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# Thermodynamics of Retention in Supercritical Fluid Chromatography: A Refined Model

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Expressions have been obtained giving the pressure and temperature derivatives of the solute retention in supercritical fluid chromatography (SFC) in terms of measurable quantities. Unlike most previous thermodynamic models, the pressure- or temperature-induced changes in composition and amount of the stationary phase ("swelling") are explicitly included. The expressions obtained apply to a *local* value of the solute capacity ratio; i.e., the pressure drop across the column is not taken into account. Emphasis is placed on the pressure dependence of retention in capillary SFC with cross-linked polymeric stationary phases. In a particular model system close to the critical point of the mobile phase, the effect of the swelling has been found to counter those of the solute partial molar volumes and of the mobile-phase compressibility. Further, occurrence of the retention minima at high mobile-phase densities is discussed in terms of the macroscopic thermodynamic properties involved.

## Introduction

Effects of the experimental parameters on solute retention in supercritical fluid chromatography (SFC) have been studied since the advent of this chromatographic technique. The amount of work on the physicochemical fundamentals of retention in SFC has been modest compared to the large number of papers on applications of SFC. However, a proper understanding of the retention mechanism in SFC is essential for the development of SFC as an analytical technique.<sup>1</sup>

The solvating power of a supercritical fluid is determined by temperature and density. In this respect, the density is a more important variable than the pressure since it is the density rather than pressure which controls the dielectric constant of the fluid.<sup>2</sup> Under typical operating conditions in SFC, however, the pressure is much easier to measure and control than is the density. For this reason, the solute retention in SFC is usually expressed as a function of temperature and pressure.

A quantitative description and/or prediction of the solute retention in SFC is a formidable task. It is not surprising, therefore, that a number of diverse approaches were employed with varying degrees of success to reach this goal. Sie et al.<sup>3</sup> attempted to describe the retention in high-pressure gas chromatography using second virial coefficients only. Giddings et al.<sup>4,5</sup> suggested a scale of solvating power for various supercritical fluids on the basis of a solubility parameter concept. Cruickshank et al.<sup>6,7</sup> and Wičar et al.<sup>8,9</sup> presented rather detailed thermodynamic analyses of retention in high-pressure gas chromatography. In their models, the solubility of the mobile phase in the stationary liquid has been explicitly taken into account. Referring specifically to SFC, van Wasen and Schneider<sup>1,10</sup> presented their equation for the isothermal pressure derivative of the logarithm of the solute capacity ratio. This equation contains the infinite-dilution partial molar volumes of the solute in both phases and the isothermal compressibility of the pure mobile-phase fluid. A similar equation was later suggested<sup>11</sup> and criticized<sup>12</sup> as a means to deduce the

partial molar volume of the solute in the mobile-phase fluid from SFC retention data. Schoenmakers<sup>13</sup> developed a thermodynamic model for solute retention employing the Lee-Kesler correlation<sup>14</sup> and the solubility parameter concept. Simple thermodynamic treatments of the effects of pressure and temperature on retention in SFC were presented by Yonker et al.<sup>15,16</sup> and by Chester and Innis.<sup>17</sup> The expressions for the pressure and temperature derivatives of the solute retention were also given by Brown et al.<sup>18</sup>

In the early studies of high-pressure gas chromatography,<sup>3,6-9</sup> the importance of the carrier gas dissolution in the stationary phase has been emphasized. One may naturally expect that this effect will be equally or more important in SFC. However, in the recent thermodynamic studies mentioned above, either the pressure- or temperature-induced changes in composition and volume of the stationary phase ("swelling") have been ignored or they have been included only implicitly within the framework of a constant-composition model.<sup>19</sup>

A specific position among the theoretical treatments of the solute retention in SFC has been taken by Martire's unified molecular theory of both partition<sup>20,21</sup> and adsorption<sup>22,23</sup> chromatography. This theory is based upon the mean-field lattice model, and it is the only theoretical treatment addressing *absolute* retention in SFC. The swelling of the stationary phase is taken into account, but its overall effect on solute retention is considered to be negligible.<sup>20</sup> The experimental support for this conclusion is partly based upon the swelling of poly(methyl methacrylate) by CO<sub>2</sub> at 41.8 °C. At this temperature, however, poly(methyl methacrylate) is probably in a glassy state. On the other hand, typical siloxane-based stationary polymers used in capillary SFC are in a rubbery state even though some amount of cross-linking has to be introduced to render the polymer insoluble in the mobile-phase fluid. Recently, the rubbery and glassy polymers have been shown<sup>24,25</sup> to behave differently when sorbing CO<sub>2</sub> at elevated

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pressures. Further, appreciable swelling has been found<sup>26,27</sup> by an indirect chromatographic method in systems comprising siloxane-based stationary phases and supercritical butane or carbon dioxide.

The purpose of this paper is to modify the thermodynamic expressions for the pressure and temperature derivatives of solute retention in SFC to accommodate the effect of swelling of the stationary phase. For a particular chromatographic system, the relative significance of the individual contributions to the pressure change of retention will be discussed. Similarly as in the unified theory of chromatography,<sup>20</sup> the pressure drop across the column is not taken into account in the present form of the following treatment. A macroscopic thermodynamic model certainly lacks the internal consistency, universality, predictive ability, and elegance of the unified molecular theory.<sup>20-23</sup> However, the significant advantage of a macroscopic model is that the experimental values of various thermodynamic properties may be used directly. This quality is rather important because, in near-critical fluids, certain thermodynamic properties are very difficult to interpret theoretically. In particular, the infinite-dilution partial molar volumes of solutes in near-critical solvents still resist a successful theoretical interpretation even within the frame of the decorated lattice-gas models,<sup>28,29</sup> at least for the solute-solvent systems of interest in SFC.

