a(m)}) \quad (13)$$

Regarding component d (here, always a principal stationary-phase component) as virtually inextractable by and, hence, absent from the mobile phase,³⁷ i.e., letting $\theta_{d(m)} \approx 0$, we have from eq 12 and 13

$$\ln K = r_a \ln \left(1 - \sum_{i=b}^d \theta_{i(s)} \right) - (zr_a/k_B T) \sum_{i=b}^d \theta_{i(s)} \epsilon_{ai} - r_a \ln \left(1 - \sum_{i=b}^c \theta_{i(m)} \right) + (zr_a/k_B T) \sum_{i=b}^c \theta_{i(m)} \epsilon_{ai} \quad (14)$$

which is subject to eq 8 and where we have made the usual assumption that, since both phases are fluid phases, $q_{a(s)} \approx q_{a(m)}$; i.e., that q_a is virtually independent of the fluid environment.²⁶

In the limit $\theta_a \rightarrow 0$ and with $\theta_{d(m)} \approx 0$, eq 7 and 8 give

$$\ln \left(1 - \sum_{i=b}^d \theta_{i(s)} \right) + \sum_{i=b}^d (1 - r_i^{-1}) \theta_{i(s)} - (z/2k_B T) \sum_{i,j=b}^d \theta_{i(s)} \theta_{j(s)} \epsilon_{ij} = \ln \left(1 - \sum_{i=b}^c \theta_{i(m)} \right) + \sum_{i=b}^c (1 - r_i^{-1}) \theta_{i(m)} - (z/2k_B T) \sum_{i,j=b}^c \theta_{i(m)} \theta_{j(m)} \epsilon_{ij} \quad (15)$$

Multiplying both sides of eq 15 by r_a , transposing the left-hand side to the right-hand side, and adding the result to eq 14, we obtain a useful alternative form for $\ln K$:

$\ln K =$

$$-r_a \sum_{i=b}^d (1 - r_i^{-1}) \theta_{i(s)} - (zr_a/k_B T) [\sum_{i=b}^d \theta_{i(s)} \epsilon_{ai} - \sum_{i,j=b}^d \theta_{i(s)} \theta_{j(s)} \epsilon_{ij}/2] + r_a \sum_{i=b}^c (1 - r_i^{-1}) \theta_{i(m)} + (zr_a/k_B T) [\sum_{i=b}^c \theta_{i(m)} \epsilon_{ai} - \sum_{i,j=b}^c \theta_{i(m)} \theta_{j(m)} \epsilon_{ij}/2] \quad (16)$$

An additional general equation is required to apply eq 14 or 16. This equation, along with eq 15, may be used to establish the equilibrium compositions and occupied volume fractions of the two chromatographic phases (see later). From eq 10 and 11, with $\theta_{a(s)} = 0$, $\theta_{a(m)} = 0$, $\theta_{d(m)} \approx 0$, and $q_{h(s)} \approx q_{h(m)}$, we have

$$\ln \theta_{h(s)} - r_h \ln \left(1 - \sum_{i=b}^d \theta_{i(s)} \right) + (zr_h/k_B T) \sum_{i=b}^d \theta_{i(s)} \epsilon_{ih} = \ln \theta_{h(m)} - r_h \ln \left(1 - \sum_{i=b}^c \theta_{i(m)} \right) + (zr_h/k_B T) \sum_{i=b}^c \theta_{i(m)} \epsilon_{ih} \quad (17)$$

where $h = b$ or c . Multiplying both sides of eq 15 by r_h and adding the result to eq 17 gives

$$\ln \theta_{h(s)} + r_h \sum_{i=b}^d (1 - r_i^{-1}) \theta_{i(s)} + (zr_h/k_B T) [\sum_{i=b}^d \theta_{i(s)} \epsilon_{ih} - \sum_{i,j=b}^d \theta_{i(s)} \theta_{j(s)} \epsilon_{ij}/2] = \ln \theta_{h(m)} + r_h \sum_{i=b}^c (1 - r_i^{-1}) \theta_{i(m)} + (zr_h/k_B T) [\sum_{i=b}^c \theta_{i(m)} \epsilon_{ih} - \sum_{i,j=b}^c \theta_{i(m)} \theta_{j(m)} \epsilon_{ij}/2] \quad (18)$$

where $h = b$ or c . Also, in eq 14-18, $\theta_{0(s)} + \sum_{i=b}^d \theta_{i(s)} = 1$ and $\theta_{0(m)} + \sum_{i=b}^c \theta_{i(m)} = 1$.

Finally, we note that the chromatographic retention quantities normally measured and reported are the net retention volume, V_N , and the capacity factor, k . These extensive quantities are related to the intensive thermodynamic distribution constant, K , as

$$K = V_N/V_s = k(V_m/V_s) \quad (19)$$

where V_m and V_s are the total volumes of the mobile and stationary phases, respectively.

The Mobile-Phase Fluid

Equation 7, with $x = m$ and $\theta_{a(m)} = \theta_{c(m)} = \theta_{d(m)} = 0$, yields the equation of state of a pure mobile-phase fluid consisting of component b :

$$\Phi_{b(m)} = P v_0 / k_B T = -\ln (1 - \theta_{b(m)}) - (1 - r_b^{-1}) \theta_{b(m)} + (z \epsilon_{bb} / 2 k_B T) \theta_{b(m)}^2 \quad (20)$$

Employing the following reduction parameters³¹

$$V_b^* = N_b r_b v_0, \quad T_b^* = -z \epsilon_{bb} / 2 k_B, \quad P_b^* = -z \epsilon_{bb} / 2 v_0 \quad (21)$$

and noting that $\theta_{b(m)} = N_b r_b v_0 / M v_0 = V_b^* / V_b$ (where V_b and V_b^* are the actual and close-packed volumes, respectively), we retrieve, as expected, the Sanchez-Lacombe (SL)³¹ reduced equation of state for a single-component system (here, component b)

$$\tilde{P}_b + \tilde{p}_b^2 + \tilde{T}_b [\ln (1 - \tilde{p}_b) + \tilde{p}_b (1 - r_b^{-1})] = 0 \quad (22)$$

where

$$\tilde{p}_b = \tilde{V}_b^{-1} = V_b^* / V_b, \quad \tilde{T}_b = T_b / T_b^*, \quad \tilde{P}_b = P_b / P_b^* \quad (23)$$

where V_b , T_b , and P_b are the experimental variables, and where \tilde{p}_b , \tilde{V}_b , \tilde{T}_b , and \tilde{P}_b are respectively the SL reduced density, volume, temperature, and pressure.

Although the reduction parameters given by eq 21 lead to a compact reduced equation of state, the reduction parameters of interest from a practical standpoint are the critical constants, which may be obtained from eq 20 in the usual manner. Substituting $r_b N_b / M$ for $\theta_{b(m)}$ and applying

$$(\partial P / \partial V)_{T, N_b} = (\partial \Phi_{b(m)} / \partial M)_{T, N_b} = 0 \quad (24a)$$

$$(\partial^2 P / \partial V^2)_{T, N_b} = (\partial^2 \Phi_{b(m)} / \partial M^2)_{T, N_b} = 0 \quad (24b)$$

we obtain the following relations for the critical constants (subscript cr) of pure fluid b

$$V_{cr} = N_b r_b v_0 (1 + r_b^{1/2}) = V_b^* (1 + r_b^{1/2}) \quad (25a)$$

$$T_{cr} = -z \epsilon_{bb} r_b / k_B (1 + r_b^{1/2})^2 \quad (25b)$$

$$P_{cr} = -[z \epsilon_{bb} / v_0 (1 + r_b^{1/2})^2] [2r_b \ln(1 + r_b^{1/2}) + (1 - 2r_b^{1/2})] \quad (25c)$$

where we note that the closer-packed volume V_b^* is proportional to the number of molecular segments, r_b . The commonly used reduced quantities (subscript R) are defined as follows:

$$\rho_R = V_R^{-1} = V_{cr} / V_b, \quad T_R = T_b / T_{cr}, \quad P_R = P_b / P_{cr} \quad (26)$$

Focussing on the reduced density and reduced temperature, we have from eq 25 and 26

$$\rho_R = (V_b^* / V_b) (1 + r_b^{1/2}) = \theta_{b(m)} (1 + r_b^{1/2}) \quad (27a)$$

$$T_R^{-1} = -(z \epsilon_{bb} / k_B T_b) (r_b / (1 + r_b^{1/2})^2) \quad (27b)$$

which will provide a link between model parameters and experimental variables in supercritical fluid and gas chromatography. Note, for example, that both the density (ρ) and reduced density (ρ_R) are proportional to the occupied volume fraction, $\theta_{b(m)}$.

A comprehensive discussion of the thermodynamic properties of pure Ising-model fluids, including comparison with other theories and favorable comparison with experimental results, is presented elsewhere³¹ and will not be pursued here.

To provide additional links, we return to eq 7 to relate second virial coefficients (B_{ij} ; $i, j = a, b$) and model parameters. Letting $x = m$ and $\theta_{c(m)} = \theta_{d(m)} = 0$, and considering a binary vapor-phase mixture of a + b:

$$Pv_0 / k_B T = -\ln(1 - \sum_{i=a}^b \theta_{i(m)}) - \sum_{i=a}^b \theta_{i(m)} (1 - r_i^{-1}) + (z / 2k_B T) \sum_{i,j=a}^b \theta_{i(m)} \theta_{j(m)} \epsilon_{ij} \quad (28)$$

Expanding the logarithmic term through θ^2 and collecting terms, we get

$$Pv_0 / k_B T = \sum_{i=a}^b (\theta_{i(m)} / r_i) + (1/2) \sum_{i,j=a}^b \theta_{i(m)} \theta_{j(m)} [1 + (z \epsilon_{ij} / k_B T)] \quad (29)$$

Recalling that $\theta_{i(m)} = N_i r_i / M$, $N_i r_i v_0 = V_i^*$, $Mv_0 = V$ and letting $N_a + N_b = L$ (Avogadro's number), we obtain from eq 29

$$PV^0 / RT = 1 + (1/V^0) \sum_{i,j=a}^b (y_{i(m)} y_{j(m)}) (r_i V_j^* / 2) [1 + (z \epsilon_{ij} / k_B T)] \quad (30)$$

where V^0 and V_j^* are the molar volume of the mixture and the molar close-packed volume of component j, respectively, and y is the mole fraction ($y_i = N_i / N_a + N_b$). Comparing eq 30 and the macroscopic expression

$$PV^0 / RT = 1 + (1/V^0) \sum_{i,j=a}^b y_{i(m)} y_{j(m)} B_{ij} \quad (31)$$

it is clear that the second virial coefficients are given by

$$B_{ij} = (r_i V_j^* / 2) [1 + (z \epsilon_{ij} / k_B T)] \quad (32)$$

where $i, j = a, b$.

For pure b

$$B_{bb} = (r_b V_b^* / 2) [1 + (z \epsilon_{bb} / k_B T)] \quad (33)$$

Using eq 25a and 25b we obtain B_{bb} in reduced form:

$$B_{bb} / V_{cr} = [1 - \{(1 + r_b^{1/2})^2 / (r_b T_R)\}] [r_b / 2(1 + r_b^{1/2})] \quad (34)$$

At the Boyle temperature, $B_{bb} = 0$. Thus

$$(T_R)_{Boyle} = T_{Boyle} / T_{cr} = (1 + r_b^{1/2})^2 / r_b \quad (35a)$$

In principle, eq 35a provides a means of estimating the molecular

parameter r_b for a given (pure) mobile-phase fluid from accessible experimental data. Alternatively, r_b could be estimated from the ratio of a low-temperature solid density ($\approx \rho^*$, the close-packed density) to the critical density, ρ_{cr} , according to eq 25a or 27a:

$$\rho_b^* / \rho_{cr} = 1 + r_b^{1/2} \quad (35b)$$

These and other methods of estimating r_b need to be ultimately judged on the basis of how well experimental data for pure compounds^{31,32} and/or mixtures³²⁻³⁵ are fit using that r_b value (see later).

Gas-Liquid Chromatography

In this section we apply the general model equations for fluid-liquid chromatography to ideal and moderately nonideal gas-liquid chromatography (GLC). We examine a single-component (b) mobile phase and, in general, a homogeneous stationary phase consisting of two principal components (c and d). Since the mobile-phase column pressures (and densities) are quite low in conventional GLC, we may safely neglect absorption of component b by the stationary phase; thus, $\theta_{b(s)} = 0$ and $\theta_{0(s)} + \theta_{c(s)} + \theta_{d(s)} = 1$. Also, we continue to make the reasonable assumption that the stationary phase is not extracted to any notable extent by the mobile phase;³⁷ thus, $\theta_{c(m)} = 0$, $\theta_{d(m)} = 0$, and $\theta_{0(m)} + \theta_{b(m)} = 1$, where $\theta_{b(m)}$ is proportional to the density of the mobile phase. Accordingly, the two chromatographic phases are treated as being completely immiscible. This is clearly valid as $\theta_{b(m)} \rightarrow 0$ (zero density, corresponding to ideal GLC) and is an excellent approximation for $\theta_{b(m)} \ll 1$ (very low density, corresponding to moderately nonideal GLC). With the above assumptions and additional, tenable approximations, it will be shown that the general equation for $\ln K$ yields familiar retention equations for ideal and moderately nonideal GLC.