### Theory

In the first part of this section, general equations for the pressure and temperature derivatives of solute retention will be presented. In the second part, specific forms of the general equations will be derived for the case in which a cross-linked rubbery polymer serves as a principal component of the stationary phase. For simplicity, the treatment will be given for neat (i.e., single-component) mobile phases only. The extension to binary or multi-component mobile phases is possible although some care is needed when taking the composition derivatives. An example of the resultant relationships for a binary mobile phase will be shown at a proper place below. In the symbols employed, subscript 1 refers to the solute, subscript 2 to the principal component of the stationary phase, and subscript 3 to the (neat) mobile phase. The term "principal component of the stationary phase" denotes the pure active material of the stationary phase (e.g., a pure siloxane polymer or the alkyl chains chemically bonded to the surface of a silica particle) while the term "stationary phase" refers to an equilibrium mixture of the principal component of the stationary phase with the absorbed mobile phase. The quantities pertaining to the stationary and the mobile phases are identified by subscripts *s* and *m*, respectively.

**General Equations.** The most natural (and the most widely used) way to quantify chromatographic retention is provided by the capacity ratio of the solute

$$k_1 = (t_R - t_0)/t_0 \quad (1)$$

where  $t_R$  is the retention time of the solute and  $t_0$  is the retention time of a nonsorbed marker. The capacity ratio may also be expressed by

$$k_1 = (x_{1s}/x_{1m})(n_s/n_m) \quad (2)$$

where the  $x_i$ 's are the mole fractions of the solute in the respective phases and the  $n$ 's are the total mole numbers in the respective phases. Let us suppose that the retention time  $t_R$  is measured to that point within the chromatographic zone where the ratio of the solute concentrations in both phases is the same as it would

be in a physically and chemically analogous system under static conditions.<sup>30</sup> At that point, the solute fugacities in both phases are equal, i.e.

$$\varphi_{1s}x_{1s}P = \varphi_{1m}x_{1m}P \quad (3)$$

where the  $\varphi_i$ 's are the fugacity coefficients of the solute in the two phases and  $P$  is the pressure. Substituting for the ratio  $x_{1s}/x_{1m}$  from eq 3 into the logarithmic form of eq 2, one obtains

$$\ln k_1 = \ln \varphi_{1m}^\infty - \ln \varphi_{1s}^\infty + \ln n_s - \ln n_m \quad (4)$$

where the superscript  $\infty$  indicates an infinite dilution of the solute in the respective phase, i.e., the absence of the solute-solute interactions.

In general, each of the four terms on the right-hand side (rhs) of eq 4 is a function of temperature, pressure, and composition of the respective phase. Thus, the total differential of  $\ln \varphi_{1s}^\infty$  is given by

$$d \ln \varphi_{1s}^\infty = (\partial \ln \varphi_{1s}^\infty / \partial T)_{P,x} dT + (\partial \ln \varphi_{1s}^\infty / \partial P)_{T,x} dP + (\partial \ln \varphi_{1s}^\infty / \partial x_{3s})_{T,P,n_{1s},n_{2s}} dx_{3s} \quad (5)$$

where  $T$  is the thermodynamic temperature and  $n_{1s}$  and  $n_{2s}$  are the mole numbers of the solute and component 2 in the stationary phase, respectively. The subscripts in the derivatives indicate the quantities that are to be kept constant upon differentiation, the symbol  $x$  denoting constant composition (in eq 5, of the stationary phase).

The assumption  $n_{2s} = \text{constant}$  states that the principal component of the stationary phase is insoluble in the mobile-phase fluid, a necessary precaution in a SFC experiment. The value of  $n_{1s}$  is supposed to be constant and very small ( $n_{1s} \rightarrow 0$ ). The temperature and pressure derivatives in eq 5 are related to measurable quantities by<sup>31</sup>

$$(\partial \ln \varphi_{1s}^\infty / \partial T)_{P,x} = (h_1^* - \bar{h}_{1s}^\infty) / (RT^2) \quad (6)$$

and

$$(\partial \ln \varphi_{1s}^\infty / \partial P)_{T,x} = \bar{v}_{1s}^\infty / (RT) - 1/P \quad (7)$$

where  $h_1^*$  is the molar enthalpy of the solute in a perfect-gas state at the temperature  $T$ ,  $\bar{h}_{1s}^\infty$  is the infinite-dilution partial molar enthalpy of the solute in the stationary phase at the temperature  $T$  and pressure  $P$ , and  $\bar{v}_{1s}^\infty$  is the infinite-dilution partial molar volume of the solute in the stationary phase at the same conditions. The composition derivative of  $\ln \varphi_{1s}^\infty$  will be discussed at the end of this section.

Since the principal component of the stationary phase is supposed to be insoluble in the mobile phase, the composition of the mobile phase is constant ( $x_{1m} \rightarrow 0$ ,  $x_{3m} \rightarrow 1$ ,  $dx_{2m} = 0$ ,  $dx_{3m} = 0$ ) so that

$$d \ln \varphi_{1m}^\infty = (\partial \ln \varphi_{1m}^\infty / \partial T)_{P,x} dT + (\partial \ln \varphi_{1m}^\infty / \partial P)_{T,x} dP \quad (8)$$

The partial derivatives in eq 8 are given by expressions analogous to eqs 6 and 7.

The total differential of the total mole number in the stationary phase may formally be written as

$$d \ln n_s = (\partial \ln n_s / \partial T)_{P,x} dT + (\partial \ln n_s / \partial P)_{T,x} dP + (\partial \ln n_s / \partial x_{3s})_{T,P,n_{1s},n_{2s}} dx_{3s} \quad (9)$$

The assumption  $n_{2s} = \text{constant}$  means that the partial derivatives at constant composition in eq 9 are zero. The third term on the rhs of eq 9 may be evaluated as follows. Obviously,  $dn_s = dn_{3s}$ , where  $n_{3s}$  is the number of moles of component 3 present in the stationary phase at equilibrium. Further, as  $n_{3s} = n_s x_{3s}$ , one may write

$$dn_s = x_{3s} dn_s + n_s dx_{3s} \quad (10)$$

Dividing eq 10 by  $n_s$ , recognizing that  $dn_s/n_s = d \ln n_s$ , and rearranging, one obtains

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$$(\partial \ln n_s / \partial x_{3s})_{T,P,n_{1s},n_{2s}} = 1/(x_{1s} + x_{2s}) \quad (11)$$

If the component 2 is a high polymer and the stationary phase is appreciably swollen by the absorbed mobile phase, then  $x_{3s} \rightarrow 1$ ,  $x_{2s} \rightarrow 0$ , and  $x_{1s} \rightarrow 0$  so that the ratio  $1/(x_{1s} + x_{2s})$  diverges. It will become clear, however, that the divergence does not introduce any singularity or inconsistency into the treatment below.

The total differential of the total mole number in the mobile phase is given by

$$d \ln n_m = (\partial \ln n_m / \partial T)_{P,x} dT + (\partial \ln n_m / \partial P)_{T,x} dP \quad (12)$$

where the composition term has been dropped for the same reason as in eq 8. Unlike the stationary phase, the mobile phase is "open" so that the derivatives in eq 12 are nonzero even at constant composition (cf. eq 9). The isothermal pressure derivative of  $\ln n_m$  may be obtained as follows. Let us denote the total volumes of the mobile and the stationary phases in the column by  $V_m$  and  $V_s$ , respectively, and let us make a reasonable assumption that  $V_m + V_s = \text{constant}$ . At constant temperature and composition,  $\ln n_m$  is a function of  $V_m$  and  $P$

$$d \ln n_m = (\partial \ln n_m / \partial V_m)_{T,P,x} dV_m + (\partial \ln n_m / \partial P)_{T,V_m,x} dP \quad (13)$$

Since  $V_m + V_s = \text{constant}$ ,  $dV_m = -dV_s$  and eq 13 may be recast into the form

$$d \ln n_m = -(1/V_m)(\partial \ln n_m / \partial \ln V_m)_{T,P,x} dV_s + (\partial \ln n_m / \partial \ln v_m)_{T,V_m,x} (\partial \ln v_m / \partial P)_{T,x} dP \quad (14)$$

where  $v_m$  is the molar volume of the mobile-phase fluid. It may easily be verified that  $(\partial \ln n_m / \partial \ln V_m)_{T,P,x} = 1$  and  $(\partial \ln n_m / \partial \ln v_m)_{T,V_m,x} = -1$ . Employing the identity  $dV_s = V_s d \ln V_s$ , one finally obtains

$$(\partial \ln n_m / \partial P)_{T,x} = \beta_{mT} + (V_s/V_m)\beta_{sT} \quad (15)$$

where  $\beta_{mT}$  and  $\beta_{sT}$  are the isothermal compressibilities of the mobile and the stationary phases, respectively. It should be noted that  $\beta_{mT}$  refers to the pure mobile-phase fluid while  $\beta_{sT}$  refers to the swollen stationary phase. In a similar way, one finds that

$$(\partial \ln n_m / \partial T)_{P,x} = -\alpha_{mP} - (V_s/V_m)\alpha_{sP} \quad (16)$$

where  $\alpha_{mP}$  and  $\alpha_{sP}$  are the isobaric expansivities of the mobile and the stationary phases, respectively.

Now, it is possible to differentiate eq 4 and to substitute for the total differentials on the rhs from eqs 5-9, 11-13, 15, and 16. From the resultant relationship, equations for the pressure and temperature derivatives of  $\ln k_1$  are readily obtained. The isothermal pressure derivative may be written as a sum of three terms

$$(\partial \ln k_1 / \partial P)_T = p_v + p_\beta + p_s \quad (17)$$

where  $p_v$  is the volume term

$$p_v = (\bar{v}_{1m}^\infty - \bar{v}_{1s}^\infty)/(RT) \quad (18)$$

$p_\beta$  is the compressibility term

$$p_\beta = -\beta_{mT} - (V_s/V_m)\beta_{sT} \quad (19)$$

and  $p_s$  is the pressure-swelling term

$$p_s = [(\partial \ln n_s / \partial x_{3s})_{T,P,n_{1s},n_{2s}} - (\partial \ln \varphi_{1s}^\infty / \partial x_{3s})_{T,P,n_{1s},n_{2s}}](\partial x_{3s} / \partial P)_T \quad (20)$$

$$= [1/(x_{1s} + x_{2s}) - (\partial \ln \varphi_{1s}^\infty / \partial x_{3s})_{T,P,n_{1s},n_{2s}}](\partial x_{3s} / \partial P)_T$$

where the derivative  $(\partial x_{3s} / \partial P)_T$  may be obtained from independent (nonchromatographic) experimental data.