From eq 16 with $\theta_{b(s)} = 0$ and $\theta_{c(m)} = 0$, we have for the mixed stationary liquid phase (c + d)

$$\ln K_{c+d} = -r_a (1 - r_c^{-1}) \theta_{c(s)} - r_a (1 - r_d^{-1}) \theta_{d(s)} - (z r_a / k_B T) (\theta_{c(s)} \epsilon_{ac} + \theta_{d(s)} \epsilon_{ad}) + (z r_a / k_B T) [(\theta_{c(s)}^2 \epsilon_{cc} / 2) + \theta_{c(s)} \theta_{d(s)} \epsilon_{cd} + (\theta_{d(s)}^2 \epsilon_{dd} / 2)] + r_a (1 - r_b^{-1}) \theta_{b(m)} + (z r_a / k_B T) [(\theta_{b(m)} \epsilon_{ab}) - (\theta_{b(m)}^2 \epsilon_{bb} / 2)] \quad (36)$$

or

$$\ln K_{c+d} = \ln K_{c+d}^0 + r_a (1 - r_b^{-1}) \theta_{b(m)} + (z r_a / k_B T) [(\theta_{b(m)} \epsilon_{ab}) - (\theta_{b(m)}^2 \epsilon_{bb} / 2)] \quad (37)$$

where

$$\ln K_{c+d}^0 = -r_a (1 - r_c^{-1}) \theta_{c(s)} - r_a (1 - r_d^{-1}) \theta_{d(s)} - (z r_a / k_B T) (\theta_{c(s)} \epsilon_{ac} + \theta_{d(s)} \epsilon_{ad}) + (z r_a / k_B T) [(\theta_{c(s)}^2 \epsilon_{cc} / 2) + \theta_{c(s)} \theta_{d(s)} \epsilon_{cd} + (\theta_{d(s)}^2 \epsilon_{dd} / 2)] \quad (38)$$

The separability of the stationary-phase contribution (subscript s terms) and the mobile-phase one (subscript m terms) is evident in the above equations. K_{c+d}^0 is the solute partition coefficient extrapolated to zero column density or pressure ($\theta_{b(m)} \rightarrow 0$) and, hence, pertains to ideal GLC. It depends only on the nature of the solute and the stationary liquid (through the molecular parameters r_i and ϵ_{ij}) and is a function of temperature only (through the occupied volume fractions $\theta_{c(s)}$ and $\theta_{d(s)}$, and T). Also, for neat c ($\theta_{d(s)} = 0$) and neat d ($\theta_{c(s)} = 0$) as single-component stationary liquids, eq 38 gives

$$\ln K_c^0 = -r_a (1 - r_c^{-1}) \theta_{c(s)}^0 - (z r_a / k_B T) [\theta_{c(s)}^0 \epsilon_{ac} - (\theta_{c(s)}^0)^2 \epsilon_{cc} / 2] \quad (39)$$

(37) Modern, presumably absorbent-type stationary phases normally consist of (a) long-chain molecules immobilized on a solid support (e.g., *n*-octadecyl or polymeric CBSP³⁶ for packed columns), in liquid, supercritical fluid and gas chromatography; (b) high molecular weight and generally cross-linked polymers (for capillary columns), in supercritical fluid and gas chromatography; (c) solid supports or capillaries coated with a sufficiently high molecular weight liquid to be essentially nonvolatile, in gas chromatography. Therefore, it is reasonable to assume that such stationary phases are not extracted into the mobile phase to any notable extent.

$$\ln K_d^0 = -r_a(1 - r_d^{-1})\theta_{d(s)}^0 - (zr_a/k_B T)[\theta_{d(s)}^0\epsilon_{ad} - (\theta_{d(s)}^0)^2\epsilon_{dd}/2] \quad (40)$$

where we have distinguished the occupied volume fractions for the neat solvents from those in the mixed liquid phase via superscripts 0.

We introduce a simplification (to be justified later) by letting $\theta_{c(s)} + \theta_{d(s)} \approx 1$, $\theta_{c(s)}^0 \approx 1$ and $\theta_{d(s)}^0 \approx 1$. This neglect of the small volume fraction of unoccupied space ($\theta_{0(s)} \approx 0$) in the stationary liquid phase of the model system precludes examination of second-order thermal expansion effects. With this simplification, algebraic manipulation of eq 38–40 yields two recognizable and well-tested forms^{38,39}

$$\ln K_{c+d}^0 = \ln K_d^0 + r_a(r_c^{-1} - r_d^{-1})\theta_{c(s)} + r_a(\chi_{ad} - \chi_{ac} + \chi_{cd})\theta_{c(s)} - r_a\chi_{cd}\theta_{c(s)}^2 \quad (41)$$

$$\ln K_{c+d}^0 = \theta_{c(s)} \ln K_c^0 + \theta_{d(s)} \ln K_d^0 + r_a\chi_{cd}\theta_{c(s)}\theta_{d(s)} \quad (42)$$

where the interaction parameter χ_{ij} is given by

$$\chi_{ij} = (z/k_B T)\Delta\epsilon_{ij} = (z/k_B T)[\epsilon_{ij} - (\epsilon_{ii} + \epsilon_{jj})/2] \quad (43)$$

and where $\theta_{h(s)} = r_h N_h / (r_c N_c + r_d N_d)$, with $h = c, d$ and $\theta_{c(s)} + \theta_{d(s)} = 1$, may be regarded as the experimental volume fraction of component h in applying eq 41 and 42.³⁸

We now derive the relationship between eq 40 and the corresponding equation for $\ln K_d^0$ in terms of macroscopic variables. Although the following analysis is readily extendible to multi-component stationary phases, we facilitate the treatment by considering only a single-component (d) stationary phase.

Let us first examine the equilibrium between the pure solute vapor and liquid (component a) at T and p_a^0 (saturated vapor pressure). From eq 29 with $\theta_{b(m)} = 0$, we have for the pure solute vapor (subscript v)

$$p_a^0 v_0 / k_B T = (\theta_{a(v)} / r_a) [1 + \{\theta_{a(v)} r_a / 2\} \{1 + (z\epsilon_{aa} / k_B T)\}] \quad (44)$$

Since $\theta_{a(v)} = V_a^* / V_{a(v)}^0$, where V_a^* is the molar close-packed volume and $V_{a(v)}^0$ is the actual vapor-phase molar volume of the pure solute, and $Lr_a v_0 / Lk_B = V_a^* / R$, where L is Avogadro's number, eq 44 may be written as

$$(p_a^0 V_a^* / RT) = \theta_{a(v)} [1 + \{r_a V_a^* / 2V_{a(v)}^0\} \{1 + (z\epsilon_{aa} / k_B T)\}] \quad (45)$$

which, with eq 32 for $i = j = a$, gives

$$(p_a^0 V_a^* / RT) = \theta_{a(v)} [1 + (B_{aa} / V_{a(v)}^0)] \quad (46)$$

where B_{aa} is the second virial coefficient of pure a.

Taking eq 7 (for $x = v$ or $x = l$, vapor or liquid, respectively), multiplying both sides by r_a , subtracting the result from eq 10 (for $h = a$ and $x = v$ or l), and letting $\theta_b = \theta_c = \theta_d = 0$, we obtain

$$(\mu_{a(v)} / k_B T) - r_a \Phi_{a(v)} = \ln(\theta_{a(v)} / r_a) + (r_a - 1)\theta_{a(v)} - r_a \ln q_{a(v)} + [r_a z \epsilon_{aa} / k_B T][\theta_{a(v)} - (\theta_{a(v)}^2 / 2)] - (r_a - 1) \ln(z - 1) \quad (47)$$

$$(\mu_{a(l)} / k_B T) - r_a \Phi_{a(l)} = \ln(\theta_{a(l)} / r_a) + (r_a - 1)\theta_{a(l)} - r_a \ln q_{a(l)} + [r_a z \epsilon_{aa} / k_B T][\theta_{a(l)} - (\theta_{a(l)}^2 / 2)] - (r_a - 1) \ln(z - 1) \quad (48)$$

At equilibrium, the left-hand side (lhs) (hence, the right-hand side (rhs)) of eq 47 and 48 must be equal. Neglecting the term in $\theta_{a(v)}^2$, again setting the occupied volume fraction in the condensed phase approximately equal to unity ($\theta_{a(l)} \approx 1$) and, as before, letting $q_{a(v)} \approx q_{a(l)}$, we obtain from eq 47 and 48

$$\ln(\theta_{a(v)}) - \theta_{a(v)} + [\theta_{a(v)} r_a][1 + (z\epsilon_{aa} / k_B T)] = (r_a - 1) + (r_a z \epsilon_{aa} / 2k_B T) \quad (49)$$

which, with eq 32 and 46, gives

$$\ln(p_a^0 V_a^* / RT) - \ln[1 + (B_{aa} / V_{a(v)}^0)] - (V_a^* / V_{a(v)}^0) + 2(B_{aa} / V_{a(v)}^0) = (r_a - 1) + (r_a z \epsilon_{aa} / 2k_B T) \quad (50)$$

where $V_a^* / V_{a(v)}^0 = \theta_{a(v)}$. Expanding $\ln[1 + (B_{aa} / V_{a(v)}^0)]$ through first order in $(V_{a(v)}^0)^{-1}$, approximating $V_{a(v)}^0$ by RT/p_a^0 and collecting terms, we have

$$\ln(p_a^0 / RT) + [p_a^0(B_{aa} - V_a^*) / RT] = -\ln V_a^* + (r_a - 1) + (r_a z \epsilon_{aa} / 2k_B T) \quad (51)$$

Adding $\ln V_d^*$ to both sides of eq 51 and recognizing that $V_d^* / V_a^* = r_d / r_a$, we obtain

$$\ln(p_a^0 V_d^* / RT) + [p_a^0(B_{aa} - V_a^*) / RT] = \ln(r_d / r_a) + (r_a - 1) + (r_a z \epsilon_{aa} / 2k_B T) \quad (52)$$

where V_d^* is the molar close-packed volume of pure component d.

In the same limit where the occupied volume fraction of the condensed phase approaches unity, it can also be shown^{38,39} that

$$\ln \gamma_{a(d)}^\infty = \ln(r_a / r_d) + r_a(r_a^{-1} - r_d^{-1}) + r_a \chi_{ab} \quad (53)$$

where χ_{ab} is given by eq 43, and where $\gamma_{a(d)}^\infty$ is the solute activity coefficient at infinite dilution in the stationary liquid, based on the convention that $\gamma_a \rightarrow 1$ as $y_a \rightarrow 1$ (where y_a is the solute mole fraction). Combining eq 52 and 53, we obtain

$$\ln[RT / V_d^* p_a^0 \gamma_{a(d)}^\infty] - [p_a^0(B_{aa} - V_a^*) / RT] = -r_a(1 - r_d^{-1}) - (zr_a / k_B T)[\epsilon_{ad} - (\epsilon_{dd} / 2)] \quad (54)$$

the rhs of which we recognize as the rhs of eq 40 with $\theta_{d(s)}^0 \approx 1$. Therefore

$$\ln K_d^0 = \ln[RT / V_d^* p_a^0 \gamma_{a(d)}^\infty] - [p_a^0(B_{aa} - V_a^*) / RT] \quad (55)$$

which would be identical with the well-known GLC equation in terms of macroscopic pure-component and solution thermodynamic properties⁴⁰ if $V_d^* = V_{d(l)}^0$ and $V_a^* = V_{a(l)}^0$, which they are under the model-system approximation used in deriving eq 54 (actual volume \approx close-packed volume in liquid phases; see Appendix I). Note, however, that a more elaborate (and much lengthier) derivation with this restriction removed would show exact correspondence. Also note that eq 55 is fully corrected for the vapor-phase nonideality of the pure solute.

We complete our treatment of ideal GLC by examining the temperature dependence of $\ln K_d^0$ and $\ln k_d^0$ (capacity factor). Again if we let $\theta_{d(s)}^0 \approx 1$ and neglect $R[d \ln(V_m / V_s) / d(1/T)] = \alpha_d RT$, where α_d is the thermal expansion coefficient of d, eq 19 and 40 give

$$R[d \ln K_d^0 / d(1/T)] = R[d \ln k_d^0 / d(1/T)] = -R(r_a z / k_B)[\epsilon_{ad} - (\epsilon_{dd} / 2)] = \Delta \bar{E}_{a(d)}^\infty \quad (56)$$

where $\Delta \bar{E}_{a(d)}^\infty$ is the infinite-dilution solute partial molar energy of vaporization from the stationary liquid to an ideal vapor phase at T . Applying eq 25b to eq 56

$$R[d \ln k_d^0 / d(1/T)] = \Delta \bar{E}_{a(d)}^\infty = (RT_{cr})[(r_a / r_b)(1 + r_b^{1/2})^2][(\epsilon_{ad} / \epsilon_{bb}) - (\epsilon_{dd} / 2\epsilon_{bb})] \quad (57)$$

where T_{cr} is the critical temperature of pure mobile phase b, a result which will be used in the section on supercritical fluid chromatography. Since $r_a = e + f n_a$ for a homologous solute series, where e and f are constants and n_a is the number of solute carbon atoms or methylene groups, eq 40 and 57 predict that both $\ln k_d^0$ and $d \ln k_d^0 / d(1/T)$ should be linear functions of n_a , as is observed in ideal and nearly ideal GLC.

The corresponding macroscopic expression is derived from eq 19 and 55. Employing the less approximate version by letting $V_d^* = V_{d(l)}^0$ and $V_a^* = V_{a(l)}^0$ in eq 55, noting there that $B_{aa} \gg V_{a(l)}^0$,⁴⁰ and letting $V_s = V_d$ in eq 19, we obtain

(38) Harbison, M. W. P.; Laub, R. J.; Martire, D. E.; Purnell, J. H.; Williams, P. S. *J. Phys. Chem.* **1979**, *83*, 1262.

(39) Martire, D. E. *J. Phys. Chem.* **1983**, *87*, 2425 and references therein.

(40) Laub, R. J.; Pecsok, R. L. *Physicochemical Applications of Gas Chromatography*; Wiley: New York, 1978; Chapter 4.

$$\ln k_d^0 = \ln [RTn_d/f_a^0\gamma_{a(d)}^\infty V_m] \quad (58)$$

where $n_d = V_d/V_{d(i)}^0$ is the number of moles of stationary liquid, f_a^0 is the vapor-phase fugacity of the pure solute at T and p_a , and where $\ln f_a^0 = \ln p_a^0 + (B_{aa}V_{a(i)}^0/RT)$.⁴⁰ It follows that

$$R[d \ln k_d^0/d(1/T)] = -RT - R[d \ln f_a^0/d(1/T)] - R[d \ln \gamma_{a(d)}^\infty/d(1/T)] \\ = -RT + \Delta \bar{H}_{a(\text{vap})}^0 - \bar{H}_{a(d)}^{\infty, \text{ex}} = \Delta \bar{H}_{a(d)}^\infty - RT \quad (59)$$

where $\Delta \bar{H}_{a(\text{vap})}^0$ is the molar enthalpy of vaporization of the pure solute, $\bar{H}_{a(d)}^{\infty, \text{ex}}$ is the infinite-dilution solute partial molar excess solution enthalpy, and $\Delta \bar{H}_{a(d)}^\infty$ is the infinite-dilution solute partial molar enthalpy of vaporization from solution, all at T and corrected for vapor-phase nonideality. Comparing eq 56 (or 57) and 59, it is seen that $\Delta \bar{E}_{a(d)}^\infty = \Delta \bar{H}_{a(d)}^\infty - RT$, confirming the internal consistency of the approximations made.