Similarly, the isobaric temperature derivative of  $\ln k_1$  is given by

$$(\partial \ln k_1 / \partial T)_P = t_h + t_\alpha + t_s \quad (21)$$

where  $t_h$  is the enthalpy term

$$t_h = (\bar{h}_{1s}^\infty - \bar{h}_{1m}^\infty)/(RT^2) \quad (22)$$

$t_\alpha$  is the expansivity term

$$t_\alpha = \alpha_{mP} + (V_s/V_m)\alpha_{sP} \quad (23)$$

and  $t_s$  is the temperature-swelling term

$$t_s = [1/(x_{1s} + x_{2s}) - (\partial \ln \varphi_{1s}^\infty / \partial x_{3s})_{T,P,n_{1s},n_{2s}}](\partial x_{3s} / \partial T)_P \quad (24)$$

If a binary mixture is employed as the mobile-phase fluid, eqs 17 and 21 contain two separate swelling terms. Denoting the second component (modifier) of the mobile phase by subscript 4, the isothermal pressure derivative of  $\ln k_1$  is given by

$$(\partial \ln k_1 / \partial P)_T = (\bar{v}_{1m}^\infty - \bar{v}_{1s}^\infty)/(RT) - \beta_{mT} - (V_s/V_m)\beta_{sT} + [1/(x_{1s} + x_{2s}) - (\partial \ln \varphi_{1s}^\infty / \partial x_{3s})_{T,P,n_{1s},n_{2s},x_{4s}}](\partial x_{3s} / \partial P)_T + [1/(x_{1s} + x_{2s}) - (\partial \ln \varphi_{1s}^\infty / \partial x_{4s})_{T,P,n_{1s},n_{2s},x_{3s}}](\partial x_{4s} / \partial P)_T \quad (25)$$

where the term  $1/(x_{1s} + x_{2s})$  comes from the relation

$$(\partial \ln n_s / \partial x_{3s})_{T,P,n_{1s},n_{2s},x_{4s}} = (\partial \ln n_s / \partial x_{4s})_{T,P,n_{1s},n_{2s},x_{3s}} = 1/(x_{1s} + x_{2s}) \quad (26)$$

The corresponding equation for the temperature derivative of  $\ln k_1$  may easily be obtained from eq 21. The following discussion will again be restricted to neat mobile phases only.

The conditions of validity of eqs 17 and 21 are (1) the component 2 is not extracted by the mobile phase, (2) the solute-solute interactions are absent from both phases (infinite dilution of the solute), and (3)  $V_s + V_m = \text{constant}$ . If these conditions are fulfilled, eqs 17 and 21 apply to any kind of column chromatography. For any particular kind of chromatography, specific forms of eqs 20 and 24 may be derived by seeking a proper way to express the quotient  $\partial \ln \varphi_{1s}^\infty / \partial x_{3s}$  as a function of measurable quantities. Since there is no such way within the formalism of classical thermodynamics, an equation of state or a mixture model is required. In the following section, specific forms of eqs 20 and 24 will be obtained for the case in which a rubbery polymer is employed as the principal component of the stationary phase.

**Approximations for Polymeric Stationary Phases.** Before starting with the proper treatment, two arrangements should be made to simplify notation within this section. First, as all composition derivatives mentioned within this section are to be taken at constant  $T$ ,  $P$ ,  $n_{1s}$ , and  $n_{2s}$ , the respective subscripts in the composition derivatives will be dropped. Second, as all the symbols within this section refer to the stationary phase only, the subscript  $s$  will also be dropped.

Rubbery (amorphous) polymers possess certain liquidlike characteristics so that the thermodynamic properties of solutions of the rubbery polymers are usually treated<sup>32</sup> in terms of excess functions and activity coefficients. It is expedient, therefore, to convert the derivative  $\partial \ln \varphi_1^\infty / \partial x_3$  in eqs 20 and 24 to the quotient  $\partial \ln \gamma_1^\infty / \partial x_3$  where  $\gamma_1$  is a mole-fraction-based activity coefficient of the solute. As we are interested here in the derivative  $\partial \ln \gamma_1^\infty / \partial x_3$  only, the choice of the standard state is not critical. It is convenient to choose the (hypothetical) pure liquid solute at  $T$  and  $P$  as the standard state so that the normalization of the activity coefficient is  $\gamma_1 \rightarrow 1$  as  $x_1 \rightarrow 1$ . Employing fundamental thermodynamic concepts<sup>31</sup> and keeping in mind the conditions of differentiation (see above), one may write

$$\begin{aligned} \partial \ln \varphi_1^\infty / \partial x_3 &= \partial \ln f_1^\infty / \partial x_3 - \partial \ln x_1 / \partial x_3 \\ &= (\partial \mu_1^\infty / \partial x_3)/(RT) - \partial \ln x_1 / \partial x_3 \\ &= \partial \ln \gamma_1^\infty / \partial x_3 + \partial \ln x_1 / \partial x_3 - \partial \ln x_1 / \partial x_3 \\ &= \partial \ln \gamma_1^\infty / \partial x_3 \end{aligned} \quad (27)$$

where  $f_1^\infty$  and  $\mu_1^\infty$  are the fugacity and the chemical potential of the solute in the stationary phase. It should be noted that, although the solute is infinitely diluted by the stationary phase, the solute mole fraction  $x_1$  does not approach zero when component 2 is a high polymer and  $x_3 \rightarrow 0$ . Such a situation occurs in gas chro-

matography (GC), and it leads to conceptual difficulties<sup>33,34</sup> in coupling the values of  $\ln \gamma_1^\infty$  with GC retention data.

If the principal component of the stationary phase is a high polymer, the use of mole fractions to represent the pressure- or temperature-induced composition changes becomes inconvenient. Therefore, eqs 20 and 24 may be rewritten as

$$p_s = S(\partial w_3 / \partial P)_T \quad (28)$$

and

$$t_s = S(\partial w_3 / \partial T)_P \quad (29)$$

where  $w_3$  is the mass fraction of component 3 in the stationary phase at equilibrium and  $S$  is given by

$$S = [1/(x_1 + x_2) - \partial \ln \gamma_1^\infty / \partial x_3](\partial x_3 / \partial w_3) \quad (30)$$

To obtain a usable expression for  $S$ , let us consider the simpler derivative  $\partial x_3 / \partial w_3$  first. The mass fraction ( $w_i$ ) and the mole fraction ( $x_i$ ) of component  $i$  in a mixture are related by

$$x_i = w_i \bar{M}_n / M_i \quad (31)$$

where  $M_i$  is the molar mass of component  $i$  and  $\bar{M}_n$  is the number-average molar mass of the mixture

$$\bar{M}_n = \sum x_i M_i = 1 / \sum (w_i / M_i) \quad (32)$$

where the summations are over all components of the mixture. In the present case of a three-component mixture, keeping in mind the conditions of differentiation (see above), one may write

$$\partial x_3 / \partial w_3 = \bar{M}_n / M_3 + (w_3 / M_3)(\partial \bar{M}_n / \partial n_3) / (\partial w_3 / \partial n_3) \quad (33)$$

Substituting from eq 32 to eq 33, differentiating, and rearranging, one finally obtains

$$\partial x_3 / \partial w_3 = (\bar{M}_n / M_3)(x_1 + x_2) / (w_1 + w_2) \quad (34)$$

To express the composition dependence of  $\ln \gamma_1^\infty$ , the classical semiempirical combination<sup>35</sup> of the Scatchard-Hildebrand regular solution theory with the Flory-Huggins theory of athermal solutions will be employed. This treatment is applicable to mixtures of nonpolar flexible-chain molecules. Within the scope of the Scatchard-Hildebrand-Flory-Huggins treatment, the activity coefficient  $\gamma_1$  of the solute in a ternary mixture may be written as<sup>36-39</sup>

$$\ln \gamma_1 = \ln (v_1 / v_M) + 1 - v_1 / v_M + \chi_{12} \Phi_2 (\Phi_2 + \Phi_3) + \chi_{13} \Phi_3 (\Phi_2 + \Phi_3) - (v_1 / v_3) \chi_{32} \Phi_2 \Phi_3 \quad (35)$$

where  $v_M$  is the molar volume of the ternary mixture ( $1 + 2 + 3$ ),  $v_i$  is the molar volume of component  $i$  in the mixture,  $\Phi_i$  is the volume fraction of component  $i$ , and  $\chi_{ij}$  is the Flory-type interaction parameter.<sup>37</sup> The superscript  $\infty$  at  $\gamma_1$  has been omitted because eq 35 is not restricted to infinite dilution of the solute. Assuming that the excess volume of the mixture is zero, the volume fraction of component  $i$  is given by

$$\Phi_i = x_i v_i / (x_1 v_1 + x_2 v_2 + x_3 v_3) = x_i v_i / v_M \quad (36)$$

To conform to the assumption of zero excess volume,  $v_i$  should be treated as a partial molar volume, i.e., as a composition-dependent quantity. In such a case, however, the differentiation would be cumbersome, and, what is more important, there are

virtually no data in the literature to evaluate the composition dependence of  $v_i$  for systems of interest in capillary SFC. Therefore, the  $v_i$ 's will be treated as composition-independent parameters. For the same reasons, the interaction parameters will also be treated as composition-independent quantities. Under these assumptions, and keeping in mind the conditions of differentiation, the quotient  $\partial \ln \gamma_1 / \partial x_3$  is readily obtained from the relationships

$$\partial \Phi_2 / \partial x_3 = -v_2 v_3 x_2 / [v_M^2 (x_1 + x_2)] \quad (37)$$

$$\partial \Phi_3 / \partial x_3 = v_3 (v_1 x_1 + v_2 x_2) / [v_M^2 (x_1 + x_2)] \quad (38)$$

$$\partial v_M / \partial x_3 = v_3 - (v_1 x_1 + v_2 x_2) / (x_1 + x_2) \quad (39)$$

Substituting from eqs 37-39 into the differential form of eq 35 and rearranging, one obtains

$$\partial \ln \gamma_1 / \partial x_3 = [v_1 v_3 / v_M^2 - v_1 / v_M - v_3 / v_M + 1 + (v_3 / v_M) \times \{\chi_{12}(\Phi_2 - 2\Phi_2^2 - 2\Phi_2\Phi_3) + \chi_{13}(\Phi_2 + 2\Phi_3 - 2\Phi_3^2 - 2\Phi_2\Phi_3) + \chi_{32}(v_1 / v_3)(2\Phi_2\Phi_3 - \Phi_2)\}] / (x_1 + x_2) \quad (40)$$