Finally, turning to moderately nonideal GLC ($\theta_{b(m)} \ll 1$), we examine eq 37. Neglecting the term in $\theta_{b(m)}^2$ and rearranging we obtain

$$\ln K_{c+d} = \ln K_{c+d}^0 + [r_a V_b^*/V_{b(v)}^0][1 + (z\epsilon_{ab}/k_B T)] - (r_a V_b^*/r_b V_{b(v)}^0) \quad (60)$$

where we have utilized $\theta_{b(m)} = V_b^*/V_{b(v)}^0$. Noting that $r_a V_b^*/r_b = V_a^*$ and applying eq 32 (with $i = a$ and $j = b$), we have

$$\ln K_{c+d} = \ln K_{c+d}^0 + [(2B_{ab} - V_a^*)/RT](P_b) \quad (61)$$

where we have utilized $V_{b(v)}^0 = RT/(P_b)$, and where $\langle P_b \rangle$ is the average mobile-phase column pressure and B_{ab} is the mixed (solute-carrier) or interaction second virial coefficient. Once again we see that the general model equations yield a familiar result⁴⁰—in this case the first correction for mobile-phase nonideality in GLC—with only a minor departure, viz., the appearance in eq 61 of V_a^* instead of $\bar{V}_{a(d)}^\infty$,⁴⁰ the infinite-dilution solute partial molar volume in the stationary liquid. However, consistent with the model-system approximations used throughout this section, $\bar{V}_{a(d)}^\infty$ approaches V_a^* as close-packed conditions are approached in the stationary liquid (see Appendix I).

Liquid-Liquid Chromatography

In this section we apply the general retention equation for fluid-liquid chromatography (eq 16) to liquid-liquid (absorption) chromatography (LLC). We examine a two-component liquid mobile phase ($b + c$) and a stationary phase consisting of a single principal component (d), but where absorption of component b into the stationary phase is possible. In the case of virtually immiscible single-component mobile and stationary phases, the ensuing treatment should be applicable to traditional liquid-liquid chromatographic systems with coated stationary phases,²³ which, however, are not truly practical systems for modern analytical applications. It should also be applicable to some extent to modern RPLC with two-component mobile phases (see below), since there is evidence that many of the commonly used CBSP are predominantly absorptive phases.³⁶ In the latter case, d may be a long-chain paraffinic or polymeric CBSP,³⁷ b the "good" organic solvent such as ethanol or acetonitrile, and c the "poor" solvent such as water (which we assume is not absorbed to any notable extent by the stationary phase, i.e., $\theta_{c(s)} \approx 0$). We continue to assume virtual absence of d in the mobile phase³⁷ ($\theta_{d(m)} = 0$) and that the volume fraction of unoccupied space in condensed phases (here, both the mobile and stationary ones) is sufficiently small to neglect ($\theta_{0(m)} \approx 0$, $\theta_{0(s)} \approx 0$). Therefore, $\theta_{b(m)} + \theta_{c(m)} = 1$ and $\theta_{b(s)} + \theta_{d(s)} = 1$. It will be shown that, with these (usual) assumptions, eq 16 yields familiar retention equations for one- and two-component mobile phases.

Under the assumed conditions, eq 16 gives the following solute partition coefficient with a mixed liquid carrier, $b + c$

$$\ln K_{b+c} = -r_a(1 - r_b^{-1})\theta_{b(s)} - r_a(1 - r_d^{-1})\theta_{d(s)} - \\ r_a[\chi_{ab}\theta_{b(s)} + \chi_{ad}\theta_{d(s)} - \chi_{bd}\theta_{b(s)}\theta_{d(s)}] + r_a(1 - r_b^{-1})\theta_{b(m)} + r_a(1 - \\ r_c^{-1})\theta_{c(m)} + r_a[\chi_{ab}\theta_{b(m)} + \chi_{ac}\theta_{c(m)} - \chi_{bc}\theta_{b(m)}\theta_{c(m)}] \quad (62)$$

where we have utilized eq 43. For pure c as a mobile phase ($\theta_{b(m)} = \theta_{b(s)} = 0$)

$$\ln K_c = r_a(r_d^{-1} - r_c^{-1}) + r_a(\chi_{ac} - \chi_{ad}) \quad (63)$$

and for pure b as a mobile phase ($\theta_{c(m)} = 0$)

$$\ln K_b = \ln K_b' + r_a(r_b^{-1} - r_d^{-1})\theta_{b(s)} + \\ r_a[(\chi_{ad} - \chi_{ab} + \chi_{bd})\theta_{b(s)} - \chi_{bd}\theta_{b(s)}^2] \quad (64)$$

$$\ln K_b' = r_a(r_d^{-1} - r_b^{-1}) + r_a(\chi_{ab} - \chi_{ad}) \quad (65)$$

where K_b' would be the solute partition coefficient if b were also excluded from the stationary phase ($\theta_{b(s)} = 0$). Equation 63 (or 65) expresses, in terms of molecular parameters, the equilibrium distribution of solute between two virtually immiscible pure solvents. In terms of volume-fraction-based solute activity coefficients at infinite dilution, $\eta_{a(i)}^\infty$ ($i = c$ or d), where³⁶

$$\ln \eta_{a(i)}^\infty = \ln \gamma_{a(i)}^\infty + \ln (r_i/r_a) = r_a(r_a^{-1} - r_i^{-1}) + r_a\chi_{ai} \quad (66)$$

$\eta_a \rightarrow 1$ as $\theta_a \rightarrow 1$, and $\gamma_{a(i)}^\infty$ is the corresponding mole-fraction-based solute activity coefficient (see eq 53), eq 63 and 66 give

$$\ln K_c = \ln \eta_{a(c)}^\infty - \ln \eta_{a(d)}^\infty \quad (67)$$

Except for a small compressibility-correction term, $(\langle P \rangle/RT) \cdot (\bar{V}_{a(c)}^\infty - \bar{V}_{a(d)}^\infty)$, which vanishes in the approximate model system, eq 67 is the classical LLC equation for two immiscible liquid phases.²³

If $\theta_{b(s)} = 0$ for all $\theta_{b(m)}$ (hence, $\ln K_b = \ln K_b'$), we retrieve from eq 62, 63 and 65 two familiar forms³⁶ describing the partitioning of solute between two immiscible phases, $b + c$ and d

$$\ln K_{b+c} = \ln K_c + r_a(r_c^{-1} - r_b^{-1})\theta_{b(m)} + \\ r_a[(\chi_{ab} - \chi_{ac} - \chi_{bc})\theta_{b(m)} + \chi_{bc}\theta_{b(m)}^2] \quad (68)$$

$$\ln K_{b+c} = \theta_{b(m)} \ln K_b' + \theta_{c(m)} \ln K_c - r_a\chi_{bc}\theta_{b(m)}\theta_{c(m)} \quad (69)$$

both of which also hold with the corresponding capacity factors, k , substituted for the K 's. In addition, note that even though CBSP and bulk liquids differ in their structures and related entropic contributions to $\ln K$ (or $\ln k$),³⁶ eq 68 and 69 would also apply to RPLC-CBSP, since these differences are totally contained in K_b' and K_c (or k_b' and k_c), provided $\theta_{b(s)}$ and $\theta_{c(s)}$ are negligible.⁴¹ The most general case considered in this section is a binary mobile phase ($b + c$) and a permanent stationary phase (d) which may absorb some b ($\theta_{b(s)} > 0$). This case and more complex ones (e.g., $\theta_{c(s)} > 0$ also) have been treated elsewhere³⁶ in quantitative detail for RPLC-CBSP model systems. Nevertheless, two unifying points warrant mentioning. First, note the similarity in form between eq 41 (mixed stationary phase $c + d$ and ideal gas mobile phase, in GLC) and eq 64 (mixed stationary phase $b + d$ and single-component liquid mobile phase b , in LLC). This formal similarity will appear again in a related situation for supercritical fluid chromatography.

Second, although eq 62 has the semblance of two separable contributions to $\ln K_{b+c}$, a stationary-phase one (subscript s terms) and a mobile-phase one (subscript m terms), the equilibrium composition of the stationary phase, $\theta_{b(s)}$ (where $\theta_{b(s)} + \theta_{d(s)} = 1$), depends on the composition of the mobile phase, $\theta_{b(m)}$ (where $\theta_{b(m)} + \theta_{c(m)} = 1$). Therefore, the two contributions are coupled, where $\theta_{b(s)}$ is related to $\theta_{b(m)}$ through eq 18 (with $\theta_{0(s)} = \theta_{c(s)} = 0$ and $\theta_{0(m)} = \theta_{d(m)} = 0$)

$$\ln \theta_{b(s)} + r_b(r_d^{-1} - r_b^{-1})\theta_{b(s)} + r_b\chi_{bd}(1 - \theta_{b(s)})^2 = \ln \theta_{b(m)} + \\ r_b(r_c^{-1} - r_b^{-1})\theta_{b(m)} + r_b\chi_{bc}(1 - \theta_{b(m)})^2 + r_b(r_d^{-1} - r_c^{-1}) \quad (70)$$

and where eq 43 has been employed. For example, if we let $r_c = 1$ (monomer solvent), $r_d \rightarrow \infty$ (high molecular weight stationary phase), and $r_b\chi_{bd} = 1$ (moderately nonideal mobile-phase mixture), then for pure b as the mobile phase eq 70 gives $\theta_{b(s)} = 0.31$ ($\theta_{d(s)} = 0.69$). Finally a form similar to eq 70 will be found in a related situation for supercritical fluid chromatography.

(41) Referred to in ref 36 and the "collapsed-chain limit".

Supercritical Fluid-Liquid Chromatography

In this section we apply the general model equations for fluid-liquid chromatography to supercritical fluid-liquid (absorption) chromatography (SFLC) and related problems, and subject the final equations to experimental tests. We examine a single-component supercritical fluid (SF) mobile phase (b) and a stationary phase of a single principal component (d), as well as any b absorbed by the principal component. Within the framework of the general model, a second mobile-phase component (c), a "modifier", could be readily included in the present treatment, but we defer this more complicated case for future study. Discussion of other applications, specifically the prediction of solubility enhancement in SF extraction processes and the attendant use of SFLC as a "pilot plant" for such processes, and the examination of solute partial molar volumes in SF media, conclude this section.

Preliminary Equations and Discussion. We begin by considering the case $\theta_{c(m)} = \theta_{c(s)} = 0$ and, as before, $\theta_{d(m)} = 0$,³⁷ where $\theta_{0(m)} + \theta_{b(m)} = 1$ and $\theta_{0(s)} + \theta_{b(s)} + \theta_{d(s)} = 1$, for which eq 16 becomes

$$\ln K = -r_a(1 - r_b^{-1})\theta_{b(s)} - r_a(1 - r_d^{-1})\theta_{d(s)} - (zr_a/k_B T)[\theta_{b(s)}\epsilon_{ab} + \theta_{d(s)}\epsilon_{ad} - (\theta_{b(s)}^2\epsilon_{bb}/2) - \theta_{b(s)}\theta_{d(s)}\epsilon_{bd} - (\theta_{d(s)}^2\epsilon_{dd}/2)] + r_a(1 - r_b^{-1})\theta_{b(m)} + (zr_a/k_B T)[(\theta_{b(m)}\epsilon_{ab}) - (\theta_{b(m)}^2\epsilon_{bb}/2)] \quad (71)$$

which is similar in form to eq 36 and where we initially do not neglect the volume fraction of unoccupied space in the stationary-phase ($\theta_{0(s)}$). Equation 71 (as does the LLC eq 62) has the appearance of separable stationary-phase and mobile-phase contributions. However, $\theta_{b(s)}$ and $\theta_{d(s)}$, the equilibrium occupied volume fractions in the stationary phase of, respectively, absorbed carrier molecules and principal stationary-phase molecules, depend on $\theta_{b(m)}$ and, hence, on the temperature and density of the SF carrier. Although the two contributions are strictly coupled, it is nevertheless possible to obtain a more convenient form of eq 71. If we designate $\theta_{d(s)}^0$ as the volume fraction occupied by component-d molecules when the SF mobile-phase pressure (and density) approach zero ($\theta_{b(m)} \rightarrow 0$ and $\theta_{b(s)} \rightarrow 0$), eq 71 reduces to eq 40 found earlier for ideal GLC

$$\ln K \rightarrow \ln K^0 = -r_a(1 - r_d^{-1})\theta_{d(s)}^0 - (zr_a/k_B T)[\theta_{d(s)}^0\epsilon_{ad} - (\theta_{d(s)}^0)^2\epsilon_{dd}/2] \quad (72)$$

where $\theta_{0(s)}^0 + \theta_{d(s)}^0 = 1$ and K^0 is the limiting (zero density) value. Combining eq 71 and 72, and applying eq 27, we obtain

$$\ln K = \ln K^0 + \Delta + (r_a/r_b)(r_b^{1/2} - 1)\rho_R - [r_a/r_b T_R][(1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb})\rho_R - (\rho_R^2/2)] \quad (73)$$

where T_R and ρ_R are the reduced temperature and reduced density of the SF carrier (b), $\ln K^0$ is given by eq 72 and where

$$\Delta = r_a(1 - r_d^{-1})(\theta_{d(s)}^0 - \theta_{d(s)}) + (zr_a/k_B T)(\theta_{d(s)}^0 - \theta_{d(s)})(\epsilon_{ad}) - (zr_a/k_B T)[(\theta_{d(s)}^0)^2 - \theta_{d(s)}^2](\epsilon_{dd}/2) + (zr_a/k_B T)(\theta_{b(s)}\theta_{d(s)}\epsilon_{bd}) - r_a(1 - r_b^{-1})\theta_{b(s)} - (zr_a/k_B T)(\theta_{b(s)}\epsilon_{ab} - \theta_{b(s)}^2\epsilon_{bb}/2) \quad (74)$$

With the exception of the Δ term, eq 73 now reflects a simple additivity of separable stationary-phase ($\ln K^0$) and mobile-phase (remaining terms) contributions. The Δ term, whose effect will be considered below, represents the correction to $\ln K$ in SFLC due to the external pressure acting on the stationary phase and the concomitant absorption of SF carrier molecules into the stationary phase ("swelling").

The values of $\theta_{d(s)}^0$, $\theta_{d(s)}$, and $\theta_{b(s)}$ required to evaluate Δ may be determined from eq 15 and 18. From eq 18 with $\theta_{c(s)} = 0$ and $\theta_{d(m)} = 0$, and similarly from eq 15, we find, respectively

$$\ln \theta_{b(s)} + r_b(1 - r_b^{-1})\theta_{b(s)} + r_b(1 - r_d^{-1})\theta_{d(s)} + (zr_b/k_B T)[\theta_{b(s)}\epsilon_{bb} + \theta_{d(s)}\epsilon_{bd} - (\theta_{b(s)}^2\epsilon_{bb}/2) - \theta_{b(s)}\theta_{d(s)}\epsilon_{bd} - (\theta_{d(s)}^2\epsilon_{dd}/2)] = \ln \theta_{b(m)} + r_b(1 - r_b^{-1})\theta_{b(m)} + (zr_b/k_B T)(\theta_{b(m)}\epsilon_{bb} - \theta_{b(m)}^2\epsilon_{bb}/2) \quad (75)$$

$$\ln(1 - \theta_{b(s)} - \theta_{d(s)}) + (1 - r_b^{-1})\theta_{b(s)} + (1 - r_d^{-1})\theta_{d(s)} - (z/2k_B T)(\theta_{b(s)}^2\epsilon_{bb} + 2\theta_{b(s)}\theta_{d(s)}\epsilon_{bd} + \theta_{d(s)}^2\epsilon_{dd}) = \ln(1 - \theta_{b(m)}) + (1 - r_b^{-1})\theta_{b(m)} - (z/2k_B T)\theta_{b(m)}^2\epsilon_{bb} \quad (76)$$

Applying eq 27 to eq 76 gives

$$\ln(1 - \theta_{b(s)} - \theta_{d(s)}) + (1 - r_b^{-1})\theta_{b(s)} + (1 - r_d^{-1})\theta_{d(s)}[(1 + r_b^{1/2})^2/2r_b T_R][\theta_{b(s)}^2 + 2\theta_{b(s)}\theta_{d(s)}(\epsilon_{bd}/\epsilon_{bb}) + \theta_{d(s)}^2(\epsilon_{dd}/\epsilon_{bb})] = \ln[1 - \{\rho_R/(1 + r_b^{1/2})\}] + [(r_b^{1/2} - 1)/r_b]\rho_R + (\rho_R^2/2r_b T_R) \quad (77)$$

Let us examine the effects of external pressure (as manifested through ρ_R) and thermal expansion and assume for the time being that there is negligible uptake of carrier by the stationary phase ($\theta_{b(s)} \approx 0$), in which case eq 75 (based on equality of the chemical potential of b in the two phases) would not apply and the equilibrium value of $\theta_{d(s)}$ would be determinable by eq 77 with $\theta_{b(s)} = 0$. Now, in SFLC (and GLC) the principal stationary-phase component has a much larger molecular volume (much larger r_d value) and is typically more polarizable and/or polar, per unit molecular volume, than common mobile phases such as CO₂ and N₂ (hence, $\epsilon_{ad}/\epsilon_{bb} > 1$). Therefore, to calculate some typical $\theta_{d(s)}^0$ values for the model system from eq 77, we let $\rho_R = 0$, $r_d \rightarrow \infty$, $r_b = 4.61$, $\epsilon_{dd}/\epsilon_{bb} = 1.62$, and $T_R = 1.10$ (simulating CO₂ at 61 °C and an SE-54 polymeric liquid phase; see later), giving $\theta_{d(s)}^0 = 0.876$. At $T_R = 1.05$ (~46 °C) and $T_R = 1.15$ (~77 °C), the calculated $\theta_{d(s)}^0$ values are 0.889 and 0.863, respectively. Thus, although $\theta_{0(s)}^0 (= 1 - \theta_{d(s)}^0)$ is small compared to unity, it is not negligible. Also, $\theta_{d(s)}^0 = V_d^*/V_d^0$ is slightly temperature dependent (thermal expansion coefficient, $\alpha_d^0 = -(d \ln \theta_{d(s)}^0/dT)$, of the order of 10^{-3} K^{-1}). Nevertheless, we shall sacrifice some accuracy of representation to gain tractability, while still maintaining the predominant effects on $\ln K$. That is, in the final SFLC equations we shall set $\theta_{d(s)}^0 = 1$ and, by extension to the more general case yet to be considered ($\rho_R > 0$, $\theta_{b(s)} > 0$), set $\theta_{b(s)} + \theta_{d(s)} = 1$, an approximation to be independently tested later. At a given T_R one would expect (and may readily confirm using eq 76 and 77) that the occupied volume fraction in the stationary phase at higher ρ_R ($\theta_{b(s)} + \theta_{d(s)}$) should be comparable to that at $\rho_R = 0$ ($\theta_{d(s)}^0$) due to two compensating effects: expansion due to absorption of the higher free volume carrier and compression due to higher external pressure (see below). As discussed earlier, these approximations preclude examination of (usually small) effects related to thermal expansion of the stationary phase (at fixed ρ_R).

Turning to the effect of external pressure per se on $\theta_{d(s)}$, again with $\theta_{b(s)} \approx 0$, eq 77 evaluated at $\rho_R = 1.0$ ($\rho = 0.468 \text{ g cm}^{-3}$ for CO₂) and $T_R = 1.10$ gives $\theta_{d(s)} = 0.884$ compared to $\theta_{d(s)}^0 = 0.876$. To assess its effect on $\ln K$, as contained in the Δ term, we set $\theta_{b(s)} = 0$ and let $r_d \rightarrow \infty$ in eq 74, and apply eq 27b

$$\Delta = (r_a/r_b)\{r_b(\theta_{d(s)}^0 - \theta_{d(s)}) - [(1 + r_b^{1/2})^2/T_R][\theta_{d(s)}^0 - \theta_{d(s)}] \times [(\epsilon_{aa}/\epsilon_{bb})^{1/2}(\epsilon_{dd}/\epsilon_{bb})^{1/2}] + [(1 + r_b^{1/2})^2/2T_R][(\theta_{d(s)}^0)^2 - \theta_{d(s)}^2][\epsilon_{dd}/\epsilon_{bb}]\} \quad (78)$$

where $\epsilon_{ad} \approx (\epsilon_{aa}\epsilon_{dd})^{1/2}$. Using $(\epsilon_{aa}/\epsilon_{bb})^{1/2} = 0.884$ to simulate an *n*-alkane solute (see later) we calculate $\Delta = (r_a/r_b)(-0.058)$, which indicates that external pressure per se (with no uptake of carrier by the stationary phase) acts to lower $\ln K$ and reduce solute retention. This is fully consistent with the Poynting effect, i.e., application of external pressure increases the partial pressure of the solute and its concentration in the mobile phase, hence lowering $\ln K$ (see eq 13). Comparing the above Δ correction with the primary reduced density contribution to $\ln K$, as shown in eq 73 and denoted here by $F(T_R, \rho_R)$, we again let $r_b = 4.61$, $\epsilon_{ab}/\epsilon_{bb} = 0.884$, $\rho_R = 1.0$, and $T_R = 1.10$, and calculate $F(T_R, \rho_R) = (r_a/r_b)(-0.928)$. Thus, the correction is relatively small and, as we shall see in subsequent analyses, acts in the opposite direction of the contribution to Δ arising from absorption of the carrier by the stationary phase. In any event, by letting $\theta_{d(s)}^0 = 1$ and $\theta_{b(s)} + \theta_{d(s)} = 1$, we also preclude further examination of (small) effects due to external pressure per se.

Accordingly, in the final SFLC equations to be applied in the present treatment, we shall allow for absorption of the SF carrier

(component b) by the principal stationary-phase component (d) and employ the approximations $\theta_{d(s)}^0 = \theta_{b(s)} + \theta_{d(s)} = 1$. Using these approximations and rephrasing eq 75 in terms of interaction parameters (eq 43), we obtain

$$\ln \theta_{b(s)} + r_b(r_d^{-1} - r_b^{-1})\theta_{b(s)} + r_b\chi_{bd}(1 - \theta_{b(s)})^2 = \ln \theta_{b(m)} + r_b(1 - r_b^{-1})\theta_{b(m)} + r_b(-z\epsilon_{bb}/2k_B T)(1 - \theta_{b(m)})^2 + r_b(r_d^{-1} - 1) \quad (79)$$

Comparison of eq 79 and 70 is revealing. The latter equation describes the equilibrium distribution in LLC of the good solvent (b) between the stationary phase and the mobile phase, where the poor solvent (c) resides only in the mobile phase and where $\chi_{bc} = (z/2k_B T)(2\epsilon_{bc} - \epsilon_{bb} - \epsilon_{cc})$. If we were to replace the poor solvent by holes or space in the mobile phase, then $r_c = 1$, $\epsilon_{bc} = \epsilon_{cc} = 0$, and eq 70 would reduce to eq 79. This indicates that the poor solvent in liquid chromatography is formally equivalent to the free space in supercritical fluid chromatography, and similarly for the good solvent and occupied space (or molecules), implying that replacing poor solvent by good solvent via changing composition in LLC is analogous to replacing empty space by molecules via increasing density in SFLC.

There is another (and, perhaps, more compelling) indication of this interesting and exploitable correspondence. If, in the mobile-phase terms of eq 62 for LLC retention, we were to let component c be holes ($r_c = 1$ and $\epsilon_{ic} = 0$) and component b be molecules (unoccupied and occupied space, respectively), then, applying eq 43, eq 62 reduces to eq 71 for SFLC. That is, in the primary mobile-phase terms, the quadratic dependence of $\ln K$ on the volume fraction ($\theta_{b(m)}$) of good solvent in LC with binary mobile phases (see eq 68) is mirrored by the quadratic dependence of $\ln K$ on reduced density in SFC (see eq 73). Thus, in terms of retention behavior, this analogy holds and further suggests that modifying solute retention through density-gradient elution in SFLC is akin to modifying it by solvent-gradient elution in LLC.

Final Equations and Their Implications. If we let $\theta_{c(m)} = \theta_{d(m)} = 0$, $\theta_{c(s)} = 0$, and $\theta_{d(s)}^0 = \theta_{b(s)} + \theta_{d(s)} = 1$, as discussed above, then the solute (a) partition coefficient in SFLC with a single-component SF mobile phase (b) and a stationary phase consisting of the principal component (d) and any absorbed SF is given by eq 72 (with 27b), 73, and 74 (with 43)

$$\ln K = \ln K^0 + F(T_R, \rho_R) + \Delta \quad (80)$$

where the main stationary-phase term is

$$\ln K^0 = (r_a/r_b)\{[r_b(r_d^{-1} - 1)] + [(1 + r_b^{1/2})^2/T_R][(\epsilon_{ad}/\epsilon_{bb}) - (\epsilon_{dd}/2\epsilon_{bb})]\} \quad (81)$$

where the main mobile-phase term is

$$F(T_R, \rho_R) = (r_a/r_b)\{(r_b^{1/2} - 1)\rho_R - [T_R^{-1}]\{(1 + r_b^{1/2}) \times (\epsilon_{ab}/\epsilon_{bb})\rho_R - (\rho_R^2/2)\}\} \quad (82)$$

where the correction term, which depends on both phases (through eq 79), is

$$\Delta = r_a(r_b^{-1} - r_d^{-1})\theta_{b(s)} + r_a[(\chi_{ad} - \chi_{ab} + \chi_{bd})\theta_{b(s)} - \chi_{bd}\theta_{b(s)}^2] \quad (83)$$

and where small contributions to $\ln K$ due to the thermal expansion of and external pressure acting on the stationary phase have been neglected.

Again, $\ln K^0$ is the zero-density or limiting value, corresponding to ideal GLC. As might be clearer from eq 72 (with $\theta_{d(s)}^0 = 1$), the unreduced counterpart of eq 81, it depends only on the temperature and the nature of the solute (a) and principal stationary-phase component (d).

As is seen in eq 82, the natural mobile-phase variables are the reduced density (ρ_R) and reduced temperature (T_R) of the SF, and the primary mobile-phase contribution to $\ln K$ is a quadratic function of ρ_R . The first term, $(r_a/r_b)(r_b^{1/2} - 1)\rho_R$, arises from the configurational entropy, is independent of T_R , and leads to an increase in $\ln K$ with increasing ρ_R . The second and dominant term, $-(r_a/r_b)(1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb})(\rho_R/T_R)$, stems from solute-SF attractive interactions and leads to a decrease in $\ln K$ with in-

creasing ρ_R , more so when solute-SF interactions (ϵ_{ab}) are strong compared to SF-SF ones (ϵ_{bb}) and as T_R decreases. The third term, $(r_a/r_b)(\rho_R^2/2T_R)$, reflects repulsive interactions, which become more important at high ρ_R and lead to an increase in $\ln K$ with increasing ρ_R . Note that, at a given ρ_R and T_R , $F(T_R, \rho_R)$ increases in magnitude with increasing r_a and, hence, with increasing solute carbon number for a homologous solute series.