Substitution from eqs 34 and 40 into eq 30 now yields

$$S = \{\bar{M}_n v_3 / [M_3 v_M (1 - w_3)]\} [1 + (v_1 / v_3) \times (1 - v_3 / v_M) + \chi_{12}(2\Phi_2^2 + 2\Phi_2\Phi_3 - \Phi_2) + \chi_{13}(2\Phi_3^2 + 2\Phi_2\Phi_3 - 2\Phi_3 - \Phi_2) + \chi_{32}(v_1 / v_3)(\Phi_2 - 2\Phi_2\Phi_3)] \quad (41)$$

Under typical conditions in capillary SFC, the solute is at infinite dilution ( $w_1 \rightarrow 0$ ,  $\Phi_1 \rightarrow 0$ ), and the principal component of the stationary phase is a high polymer ( $M_2 \rightarrow \infty$ ,  $v_2 \rightarrow \infty$ ). Therefore,  $\Phi_2 = 1 - \Phi_3$

$$\lim_{M_2 \rightarrow \infty} \bar{M}_n v_3 / (M_3 v_M) = \Phi_3 / w_3 \quad (42)$$

and

$$\lim_{M_2 \rightarrow \infty} v_3 / v_M = \Phi_3 \quad (43)$$

Accordingly, eq 41 may be simplified to give

$$S = \{\Phi_3 / [w_3 (1 - w_3)]\} [1 + (v_1 / v_3 + \chi_{12} - \chi_{13}) \times (1 - \Phi_3) + \chi_{32}(v_1 / v_3)(1 - 3\Phi_3 + 2\Phi_3^2)] \quad (44)$$

Now, assuming that all noncombinatorial contributions to the excess Gibbs energy are accounted for by the regular solution theory,<sup>35</sup> the interaction parameters may be expressed in terms of the solubility parameters,  $\delta_i$  and  $\delta_j$ , of the respective components

$$\chi_{ij} = v_i (\delta_i - \delta_j)^2 / (RT) \quad (45)$$

Substitution from eq 45 to eq 44 yields

$$S = \{\Phi_3 / [w_3 (1 - w_3)]\} [1 + [v_1 / (RT)] \{[RT / v_3 + (\delta_1 - \delta_2)^2 - (\delta_1 - \delta_3)^2](1 - \Phi_3) + (\delta_2 - \delta_3)^2(1 - 3\Phi_3 + 2\Phi_3^2)\}] \quad (46)$$

Together with the experimental values of  $(\partial w_3 / \partial P)_T$  or  $(\partial w_3 / \partial T)_P$ , the calculated value of  $S$  may be used in eq 28 or 29 to estimate the contribution of swelling to  $(\partial \ln k_1 / \partial P)_T$  or  $(\partial \ln k_1 / \partial T)_P$ .

### Application of Final Equations

In this section, the relative significance of the three contributions to the pressure derivative of retention (eqs 17-20) in a typical capillary SFC system will be estimated. The system to be considered is naphthalene (1)-poly(dimethylsiloxane) (PDMS) (2)-carbon dioxide (3) at 35 °C (308.15 K) and 74.6 bar. This particular choice is dictated by availability of the experimental data to be used in eqs 18, 28, and 46. The data sources are briefly reviewed below.

The infinite-dilution partial molar volume of naphthalene in CO<sub>2</sub> at 35 °C and 74.6 bar is  $-2110 \text{ cm}^3 \text{ mol}^{-1}$ .<sup>40</sup> This value actually refers to 35.23 °C, but the resultant error is probably less than the estimated uncertainty<sup>40</sup> of  $\pm 950 \text{ cm}^3 \text{ mol}^{-1}$ . For  $\bar{v}_{1s}^\infty$ , the value of  $123 \text{ cm}^3 \text{ mol}^{-1}$  will be employed. This number is the subcooled-liquid molar volume of naphthalene extrapolated<sup>41</sup> to 25 °C from the saturated-liquid molar volumes at temperatures

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(41) Reference 35, Appendix 5, p 214.

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(36) Reference 32, p 183, eq (7.22).

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above the melting point. For comparison, the molar volume of solid naphthalene at 25 °C is 112 cm<sup>3</sup> mol<sup>-1</sup>,<sup>42</sup> and the molar volume of liquid naphthalene at the melting point (80.2 °C) is 130.86 cm<sup>3</sup> mol<sup>-1</sup>.<sup>43</sup> At temperatures and pressures close to the critical point of the mobile phase, the volume term  $p_v$  (eqs 17 and 18) is dominated by a large negative value of  $\bar{v}_{1m}^\infty$  so that a small error in  $\bar{v}_{1s}^\infty$  is not significant. The solubility parameter of naphthalene is 20.3 (J cm<sup>-3</sup>)<sup>1/2</sup>. This value<sup>41</sup> refers to subcooled liquid naphthalene at 25 °C, and it has been obtained by applying a thermochemical cycle.<sup>44</sup> Again, the use of a value pertaining to 25 °C does not result in a significant error because the solubility parameter of naphthalene at the melting point (80.2 °C) is 19.4 (J cm<sup>-3</sup>)<sup>1/2</sup>.<sup>43</sup>

At 35 °C and 74.6 bar, the density of high-molar-mass PDMS is 0.9703 g cm<sup>-3</sup>. This value has been calculated from the specific volumes and isothermal compressibilities reported by Shih and Flory<sup>45</sup> and by Lichtenthaler et al.<sup>46</sup> At 35 °C, the solubility parameter of PDMS is 14.8 (J cm<sup>-3</sup>)<sup>1/2</sup>.<sup>47</sup> This value has been derived from GC specific retention volumes of hydrocarbon solutes.<sup>48</sup> It should be noted here that the data for PDMS refer to a linear polymer rather than to a cross-linked material.