If Δ , the correction to $\ln K$ due to uptake of the SF by the stationary phase, is sufficiently small to neglect relative to $F(T_R, \rho_R)$, then eq 80 and 82 predict that $\ln K$ as a function of ρ_R at fixed T_R (and, by extension, $\ln k$) should exhibit a minimum at high enough ρ_R . From $(\partial \ln K / \partial \rho_R)_{T_R} = 0$

$$(\rho_R)_{\min} = (1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb}) - (r_b^{1/2} - 1)T_R \quad (84)$$

which is independent of the size of the solute, but depends on its (segmental) interaction energy with the SF, ϵ_{ab} . Since the highest attainable value of ρ_R in the model system is the close-packed value, $1 + r_b^{1/2}$ (eq 27a, with $\theta_{b(m)} = 1$), this minimum would only be observable in systems where $1 > [(\epsilon_{ab}/\epsilon_{bb}) - \{(r_b^{1/2} - 1)/(r_b^{1/2} + 1)\}T_R] > 0$. We shall return to eq 84 later.

If we continue to neglect Δ and consider low enough reduced densities so that the term in ρ_R^2 may also be neglected, then with the help of eq 25a, 27b, and 32, eq 80 and 82 may be written in terms of the solute-SF interaction second virial coefficient, B_{ab} , as follows

$$\ln K = \ln K^0 + [(2B_{ab} - V_a^*)/V_{cr}]\rho_R \quad (85)$$

where B_{ab} is a function of the reduced temperature and V_{cr} is the critical molar volume of the SF. Comparing eq 61 and 85 we see that the slope of the plot of $\ln K$ (or $\ln k$) vs. the average mobile-phase column pressure ($\langle P \rangle$) under moderately nonideal GLC conditions, when multiplied by RT/V_{cr} , should provide an estimate of the initial slope of the $\ln K$ (or $\ln k$) vs. ρ_R plot in SFLC, for the same solute/mobile phase/stationary phase combination and at the same temperature. Including the ρ_R^2 term from eq 82 and substituting V_a^*/V_b^* for r_a/r_b , eq 85 becomes

$$\ln K = \ln K^0 + [(2B_{ab} - V_a^*)/V_{cr}]\rho_R + (V_a^*/V_b^*)(\rho_R^2/2T_R) \quad (86)$$

which may also be written in terms of k and k^0 , and which provides an alternative, macroscopic form for an approximate description of solute retention in SFLC. To apply eq 86 one would need to know or estimate the following: B_{ab} at the desired T_R ; V_a^* or strictly $\bar{V}_{a(d)}$ (see discussion following eq 61) which should be approximately equal to $\bar{V}_{a(l)}$,⁴⁰ the liquid molar volume of pure solute; and V_a^*/V_b^* , which may be well-approximated by the ratio of the respective van der Waals molar volumes.⁴² It remains to be determined whether eq 86 proves ultimately more useful than and as accurate as the form in terms of molecular parameters that will be applied here.

The correction term, Δ , given by eq 83, is the contribution to $\ln K$ arising from "swelling" of the fixed stationary phase by the SF and resulting in solute partitioning between a binary stationary phase (b + d, instead of pure d alone) and the SF mobile phase (b). It has exactly the same form and gives the same contribution to $\ln K$ (at a particular $\theta_{b(s)}$) as do the following two cases: (1) where there is a second component of the stationary phase in ideal GLC (eq 41, where c is the other component); (2) where there is swelling of a fixed stationary phase by a single-component mobile phase in LLC (eq 64). Note that Δ increases with increasing $\theta_{b(s)}$, the value of which may be determined at a given T_R and ρ_R from eq 27 and 79

$$\ln \theta_{b(s)} + r_b(r_d^{-1} - r_b^{-1})\theta_{b(s)} + r_b\chi_{bd}(1 - \theta_{b(s)})^2 = \ln [\rho_R/(1 + r_b^{1/2})] + (r_b^{1/2} - 1)\rho_R + [(1 + r_b^{1/2})^2/2T_R][1 - \rho_R/(1 + r_b^{1/2})] + r_b(r_d^{-1} - 1) \quad (87)$$

where $\theta_{b(s)}$ and Δ approach zero as $\rho_R \rightarrow 0$. Also, since swelling would cause a change in the phase ratio, V_m/V_s , the expression

for $\ln k$ corresponding to eq 80 would have a small additional term. With capillary columns, for example, where $V_m/V_s \gg 1$, eq 19 and 80 give

$$\ln k = \ln k^0 + F(T_R, \rho_R) + \Delta - \ln \theta_{d(s)} \quad (88)$$

where $\theta_{d(s)} = 1 - \theta_{b(s)}$.

Turning to the temperature dependence of $\ln k$ at fixed ρ_R and neglecting the temperature dependence of $\theta_{b(s)}$ and Δ , we obtain from eq 88

$$R[\partial \ln k / \partial T^{-1}]_{\rho_R} = R[d \ln k^0 / dT^{-1}] + R[\partial F(T_R, \rho_R) / \partial T^{-1}]_{\rho_R} \quad (89)$$

From the ideal GLC eq 57 and 59

$$R[d \ln k^0 / dT^{-1}] = \Delta \bar{H}_{a(d)}^\infty - RT = \Delta \bar{E}_{a(d)}^\infty = RT_{cr}(r_a/r_b)(1 + r_b^{1/2})^2[(\epsilon_{ad}/\epsilon_{bb}) - (\epsilon_{dd}/2\epsilon_{bb})] \quad (90)$$

and from eq 82

$$R[\partial F(T_R, \rho_R) / \partial T^{-1}]_{\rho_R} = -\Delta \bar{E}_{a(b)}^\infty = -RT_{cr}(r_a/r_b)[(1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb})\rho_R - (\rho_R^2/2)] \quad (91)$$

where T_{cr} is the critical temperature of the SF mobile phase, $\Delta \bar{E}_{a(d)}^\infty$ and $\Delta \bar{H}_{a(d)}^\infty$ (both > 0) are respectively the partial molar internal energy and enthalpy of solute transfer, at infinite dilution, from the pure stationary liquid (d) to an ideal mobile phase ($\rho_R = 0$), and $\Delta \bar{E}_{a(b)}^\infty$ (also > 0) is the partial molar internal energy of solute transfer, at infinite dilution, from the actual mobile phase at ρ_R to an ideal mobile phase. Therefore

$$R[\partial \ln k / \partial T^{-1}]_{\rho_R} = \Delta \bar{E}_{a(d)}^\infty - \Delta \bar{E}_{a(b)}^\infty = \Delta \bar{E}_{a(d \rightarrow b)}^\infty \quad (92)$$

where $\Delta \bar{E}_{a(d \rightarrow b)}^\infty$ reflects the actual chromatographic process at ρ_R , i.e., solute transfer from the stationary liquid phase (d) to the SF mobile phase (b), and is the slope of a $R \ln k$ vs. T^{-1} plot at fixed ρ_R .

Although eq 80–92 have been presented as SFLC equations, they apply equally to GLC ($\rho_R \ll 1$) and LLC, where the reduced density of the liquid mobile phase is expected to approach the close-packed reduced density in the model system.⁴³ Therefore, eq 89–92 predict the linearity and continuity in $R \ln k$ vs. T^{-1} plots at fixed ρ_R observed by Lauer et al.^{15,19}

Finally, we note that $-F(T, \rho_R)$ may be regarded as a measure of the solvating power of the SF mobile phase. Examining eq 82, it is clear that a simple separation into a "state effect" (depending on T_R and ρ_R) and a "chemical effect" (depending on the molecular parameters r_a , r_b , ϵ_{ab}) is hardly feasible, suggesting that solvent-strength scales based on such a concept^{1,5,12,13,25} are semi-quantitative at best.

Application to SFLC. In searching the literature for supercritical fluid data to use in testing the final equations, we focused on normal-chain solutes and fixed or cross-linked polymeric stationary phases (to render them inextractable³⁷) to correspond as closely as possible to the molecular structures prescribed in the model.^{44,45} We also sought accessible thermodynamic measurements where solute chain length and mobile-phase density, temperature, and type were varied systematically. Fortunately, a few sets of data on *n*-alkane solutes, mainly with CO₂ as the SF mobile phase, satisfying these criteria were identified, although some were in graphical form.

Assuming for the time being that the correction term Δ is small with respect to $F(T_R, \rho_R)$, our working equations are then the

(43) For example, with $\rho_{cr} = 0.468$ (g cm⁻³)³ and $r_b = 4.61$ for CO₂, one calculates a close-packed density (ρ_b^*) of 1.47 g cm⁻³ from eq 35b. Since $\rho_{liq}(40^\circ\text{C}) = 1.26$ (g cm⁻³),²⁰ the reported liquid-phase density of CO₂ at 40 °C is about 86% of the close-packed density in the model system.

(44) Although CO₂ is more properly describable as a rigid-rod molecule, one can show that the relevant thermodynamic properties of rigid-rod and flexible-chain fluids in the model are comparable for small r_b .³⁰

(45) The principal stationary-phase component (d) is modelled as a free, completely flexible chain. Immobilization and/or cross-linking are expected to reduce the entropy of d and the entropic contribution to $\ln K^0$ (and $\ln k^0$)³⁶ in eq 81, as manifested by the term $r_a(r_a^{-1} - 1)$. Accordingly, for such restricted stationary phases, eq 81 would predict too low a value for K^0 (and k^0). Equation 83 and 87 for the correction term Δ would be affected as well.

TABLE I: van der Waals Volumes,⁴² V^{\ddagger} , cm³ mol⁻¹

substance	V^{\ddagger}	r_a/r_{CO_2}
CO ₂	19.7	
C ₂ H ₆	27.3	
N ₂ O	18.9	
<i>n</i> -C ₁₀ H ₂₂	109.2	5.54
<i>n</i> -C ₁₅ H ₃₂	160.3	8.14
<i>n</i> -C ₁₆ H ₃₄	170.6	8.66
<i>n</i> -C ₁₇ H ₃₆	180.8	9.18
<i>n</i> -C ₁₈ H ₃₈	191.0	9.70
<i>n</i> -C ₁₉ H ₄₀	201.3	10.22
<i>n</i> -C ₂₀ H ₄₂	211.5	10.74
squalane ^b	313.7	15.92

^a V_i is proportional to r_i . ^b 2,6,10,15,19,23-Hexamethyltetracosane.

TABLE II: Experimental¹⁸ and Calculated^a Values of $R[\partial \ln k / \partial T^{-1}]_{\rho_R}$ (kcal mol⁻¹) for *n*-Alkane Solute/SE-54/CO₂ Systems

ρ , g cm ⁻³	solute		
	<i>n</i> -C ₁₇ H ₃₆	<i>n</i> -C ₁₈ H ₃₈	<i>n</i> -C ₁₉ H ₄₀
0.5	3.9 (4.0)	4.2 (4.3)	4.3 (4.5)
0.4	6.5 (6.3)	6.8 (6.6)	7.1 (6.9)
0.3	8.6 (8.6)	8.9 (9.1)	9.4 (9.5)
0	(17.4)	(18.4)	(19.3)
0	(18.1) ^b	(19.5) ^b	(20.9) ^b

^a Shown in parentheses are values calculated from eq 96 with $A = 1890$ cal mol⁻¹ and $B = (1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb}) = 2.784$. ^b Calculated from $\Delta H^\circ_{a(l \rightarrow v)} - RT$ at $T = 350$ K, using data in ref 47.

counterparts of eq 80–82 in terms of k and k^0 (see eq 88) and eq 89–92. For the main mobile-phase contribution, the state variables are ρ_R and T_R , and the molecular parameters are r_a/r_b , r_b , and $\epsilon_{ab}/\epsilon_{bb}$ (eq 82). The parameter r_a/r_b may be readily and accurately estimated from the ratio of the respective van der Waals molar volumes,⁴² $V_a^\ddagger/V_b^\ddagger$, leaving r_b and $\epsilon_{ab}/\epsilon_{bb}$ as the only free parameters. The values of V_i^\ddagger for the mobile phases and solutes treated here, as well as r_a/r_{CO_2} , are listed in Table I.

Considering CO₂ as the SF mobile phase, eq 35a and 35b may, in principle, be used to estimate its r_b value. From eq 35a and the known critical³ and Boyle⁴⁶ temperatures of CO₂, $T_{cr} = 304.2$ K and $T_B = 713$ K, respectively, one calculates $r_b = 3.6$. From eq 35b, the critical density of CO₂,³ $\rho_{cr} = 0.468$ g cm⁻³, and the Handbook value for the density of crystalline CO₂ at -79°C , $\rho_b^* \approx 1.56$ g cm⁻³, one calculates $r_b = 5.4$, which is close to the value assigned by Vezzetti.³⁵ Because of the uncertainty about the "best" r_b value for CO₂, we will have to treat it as an adjustable parameter and to fit it directly using SFC data. The only other adjustable parameter, $\epsilon_{ab}/\epsilon_{bb}$, depends on the nature of the solute (here, *n*-alkanes) and the SF. The best-fit values obtained for these two parameters are further tested for their internal consistency, predictive ability, and physical significance (see below).

Yonker and Smith¹⁸ have reported slopes of $R \ln k$ vs. T^{-1} plots at fixed ρ_R . Shown in Table II are their results for three *n*-alkane solute at three CO₂ densities with cross-linked 5% phenylpoly(methylphenylsiloxane) as the stationary phase (SE-54).⁴⁷ From eq 89–91, we obtain a form amenable to linear least-squares analysis of their data

$$(r_b/r_a)(R)(\partial \ln k / \partial T^{-1})_{\rho_R} - (RT_{cr})(\rho_R^2/2) = Y = A - B(RT_{cr}\rho_R) \quad (93)$$

where

$$A = (r_b/r_a)(d \ln k^0 / dT^{-1}) = (RT_{cr})(1 + r_b^{1/2})^2[(\epsilon_{ad}/\epsilon_{bb}) - (\epsilon_{dd}/2\epsilon_{bb})] \quad (94a)$$

$$B = (1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb}) \quad (94b)$$

(46) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures*; Clarendon: Oxford, U.K., 1980.