Within the scope of eq 35, the mobile-phase fluid dissolved in the stationary phase is considered to be a liquidlike additive to the principal component of the stationary phase. Therefore, the values of  $v_3$  and  $\delta_3$  to be used in eq 46 are different from those pertaining to pure supercritical CO<sub>2</sub> at 35 °C and 74.6 bar. The sorption of CO<sub>2</sub> by a cross-linked PDMS rubber has been studied by Fleming and Koros<sup>24</sup> at 35 °C and pressures up to 62 bar. Extrapolating the experimental values<sup>24</sup> of the partial molar volume of CO<sub>2</sub> to 74.6 bar, one obtains  $v_3 = 61$  cm<sup>3</sup> mol<sup>-1</sup>. This value is used in the calculation below. For comparison, the average partial molar volume of CO<sub>2</sub> at 25 °C derived<sup>49,50</sup> from solubilities of CO<sub>2</sub> in a variety of organic liquids is 55 cm<sup>3</sup> mol<sup>-1</sup>. From the same source,<sup>49,50</sup> a value of  $\delta_3 = 12.3$  (J cm<sup>-3</sup>)<sup>1/2</sup> has been adopted. The equilibrium mass fractions of CO<sub>2</sub> in a swollen sample of PDMS may be calculated from the dilation data.<sup>24</sup> At pressures below 24 bar, the mass fractions obtained agree very well with those from an independent source.<sup>51</sup> Extrapolation of the results to 74.6 bar yields  $w_{3s} = 0.25$  and  $(\partial w_{3s}/\partial P)_T = 0.0045$  bar<sup>-1</sup>. From  $w_{3s}$  and the density of PDMS, one obtains  $\Phi_{3s} = 0.31$ . At 35 °C and 74.6 bar, the isothermal compressibility of CO<sub>2</sub> may be calculated by using the Lee-Kesler correlation<sup>14</sup> which yields  $\beta_{mT} = 0.054$  bar<sup>-1</sup>. Since  $\beta_{sT} < \beta_{mT}$  and  $V_s/V_m \ll 1$ , the term  $(V_s/V_m)\beta_{sT}$  may be neglected compared to  $\beta_{mT}$ .

Employing the above data, the resultant values of the volume term (eq 18), the compressibility term (eq 19), and the pressure-swelling term (eqs 20, 28, and 46) are -0.087, -0.054, and +0.010 bar<sup>-1</sup>, respectively. Therefore, the relative contributions of the three terms to the total value of  $(\partial \ln k_1/\partial P)_T = -0.131$  bar<sup>-1</sup> are 67%, 41%, and -8%, respectively. In the particular case shown in this example, the effect on  $(\partial \ln k_1/\partial P)_T$  of the pressure-swelling term counters the contributions of the volume and compressibility terms.

## Discussion

Equation 20 clearly shows that the pressure-swelling contribution to  $(\partial \ln k_1/\partial P)_T$  results from two distinct effects. The term  $\partial \ln n_s/\partial x_{3s}$  measures the effect of the changing amount of substance in the stationary phase, i.e., the "mole-number" effect. On the other hand, the term  $\partial \ln \varphi_{1s}^\infty/\partial x_{3s}$  (or  $\partial \ln \gamma_{1s}^\infty/\partial x_{3s}$ ) reflects

the effect of the changing composition of the stationary phase, i.e., the "molecular-environment" effect. Let us consider the mole-number effect first. The derivative  $\partial \ln n_s/\partial x_{3s}$  is always positive (cf. eq 11). As the quotient  $(\partial x_{3s}/\partial P)_T$  (or  $(\partial w_{3s}/\partial P)_T$ ) is also positive, one may conclude that as the pressure increases, the mole-number effect tends to increase retention, i.e., to make  $(\partial \ln k_1/\partial P)_T$  less negative. While the mole-number effect is easy to visualize, the molecular-environment effect is less so. This is because the latter results from several contributions, and each of the contributions reflects the composition changes in a specific way so that no universal trend in  $\partial \ln \varphi_{1s}^\infty/\partial x_{3s}$  (or  $\partial \ln \gamma_{1s}^\infty/\partial x_{3s}$ ) may be identified as the pressure increases. To illustrate this statement, let us confine the discussion to the case when component 2 is a high polymer, and suppose that the energetic and free-volume contributions to  $\ln \gamma_{1s}^\infty$  are absent. In such a hypothetical case, the derivative  $\partial \ln \gamma_{1s}^\infty/\partial x_{3s}$  would be determined solely by the combinatorial entropy. An increase in  $x_{3s}$  causes a decrease in the molar volume  $v_M$ . Further, the relation  $\bar{v}_{1s}^\infty > \bar{v}_{3s}$  usually applies in SFC. (The partial molar volumes  $\bar{v}_{1s}^\infty$  and  $\bar{v}_{3s}$  may be identified with the quantities  $v_1$  and  $v_3$  of the Theory section, respectively.) Therefore, at low pressures when  $w_{3s} \rightarrow 0$  and the inequality  $\bar{v}_{1s} < v_M$  still applies, an increase in  $x_{3s}$  makes the infinite-dilution partial molar excess entropy of the solute lower so that  $\partial \ln \gamma_{1s}^\infty/\partial x_{3s} > 0$ . At high pressures when  $w_{3s} > 0$ , the relation  $\bar{v}_{1s}^\infty > v_M$  may apply if  $\bar{v}_{1s}^\infty$  is sufficiently large, and, in such a case,  $\partial \ln \gamma_{1s}^\infty/\partial x_{3s} < 0$ . However, the example given in the preceding section suggests that, under typical conditions in a real (1 + 2 + 3) mixture, the term  $\partial \ln \gamma_{1s}^\infty/\partial x_{3s}$  is not large enough to offset the contribution of  $\partial \ln n_s/\partial x_{3s}$  so that the resultant value of  $p_s$  is positive.