(47) Smith, R. D.; Udseth, H. R.; Wright, B. W. In *Supercritical Fluid Technology*; Penninger, J. M. L., Radosz, M., McHugh, M. A.; Krukonis, V. J., Eds.; Elsevier: Amsterdam, 1985; pp 191–223, in which it is conclusively demonstrated that the cross-linked SE-54 is behaving as a purely absorptive stationary liquid toward *n*-alkane solutes.

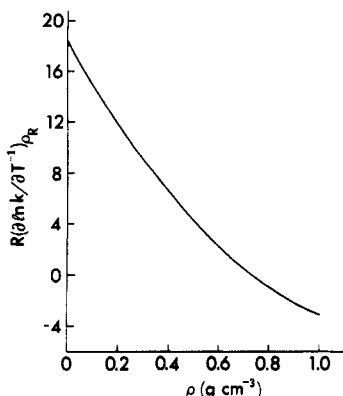


Figure 1. Plot of $R(\partial \ln k / \partial T^{-1})_{\rho_R} = \Delta \bar{H}_{a(d \rightarrow b)}^{\infty} - RT$ (in kcal mol⁻¹) vs. supercritical CO₂ density, ρ (in g cm⁻³), for the solute n -C₁₈H₃₈ and the stationary phase SE-54, as predicted by eq 96.

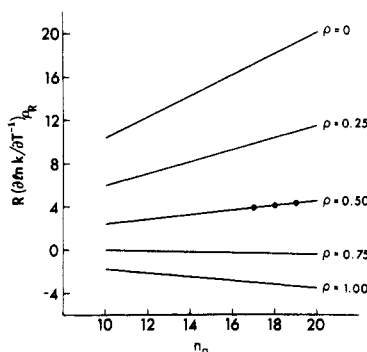


Figure 2. Plot of $R(\partial \ln k / \partial T^{-1})_{\rho_R} = \Delta \bar{H}_{a(d \rightarrow b)}^{\infty} - RT$ (in kcal mol⁻¹) vs. n -alkane solute carbon number, n_a , at different supercritical CO₂ densities, ρ (in g cm⁻³), for the stationary phase SE-54, as predicted by eq 96; ●, experimental data.

According to the model, analysis of Y as a function of $RT_{cr}\rho_R$ of the SF should yield a straight line of intercept A and slope $-B$, both of which are predicted to be independent of solute size for a given homologous solute series.

Using the data in Tables I and II, the fitting procedure yields values of $A = 1890$ cal mol⁻¹ and $B = 2.784$ with a correlation coefficient of 0.998. Rearranging eq 93 and 94 to the original form, we have

$$R(\partial \ln k / \partial T^{-1})_{\rho_R} = \Delta \bar{H}_{a(d \rightarrow b)}^{\infty} - RT = (r_a/r_b)A - (r_a/r_b)(RT_{cr})B\rho_R + (r_a/r_b)(RT_{cr})(\rho_R^2/2) \quad (95)$$

where A and B are given by eq 94. From the data in Table II we obtain $(r_a/r_b) = (V_a^{\dagger}/V_b^{\dagger}) = 0.349 + 0.519n_a$, where n_a is the number of carbon atoms in the solute molecule, which when combined with eq 95 gives

$$R(\partial \ln k / \partial T^{-1})_{\rho_R} = (661 + 983n_a) - (588 + 874n_a)\rho_R + (106 + 157n_a)\rho_R^2 \quad (96)$$

where the units are cal mol⁻¹, and which is linear in n_a and quadratic in ρ_R . Shown in parentheses in Table II are the values of $R(\partial \ln k / \partial T^{-1})_{\rho_R}$ calculated from eq 95 or 96 and of $\Delta H_{a(l \rightarrow v)}^{\circ} - RT$, where $\Delta H_{a(l \rightarrow v)}^{\circ}$ is the enthalpy of vaporization of the pure solute calculated at $T = 350$ K⁴⁸ (near the midpoint of their temperature range) and uncorrected for vapor-phase nonideality. The former parenthetical values fall within ± 0.2 kcal mol⁻¹ of the experimental values, while the latter indicate that the enthalpies of vaporization of the pure n -alkanes are slightly larger but comparable to the (extrapolated) enthalpies of solute vaporization from the stationary phase ($\Delta \bar{H}_{a(d \rightarrow b)}^{\infty}$).

Shown in Figure 1 is a plot of $R(\partial \ln k / \partial T^{-1})_{\rho_R} = \Delta \bar{H}_{a(d \rightarrow b)}^{\infty} - RT$ vs. ρ for n -C₁₈H₃₈ and, in Figure 2, linear plots of $R(\partial \ln k / \partial T^{-1})_{\rho_R}$

TABLE III: Analysis of Capacity Factors (k) for n -C₁₅H₃₂/SE-54/Mobile Phase Systems^{a,b}

conditions	mobile phase			
	CO ₂	C ₂ H ₆	N ₂ O	ln k^0
j: $T_R = 1.06$; $\rho_R = 0.72$	3.23 (3.23)	2.83 (2.89)	2.66 (2.63)	(7.85)
i: $T_R = 1.23$; $\rho_R = 0.39$	4.42 (4.42)	4.46 (4.36)	3.90 (3.95)	(4.53)
mol parameters				
r_b	4.61	6.40	4.43	
$\epsilon_{ab}/\epsilon_{bb}$	0.884	1.044	0.878	

^a Experimental data from ref 49; calculated k values given in parentheses (from eq 98). ^b Reference 49 also lists k values for the solute n -C₁₀H₂₂, which are low (0.53–0.60) and, hence, more sensitive to any systematic error in the determination of the retention time for the “unretained” compound; accordingly, these results were not analyzed.

vs. n_a at different SF mobile phases densities, both generated by using eq 96. As is seen in Figure 1, the energy change for solute transfer from the stationary phase to the mobile phase is highly positive at low ρ , decreases with increasing ρ , and is predicted to become zero at $\rho = 0.73$ g cm⁻³, where $\Delta \bar{E}_{a(d \rightarrow b)}^{\infty} = \Delta \bar{E}_{a(b \rightarrow d)}^{\infty}$ (see eq 89–92), and negative at higher ρ values, where n -alkane solutes are predicted to display an *energetic* preference for the CO₂ mobile phase over the SE-54 stationary phase. From eq 96

$$R(\partial^2 \ln k / \partial n_a \partial T^{-1})_{\rho_R} = 983 - 874\rho_R + 157\rho_R^2 = 0 \quad (97)$$

whose solution ($\rho_R = 1.56$; $\rho = 0.73$ g cm⁻³) reveals that methylene-group selectivity in these systems should be independent of temperature at $\rho = 0.73$ g cm⁻³. Relatedly, it is inferable from Figure 2 (and will become more evident later) that, provided CO₂ density is kept fixed as the temperature is varied, the selectivity should increase linearly with *increasing* reciprocal temperature for $\rho < 0.73$ g cm⁻³, but less so at higher density. For $\rho > 0.73$ g cm⁻³, the selectivity is predicted to increase linearly with *decreasing* reciprocal temperature and more so at higher density.

The analysis thus far has yielded the product $(1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb})$. To separate the molecular parameters r_b (for CO₂) and $\epsilon_{ab}/\epsilon_{bb}$ (for CO₂/ n -alkane systems), we treat the $\ln k$ data for the system n -C₁₅H₃₂/SE-54/CO₂⁴⁹ listed in Table III. From eq 80, 82, and 88 (with $\theta_{b(s)} = 0$ and $\Delta = 0$), we have

$$\ln k = \ln k^0 + (r_a/r_b)(r_b^{1/2} - 1)\rho_R - [r_a/r_b T_R][(1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb})\rho_R - (\rho_R^2/2)] \quad (98)$$

and

$$(r_a/r_b)(r_b^{1/2} - 1)(\rho_{R,j} - \rho_{R,i}) = \ln(k_j/k_i) - \ln(k_j^0/k_i^0) + (r_a/r_b)[(1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb})[(\rho_{R,j}/T_{R,j}) - (\rho_{R,i}/T_{R,i})] - [(\rho_{R,j}^2/2T_{R,j}) - (\rho_{R,i}^2/2T_{R,i})]] \quad (99)$$

where j and i refer to the experimental conditions in Table II, $(r_b^{1/2} - 1)$ on the lhs is to be determined, and all of the quantities on the rhs are known, including $\ln(k_j^0/k_i^0)$ which may be calculated from eq 96 (with $\rho_R = 0$ and $n_a = 15$):

$$\ln(k_j^0/k_i^0) = 7753(T_j^{-1} - T_i^{-1}) = 3.32 \quad (100)$$

Applying eq 99 and 100, we calculate $r_b = 4.61$ which is within the range of values from our preliminary estimates (3.6 to 5.4), and knowing $(1 + r_b^{1/2})(\epsilon_{ab}/\epsilon_{bb}) = 2.784$, we obtain $(\epsilon_{ab}/\epsilon_{bb}) = 0.884$, indicating slightly weaker attractive n -alkane–CO₂ segmental interactions compared to CO₂–CO₂ segmental interactions. Also, inserting the appropriate values into eq 98 gives the calculated (absolute) $\ln k^0$ s listed in Table III.

From the $\ln k^0$ values for n -C₁₅H₃₂ and eq 19 and 100, we find

$$\ln K_{C_{15}}^0 = -16.19 + (25.49/T_R) = \ln K_{C_{15}}^0 - \ln(V_m/V_s) \quad (101)$$

For the capillary columns used in ref 18 and 49, $(V_m/V_s) = (d/4d_f)$

(48) Dreisbach, R. R. *Physical Properties of Chemical Compounds-II*; American Chemical Society: Washington, DC, 1959.

(49) Wright, B. W.; Kalinoski, H. T.; Smith, R. D. *Anal. Chem.* **1985**, *57*, 2823.

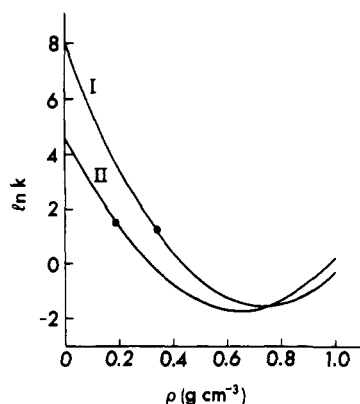


Figure 3. Plots of $\ln k$ (capacity factor) vs. supercritical CO_2 density, ρ (in g cm^{-3}) for the system $n\text{-C}_{15}\text{H}_{32}/\text{SE-54}/\text{CO}_2$ at $T_R = 1.06$ (I) and $T_R = 1.23$ (II), as predicted by eq 104; \bullet , experimental data.

= 50, where d is the internal column diameter (50 μm) and d_f is the stationary-phase film thickness (0.25 μm). Utilizing this estimate, eq 101, and the proportionality between $\ln K^0$ and r_a/r_b (eq 81), we have

$$\ln K^0 = [(r_a/r_b)/8.14][-12.27 + (25.49/T_R)] \quad (102)$$

where K^0 refers to the zero-density solute partition coefficient for any n -alkane and 8.14 is r_a/r_b for $n\text{-C}_{15}\text{H}_{32}$. Letting $r_a/r_b = 0.349 + 0.519n_a$, we obtain the following expression for $\ln k^0$ for these n -alkane/SE-54/ CO_2 systems, in terms of n_a and T_R

$$\ln k^0 = -(4.43 + 0.784n_a) + [(1.09 + 1.626n_a)/T_R] \quad (103)$$

which, when combined with a numerically substituted eq 98, gives the corresponding expression for $\ln k$ in terms of n_a , T_R , and ρ_R

$$\ln k = \ln k^0 + (0.40 + 0.596n_a)\rho_R - (0.97 + 1.446n_a)(\rho_R/T_R) + (0.17 + 0.260n_a)(\rho_R^2/T_R) \quad (104)$$

Therefore, $\ln k$ is a linear function of n_a and T_R^{-1} and a quadratic function of ρ_R .

Generated from eq 104 and shown in Figure 3 are plots of $\ln k$ vs. CO_2 density for $n\text{-C}_{15}\text{H}_{32}$ at $T_R = 1.06$ (I) and $T_R = 1.23$ (II), which intersect at $\rho = 0.73 \text{ g cm}^{-3}$, where $\Delta\bar{H}_{a(d-b)}^\infty \sim RT$ is predicted to become zero (see Figure 1). Equation 84 (or eq 104 with $0.349 + 0.519n_a = r_a/r_b$) predicts minima in these plots at $\rho_R = 2.784 - 1.148T_R$, corresponding to $\rho = 0.733$ and $\rho = 0.642 \text{ g cm}^{-3}$ at $T_R = 1.06$ and $T_R = 1.23$, respectively. In the lower density region, lower k values at higher temperatures have been observed.^{1,14,50} However, there have been no reports of the crossover seen in Figure 3 and there has been merely a mention of the existence of minima in the SFC literature. For polycyclic aromatic hydrocarbon (PAH) solute/ μ -Bondapak- NH_2/CO_2 systems at 40 $^\circ\text{C}$ Christensen⁵¹ observed common minima in retention at $P = 250 \text{ atm}$ ($\rho = 0.88 \text{ g cm}^{-3}$) for all the PAHs studied. Although the bonded stationary phase used would hardly qualify as a bulk absorbent phase, there is other evidence that these minima are largely due to mobile-phase effects, as predicted by eq 84. Schneider⁸ has reported maxima in the solubility of high-molecular-weight alkanes in supercritical CO_2 as a function of SF density. His interpretation of these maxima is the same as the source of the predicted retention minima in the present systems. That is, with increasing SF density the concentration of solute in the mobile phase initially increases due to enhanced SF-solute attractive interactions resulting from the progressive reduction in the average distance between molecules. This leads to a decrease in solute retention with increasing SF density. Then, at higher densities (and even smaller intermolecular distances) repulsive interactions become more effective, causing a subsequent

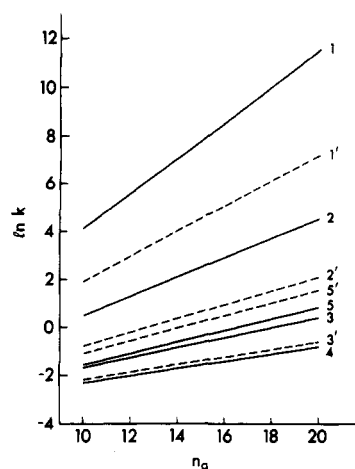


Figure 4. Plots of $\ln k$ (capacity factor) vs. solute carbon number, n_a , for n -alkane/SE-54/ CO_2 systems at the following fixed supercritical fluid densities: (1) $\rho = 0$, (2) $\rho = 0.25$, (3) $\rho = 0.50$, (4) $\rho = 0.75$, (5) $\rho = 1.00 \text{ g cm}^{-3}$, as predicted by eq 104; the primed labels correspond to $T_R = 1.23$ and the unprimed ones to $T_R = 1.06$; not shown is line 4' which lies very close to line 4.

TABLE IV: Methylene Group Selectivity, $(\partial \ln k / \partial n_a)_{T_R, \rho_R}$, at $T_R = 1.06$ and $T_R = 1.23$ and Different Mobile-Phase Densities, for n -Alkane/SE-54/ CO_2 Systems^a

$\rho, \text{g cm}^{-3}$	$(\partial \ln k / \partial n_a)_{T_R, \rho_R}$	
	$T_R = 1.06$	$T_R = 1.23$
0	0.750	0.538
0.25	0.410	0.289
0.50	0.209	0.160
0.75	0.149	0.152
1.00	0.229	0.265

^a Predicted by using eq 105.

decrease in the mobile-phase concentration of the solute and longer retention. Note that the minimum in SFLC retention for a given class of solutes is predicted to shift toward higher densities at lower temperatures, indicating that the predominance of solute-mobile phase attractive interactions is better maintained when the thermal energy is lower.

Illustrated in Figure 4 are linear plots of $\ln k$ vs. n -alkane solute carbon number, n_a , at various fixed SF densities, as generated from eq 104. The slopes of these lines may be calculated at the particular ρ_R and T_R from

$$(\partial \ln k / \partial n_a)_{T_R, \rho_R} = 0.784 + (1.626/T_R) + 0.596\rho_R - 1.446(\rho_R/T_R) + 0.260(\rho_R^2/T_R) \quad (105)$$

and are listed in Table IV. As noted earlier, both $\ln k$ and $(\partial \ln k / \partial n_a)_{T_R, \rho_R}$ (methylene group selectivity) should be independent of temperature at $\rho = 0.73 \text{ g cm}^{-3}$. At lower densities they are predicted to decrease with increasing density or temperature (with the other state variable held constant). In this density range, constant-temperature plots similar to lines 1 to 3 in Figure 4 have been often cited in the SFLC literature.^{1,5,24,52} At higher densities they are predicted to increase with increasing density or temperature.

Most of the predictions cited above remain to be experimentally confirmed. (Even semiquantitative verification would be encouraging at this stage.) However, it is possible to otherwise subject the predictive ability of the treatment thus far to an independent test. Listed in Table V are the data points interpolated from graphs of $\ln k$ as a function of ρ at 40 $^\circ\text{C}$ ($T_R = 1.030$) for three n -alkane solute/immobilized Carbowax-400 stationary phase/ CO_2 systems.^{3,5} From eq 98, with $T_R = 1.030$, $r_b = 4.61$, and $\epsilon_{ab}/\epsilon_{bb} = 0.884$, we obtain

$$\ln k = \ln k^0 - (r_a/r_b)(1.556\rho_R - 0.486\rho_R^2) \quad (106)$$

(50) Wilsch, A.; Feist, R.; Schneider, G. M. *Fluid Phase Equilib.* **1983**, *10*, 299.

(51) Christensen, R. G. J. *High Resolut. Chromatogr. Chromatogr. Commun.* **1985**, *8*, 824.

(52) Sie, S. T.; van Beersum, W.; Rijnders, G. W. A. *Sep. Sci.* **1966**, *1*, 459.

TABLE V: Experimental $\ln k$ Values^{3,5} for n -Alkane Solute/Carbowax-400/ CO_2 Systems at 40 °C and Different CO_2 Densities, ρ^a

$n\text{-C}_{10}\text{H}_{22}$		$n\text{-C}_{16}\text{H}_{34}$		$n\text{-C}_{20}\text{H}_{42}$	
$\ln k$	$\rho, \text{g cm}^{-3}$	$\ln k$	$\rho, \text{g cm}^{-3}$	$\ln k$	$\rho, \text{g cm}^{-3}$
4.32	0.06	4.09	0.23	3.36	0.33
3.72	0.09	3.71	0.25	2.44	0.38
3.17	0.12	3.26	0.27	1.44	0.45
2.58	0.15	2.84	0.29	0.64	0.52
1.84	0.21	2.16	0.33	0.30	0.55
1.37	0.25	1.57	0.38	-0.17	0.59
0.70	0.29	0.83	0.45	-0.33	0.61
0.36	0.33	0.13	0.52	-0.62	0.65
-0.04	0.38	-0.25	0.55		
-0.21	0.40	-0.56	0.59		
-0.49	0.45	-1.06	0.64		
-1.16	0.54	-1.12	0.65		

^a $\rho_R = \rho(\text{g cm}^{-3})/0.468$; $T_R = 313.2/304.2 = 1.030$.

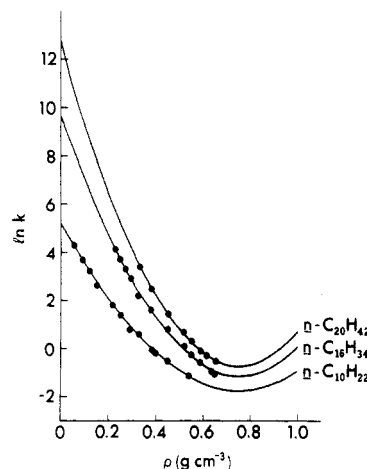


Figure 5. Plots of $\ln k$ (capacity factor) vs. supercritical CO_2 density, ρ (in g cm^{-3}), for three n -alkane solutes and the stationary phase Carbowax 400 at $T_R = 1.030$, as predicted by eq 106 and 108; ●, experimental data.

where the only unknown is $\ln k^0$, the form of which is given by eq 19 and 81:

$$\ln k^0 = \ln (V_s/V_m) + (r_a/r_b)(\text{constant}) \quad (107)$$

Least-squares analysis of the results in Table V as a function of r_a/r_b , according to eq 106 and 107, yields

$$\ln k^0 = -2.733 + (r_a/r_b)(1.430) \quad (108)$$

with a correlation coefficient in excess of 0.9999. The intercept value in eq 108 gives a phase ratio, V_m/V_s , of about 15 which is quite reasonable for the particular packed column used (100–120 mesh Porasil C as the support). The slope (1.430) is discussed below.

Shown in Figure 5 are plots of $\ln k$ vs. ρ for the three n -alkane solutes, as predicted by eq 106 and 108. The agreement between theory and experiment is excellent; the average difference in $\ln k$ is ± 0.08 . Definite curvature is evident in the experimental graphs^{3,5} and common minima are predicted from eq 106 (or 84) to occur at $\rho_R = 1.60$ or $\rho = 0.75 \text{ g cm}^{-3}$.

The reasonableness of the formulation for the primary mobile-phase contribution to $\ln k$, eq 82, may be further demonstrated by applying it to SFLC data obtained with mobile phases other than CO_2 . Listed in Table III are the experimental results for $n\text{-C}_{15}\text{H}_{32} + \text{SE-54}$ with ethane and nitrous oxide as the SF carriers.⁴⁹ Using eq 98, the r_a/r_b ($=V_a^t/V_b^t$) values from Table II, $r_b = 4.61$ ($V_b^t/V_{\text{CO}_2}^t$) and the previously determined $\ln k^0$ values (Table III), we calculate the average $\epsilon_{ab}/\epsilon_{bb}$ values listed in Table III. Note that the value for ethane is close to unity, as would be expected for n -alkane solute + alkane SF systems.

Returning to $R[\ln k^0/dT^{-1}]$ for the SE-54 systems, it was found that $A = 1890 \text{ cal mol}^{-1}$ (Table II), where A is given by

eq 94a. If we apply the geometric mean approximation for unlike interactions, i.e., $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$, then eq 94a becomes

$$A = RT_{cr}(1 + r_b^{1/2})^2[(\epsilon_{aa}/\epsilon_{bb})^{1/2}(\epsilon_{dd}/\epsilon_{bb})^{1/2} - (\epsilon_{dd}/2\epsilon_{bb})] \quad (109)$$

where $(\epsilon_{aa}/\epsilon_{bb})^{1/2} = (\epsilon_{ab}/\epsilon_{bb}) = 0.884$. With $r_b = 4.61$ and $T_{cr} = 304.2 \text{ K}$, we calculate $\epsilon_{dd}/\epsilon_{bb} = 1.618$ and $(\epsilon_{dd}/\epsilon_{bb})^{1/2} = 1.272$, indicating appreciably stronger segmental solvent–solvent attractive interactions compared to SF–SF ones.

Equation 102 describes K^0 for the SE-54 systems, which when combined with eq 19 (with $V_m/V_s = 50$), gives one the corresponding k^0 . Also, letting $r_d \rightarrow \infty$ and acknowledging the inadequacy of the present theoretical formulation of the configurational entropy contribution to $\ln K^{0.45}$ by introducing a correction factor u , we find that eq 81 becomes (after numerical substitution)

$$\ln K^0 = [(r_a/r_b)/8.14][-37.55u + (25.49/T_R)] \quad (110)$$

which, when compared with eq 102, gives $u = 0.327$. Taken at face value, this suggests that cross-linking of the SE-54 reduces the entropic contribution to $\ln K^0$ and ($\ln k^0$) to about one-third of that for a stationary liquid consisting of a comparable unrestricted polymer. Similarly, for the immobilized Carbowax 400 stationary phase, we have from eq 81 (with $r_d \rightarrow \infty$) and 108 (with $T_R = 1.030$)

$$-4.61u + 9.625[(0.884)(\epsilon_{dd}/\epsilon_{bb})^{1/2} - (\epsilon_{dd}/2\epsilon_{bb})] = 1.430 \quad (111)$$

where the geometric mean approximation has again been utilized. Although the actual entropy correction to $\ln K^0$ stemming from immobilization of the stationary phase is rather more complicated,³⁶ if we arbitrarily let $u = 1/3$ in eq 111, then we estimate that $(\epsilon_{dd}/\epsilon_{bb}) = 1.67$, which again points to relatively stronger solvent–solvent attractive interactions. Before more reliable analysis of $\ln K^0$ (and $\ln k^0$) can be conducted, the present theoretical treatment will need to be modified to include explicitly effects due to entropic restriction of the principal stationary phase component molecules.

Finally, we conclude this subsection by examining the effect of swelling of the stationary phase. First, we test the predictive ability of eq 87 by evaluating the absorption of CO_2 by squalane. At $T_R = 1.030$ (40 °C) and $P = 75 \text{ bar}$, where $\rho_R = 0.50$, it has been directly determined that the equilibrium weight fraction of absorbed CO_2 is 0.182.⁵² This corresponds to an approximate volume fraction of absorbed CO_2 of $\theta_{b(s)} = 0.12$. In eq 87

$$r_b\chi_{bd} = (zr_b/k_B T)[\epsilon_{bd} - (\epsilon_{bb} + \epsilon_{dd})/2] \quad (112)$$

If we apply eq 27b and the geometric mean approximation, eq 112 becomes

$$r_b\chi_{bd} = [(1 + r_b^{1/2})^2/2T_R][1 - (\epsilon_{dd}/\epsilon_{bb})^{1/2}]^2 \quad (113)$$

From eq 87 (with $r_d \rightarrow \infty$) and eq 113 (with $(\epsilon_{dd}/\epsilon_{bb})^{1/2} = 0.884$), we calculate $\theta_{b(s)} = 0.09$, which corresponds to a swelling percentage of $[\theta_{b(s)}/(1 - \theta_{b(s)})] \times 100 = 10\%$. This relatively small amount of predicted swelling is close to the experimental value (13% swelling) and is in line with recent, directly determined values for the swelling of poly(methyl methacrylate) by CO_2 at 41.8 °C: 12% at $P = 75 \text{ bar}$, rising to only 15% at $P = 250 \text{ bar}$.⁵³ These percentages are not in agreement with the rather appreciable swelling factors determined *indirectly* for the system $\text{CO}_2 + \text{SE-30}$.⁵⁴

With confidence in the absorption equation, we now consider the swelling correction to $\ln k$. With $T_R = 1.10$ (61 °C), $\rho_R = 1.00$, and $(\epsilon_{dd}/\epsilon_{bb})^{1/2} = 1.272$ (SE-54 value), eq 87 (with $r_d \rightarrow \infty$) and eq 113 produce a value of $\theta_{b(s)} = 0.061$. In eq 83 for the correction term Δ

$$\chi_{ij} = [(1 + r_b^{1/2})^2/2r_b T_R][(\epsilon_{ii}/\epsilon_{bb})^{1/2} - (\epsilon_{jj}/\epsilon_{bb})^{1/2}]^2 \quad (114)$$

where the procedure used in deriving eq 113 has been employed.

(53) Liao, I. S.; McHugh, M. A. In ref 47, pp 415–434.

(54) Springston, S. R.; David, P.; Steger, J.; Novotny, M. *Anal. Chem.* **1986**, *58*, 997.

With $(\epsilon_{aa}/\epsilon_{bb})^{1/2} = 0.884$ (*n*-alkane solute), eq 83 (with $r_d \rightarrow \infty$) and eq 114 yield $\Delta = (r_a/r_b)(0.078)$, a contribution which acts to increase $\ln k$. Earlier we had shown that, under the same conditions, the effect of external pressure per se (Poynting effect) gave a correction of $\Delta = (r_a/r_b)(-0.058)$, promoting a decrease in $\ln k$. The sum of these two partially compensating effects, $(r_a/r_b)(0.020)$, is clearly small with respect to the primary mobile-phase contribution for the same system and under the same conditions, $F(T_R, \rho_R)$, as given by eq 82, which was calculated to be $(r_a/r_b)(-0.928)$. Thus, as has been done in our analysis of SFLC data, it is reasonable to neglect the small correction term Δ in eq 80 and and 88, and to base treatment of SFLC retention behavior on the decoupled equation

$$\ln k = \ln k^0 + F(T_R, \rho_R) \quad (115)$$

where the capacity factors, k and k^0 , are related to the partition coefficients, K and K^0 , respectively, through eq 19. In stating eq 115 it has been assumed that any small decrease in the phase ratio, V_m/V_s , arising from absorption of the SF mobile phase by the principal stationary phase component will be more or less offset by the small increase stemming from external pressure acting on the stationary phase. (Strictly, $-\ln(1 - \theta_{b(s)})$ should appear on the rhs of eq 115 as an additional term; see eq 88.) Further justification of eq 115 may be found in the work of Sie et al.⁵² They demonstrated that even though the weight fraction of CO₂ absorbed by squalane is 0.182, and less than 0.005 by glycerol (both at 40 °C and 75 bar), for a given solute the $\ln k$ vs. P plots for these two stationary liquids are virtually superimposable when the difference in the respective $\ln k^0$ values is taken into account.

Other Applications. Let us develop the relationship between the dependence of solute retention in SFLC and solute solubility in supercritical fluid extraction (SFE) on T_R and ρ_R of the SF by using a simple thermodynamic argument. If we neglect the effects on the stationary phase in SFLC due to absorption of the SF, external pressure, and thermal expansion, then, from eq 13, 19, and 115

$$\ln(k^0/k) = \ln(c_{a(m)}/c_{a(m)}^0) = -F(T_R, \rho_R) \quad (116)$$

where $c_{a(m)}^0$ and $c_{a(m)}$ refer to the concentration of solute in the SF at $\rho_R = 0$ and $\rho_R > 0$, respectively, and where the ratio of the respective stationary-phase concentrations is approximately unity. If we also neglect these effects on the matrix in SFE and restrict consideration to solutes which are sparingly soluble in the SF (say, $\theta_{a(m)} \leq 0.01$), then the solubility enhancement factor,⁸ $E = c_{a(m)}/c_{a(m)}^0$, should be approximately equal to k^0/k

$$\ln E = \ln(k^0/k) = -F(T_R, \rho_R) \quad (117)$$

where $F(T_R, \rho_R)$ is given by eq 82. Equation 117 implies that information obtained by SFLC through studying the effects of temperature and density on solute retention (to obtain $F(T_R, \rho_R)$) should be useful in assessing the solubility enhancement in SFE of the same solute or class of solutes, provided the concentration of solute in the latter is sufficiently low. By extension, it suggests the use of SFLC as a "pilot plant" for SFE, wherein the potential of different SF and modifiers ("entrainers" in SFE) may be rapidly and economically screened. Note that eq 117 predicts solubility maxima in SFE (see eq 84), as have been observed.⁸ Note also that the theory may be readily extended to include solutes at higher concentrations in SFE and to derive a more general equation than eq 117 to link SFLC and SFE.

Another interesting, physical-chemical application of SFLC is the determination of solute partial molar volumes at infinite dilution in SF solvents, $\bar{V}_{a(b)}^\infty$.^{3,55} Highly negative values of $\bar{V}_{a(b)}^\infty$ have been observed for naphthalene in SF CO₂ at 35 °C ($T_R = 1.013$) at a pressure of approximately 80 bar, rapidly becoming less negative at higher and lower pressures. At 50 °C ($T_R = 1.062$), less negative values were found, with the most negative value at this temperature occurring at a pressure of about 100 bar, but with the negative $\bar{V}_{a(b)}^\infty$ region spread over a wider pressure range than at 35 °C.

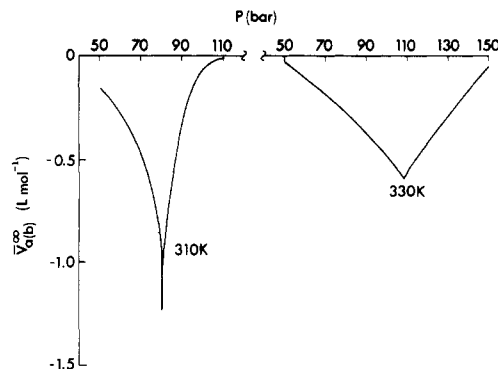


Figure 6. Representative dependence of the infinite-dilution solute partial molar volume, $\bar{V}_{a(b)}^\infty$ (in L mol⁻¹), on the pressure of the supercritical fluid solvent, P (in bar), at 310 and 330 K, as predicted by the theory (see text).

As discussed in Appendix I, $\bar{V}_{a(b)}^\infty \rightarrow -\infty$ as the critical point is approached ($T_R \rightarrow 1$ and $\rho_R \rightarrow 1$). Provided a condition analogous to eq I-12 is satisfied, eq I-7 predicts highly negative $\bar{V}_{a(b)}^\infty$ values at temperatures slightly above the critical temperature (304.2 K for CO₂) and generally less negative ones at higher temperatures. In more detail, we simulate the naphthalene + CO₂ system by letting $r_b = 4.61$, $r_a = (73.97/19.7)(4.61) = 17.31$, where the van der Waals molar volume of naphthalene (73.97 cm³ mol⁻¹)⁴² is assumed to be approximately equal to V_a^* , and $\epsilon_{ab}/\epsilon_{bb} = 1.56$

Shown in Figure 6 are plots of $\bar{V}_{a(b)}^\infty$ vs. SF pressure at 310 K ($T_R = 1.019$) and 330 K ($T_R = 1.085$), constructed by using eq I-7 to I-10 (Appendix I). The required CO₂ densities at the various pressures were obtained from tabulated values at 310 and 330 K.⁵⁷ Note that at 310 K $\bar{V}_{a(b)}^\infty$ is negative in the range 40–110 bar and reaches a value of -1250 cm³ mol⁻¹ at $P \approx 80$ bar. At 330 K the corresponding pressure range is 50–150 bar and the most negative value, ~ -600 cm³ mol⁻¹, is attained at $P \approx 110$ bar. In all, the theoretical results shown in Figure 6 are remarkably consistent with experiment.^{3,55}

Concluding Remarks

From our unified treatment it has been shown that the general equations describing the equilibrium between the mobile and stationary phases and solute retention in fluid-liquid chromatography yield well-known retention equations for ideal and moderately nonideal GLC, conventional LLC, and RPLC-CBSP. Also, solute retention in SFLC with a single-component mobile phase is well represented by eq 98, where the natural mobile-phase variables are the reduced temperature and density.

Although the present results strictly apply to completely flexible and translationally free molecules, the theoretical treatment can be extended to include other solute structures (rods, plates, etc.) and to account explicitly for immobilization and/or cross-linking of the stationary liquid in the $\ln k^0$ term of eq 98. Also, the general formalism has already been developed and can be readily applied to study the effects in SFLC of small amounts of mobile-phase modifiers^{5,6,49,58–61} and even binary mixed mobile phases.^{3,5,8,61} Work in these areas is currently under way.

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(56) From Christensen's⁵¹ observation of a retention minimum for naphthalene at 40 °C ($T_R = 1.030$) and $P = 250$ bar ($\rho = 0.88$ g cm⁻³ or $\rho_R = 1.88$ for SF CO₂), using eq 84 (with $r_b = 4.61$) we calculate $\epsilon_{ab}/\epsilon_{bb} = 0.973$. Also, since $r_a = 17.31$ for naphthalene, eq I-12 in Appendix I requires that $\epsilon_{ab}/\epsilon_{bb} > 0.767$, a condition which is apparently satisfied for the naphthalene + CO₂ system.

(57) Angus, S.; Armstrong, B.; de Reuck, K. M. *International Thermodynamic Tables of the Fluid State*; Pergamon: New York, 1976; Volume 3, Carbon Dioxide.

(58) Levy, J. M.; Ritchey, W. M. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1985**, 8, 503.

(59) Levy, J. M.; Ritchey, W. M. *J. Chromatogr. Sci.* **1986**, 24, 242.

(60) Wright, B. W.; Smith, R. D. *J. Chromatogr.* **1986**, 355, 367.

(61) Yonker, C. R.; Smith, R. D. *J. Chromatogr.* **1986**, 361, 25.

Appendix I

Here we derive expressions for the infinite-dilution partial molar volume of the solute in the stationary- and mobile-phase solvents.

From thermodynamics, the partial molar volume of component *h* in a multicomponent mixture, \bar{V}_h , is given by

$$\bar{V}_h = N(\partial\mu_h/\partial P)_{T,N} \quad (\text{I-1})$$

where *N* is the total number of molecules (Avogadro's number) and where the molecular chemical potential of component *h*, μ_h , is given by eq 10. Since $\Phi = P\bar{V}_0/k_B T$ (eq 5), it follows that

$$\bar{V}_h = N\bar{V}_0\{\partial(\mu_h/k_B T)/\partial M\}/\{\partial\Phi/\partial M\}_{T,N} \quad (\text{I-2})$$

where Φ is given by eq 7, $\Theta_i = N_i r_i/M$, and where, for the time being, we do not distinguish between the stationary- and mobile-phase mixtures. If *h* = *a* (solute component), then eq I-2, 7, and 10 give

$$\bar{V}_a = V_a^*(Y/X) \quad (\text{I-3})$$

where V_a^* is the close-packed molar volume of pure *a* and

$$Y = 1 - (1 - r_a^{-1})(1 - \sum_{i=a}^d \theta_i) + (z/k_B T)(\sum_{i=a}^d \epsilon_{ai}\theta_i)(1 - \sum_{i=a}^d \theta_i) \quad (\text{I-4})$$

$$X = \sum_{i=a}^d \theta_i - [\sum_{i=a}^d (1 - r_i^{-1})\theta_i][1 - \sum_{i=a}^d \theta_i] + (z/k_B T)(\sum_{i,j=a}^d \epsilon_{ij}\theta_i\theta_j)(1 - \sum_{i=a}^d \theta_i) \quad (\text{I-5})$$

For pure *a* ($\Theta_b = \Theta_c = \Theta_d = 0$), eq I-3 to I-5 give $\bar{V}_a = V_a/\Theta_a$, where, in general, $\Theta_a = V_a^*/V_a^0$ and $\bar{V}_a = V_a^0$, the actual molar volume of pure *a*. Under conditions where $\Theta_a \rightarrow 1$, then $\bar{V}_a = V_a^0 \rightarrow V_a^*$ (and similarly for any other pure compound).

At infinite dilution in the principal stationary-phase (*s*) component, *d*, where $\Theta_{a(s)} \rightarrow 0$ and $\Theta_{b(s)} = \Theta_{c(s)} = 0$, we have

$$\bar{V}_{a(d)}^\infty = \frac{V_a^* [1 - (1 - r_a^{-1})(1 - \theta_{d(s)}) + (z\epsilon_{ad}/k_B T)\theta_{d(s)}(1 - \theta_{d(s)})]}{\theta_{d(s)} [1 - (1 - r_d^{-1})(1 - \theta_{d(s)}) + (z\epsilon_{dd}/k_B T)\theta_{d(s)}(1 - \theta_{d(s)})]} \quad (\text{I-6})$$

where $\Theta_{d(s)} = V_d^*/V_d^0$ and $\bar{V}_{a(d)}^\infty \rightarrow V_a^*$ as $\Theta_{d(s)} \rightarrow 1$. Similarly, at infinite dilution in the principal mobile-phase (*m*) component, *b*, where $\Theta_{a(m)} \rightarrow 0$ and $\Theta_{c(m)} = \Theta_{d(m)} = 0$, the partial molar volume of the solute becomes

$$\bar{V}_{a(b)}^\infty = \frac{V_a^* [1 - (1 - r_a^{-1})(1 - \theta_{b(m)}) + (z\epsilon_{ab}/k_B T)(\theta_{b(m)})(1 - \theta_{b(m)})]}{\theta_{b(m)} [1 - (1 - r_b^{-1})(1 - \theta_{b(m)}) + (z\epsilon_{bb}/k_B T)(\theta_{b(m)})(1 - \theta_{b(m)})]} \quad (\text{I-7})$$

where $\Theta_{b(m)} = V_b^*/V_b^0$. As $\Theta_{b(m)} \rightarrow 0$ (essentially, an ideal gas), $\bar{V}_{a(b)}^\infty \rightarrow V_b^0$, the molar volume of pure *b*.

Equation I-7 may be written in terms of the reduced temperature, T_R , and reduced density, ρ_R , of *b* by substituting eq 27a and 27b into it:

$$\theta_{b(m)} = \rho_R/(1 + r_b^{1/2}) \quad (\text{I-8})$$

$$(z\epsilon_{ab}/k_B T) = -(\epsilon_{ab}/\epsilon_{bb})[(1 + r_b^{1/2})^2/r_b T_R] \quad (\text{I-9})$$

$$(z\epsilon_{bb}/k_B T) = -(1 + r_b^{1/2})^2/r_b T_R \quad (\text{I-10})$$

As the critical point of pure fluid *b* is approached ($\rho_R \rightarrow 1$, $T_R \rightarrow 1$), the denominator in eq I-7 approaches zero. (Note that this stems from the denominator in eq I-2 approaching zero; see eq 24a.) Also, in the region of the critical point of pure *b*, it can be shown from eq I-7 to I-9 that the numerator in eq I-7 will be negative, provided

$$(\epsilon_{ab}/\epsilon_{bb}) > [r_b^{1/2} + (r_b/r_a)]/[1 + r_b^{1/2}] \quad (\text{I-11})$$

For CO₂ as the solvent ($r_b = 4.61$), eq I-11 becomes

$$(\epsilon_{ab}/\epsilon_{bb}) > 0.682 + (1.466/r_a) \quad (\text{I-12})$$

where the right-hand side is expected to range from unity ($r_a = r_b$) to 0.682 ($r_a \rightarrow \infty$). Accordingly, if eq I-12 is satisfied, then $\bar{V}_{a(b)}^\infty \rightarrow -\infty$ as $\rho_R \rightarrow 1$ and $T_R \rightarrow 1$.