It should also be stressed that the above relationships give the value of  $(\partial \ln k_1/\partial P)_T$  at some particular pressure  $P$ . In their present form, the relationships apply to a hypothetical isobaric chromatographic column or, alternatively, to a local value of  $(\partial \ln k_1/\partial P)_T$  at some particular position within a real chromatographic column. Therefore, a comparison of the experimental and calculated results necessitates the use of suitable averaging procedures.<sup>52,53</sup> In general, these procedures should be employed with both packed and capillary columns since even a capillary column may display a significant pressure drop.<sup>54,55</sup>

In the preceding section, certain physical properties of a straight-chain PDMS have been used to model a cross-linked PDMS. Some indirect experimental justification for this procedure comes from the fact that neither sorption properties<sup>56,57</sup> nor transport properties<sup>58</sup> of siloxane polymers toward *n*-alkane solutes are significantly affected by a radical in situ cross-linking of the polymer.

The quotient  $\partial \ln \gamma_{1s}^\infty/\partial x_{3s}$  has been derived from eq 35 under several simplifying assumptions, e.g., composition-independent partial molar volumes, zero excess volume, and a solubility parameter approach to approximate interaction parameters. The quality of the results is highly dependent upon the validity of these approximations to any particular chromatographic system. Further, eq 35 contains the classical Flory-Huggins formula for the combinatorial contribution to  $\ln \gamma_{1s}$ . The Flory-Huggins expression applies to mixtures of linear molecules so that, as noted previously,<sup>59</sup> it should be modified to account for the effect of cross-linking. Also, the differences in molecular bulkiness of the mixture components should be taken into account. This may be done by adopting a generalized expression for the combinatorial

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(59) See ref 45 in ref 20.

entropy<sup>60,61</sup> in which the ratio of molecular surface areas is employed in addition to the ratio of molecular volumes. The results obtained with the modified expressions<sup>60-62</sup> suggest that the classical Flory-Huggins formula tends to overestimate the combinatorial entropy, and, consequently, to make the combinatorial contribution to  $\ln \gamma_{1s}$  more significant. The interaction parameters in eq 35 may be made composition-dependent provided that sufficient experimental data to warrant such a step are available. All these potential improvements would cause a substantial increase in the number of adjustable parameters to be used in eqs 35, 44, and 46.

To conclude this section, the isothermal derivative of  $\ln k_1$  with respect to the mobile-phase density ( $\rho_m$ ) will briefly be examined. Obviously

$$\begin{aligned} (\partial \ln k_1 / \partial \rho_m)_T &= (\partial P / \partial \rho_m)_T (\partial \ln k_1 / \partial P)_T \\ &= [1 / (\rho_m \beta_{mT})] (\partial \ln k_1 / \partial P)_T \end{aligned} \quad (47)$$

Substituting for  $(\partial \ln k_1 / \partial P)_T$  in eq 47 from eqs 17-19, one obtains

$$(\partial \ln k_1 / \partial \rho_m)_T = (\bar{v}_{1m}^\infty - \bar{v}_{1s}^\infty) / (RT \rho_m \beta_{mT}) - 1 / \rho_m - (V_s / V_m) \beta_{sT} / (\rho_m \beta_{mT}) + p_s / (\rho_m \beta_{mT}) \quad (48)$$

Equation 48 provides the basis to discuss the behavior of  $(\partial \ln k_1 / \partial \rho_m)_T$  at high pressures and/or densities. Under certain conditions, the unified molecular theory of chromatography<sup>20</sup> predicts a minimum in  $\ln k_1$  as a function of  $\rho_m$ . Accordingly, at a certain pressure (or density), the derivative  $(\partial \ln k_1 / \partial \rho_m)_T$  is expected to change sign from negative to positive. It follows from eq 48 that the condition  $(\partial \ln k_1 / \partial \rho_m)_T \geq 0$  requires that

$$\bar{v}_{1m}^\infty - \bar{v}_{1s}^\infty \geq RT[\beta_{mT} + (V_s / V_m) \beta_{sT} - p_s] \quad (49)$$

One may speculate that, at high pressures, the swollen stationary phase becomes saturated with the dissolved mobile-phase fluid so that  $(\partial x_{3s} / \partial P)_T \rightarrow 0$  and

$$\beta_{mT} + (V_s / V_m) \beta_{sT} > p_s \quad (50)$$

Obviously, the bracketed term in eq 49 is positive provided eq 50 applies. Therefore, the minimum in  $\ln k_1$  as a function of  $\rho_m$  at a constant temperature occurs only if the difference  $\bar{v}_{1m}^\infty - \bar{v}_{1s}^\infty$  exceeds the positive value given by the rhs of eq 49. It should be noted here that, as the pressure increases, the values of  $\bar{v}_{1m}^\infty$  ultimately become positive even at temperatures very close to the critical temperature of the mobile phase.<sup>40</sup> In the particular case of capillary SFC of polycyclic aromatic hydrocarbons with cross-linked polysiloxane stationary phases, the minima in  $\ln k_1$  have not been observed.<sup>19,63</sup> More details concerning the retention minima in SFC will be presented in a separate communication.

## Conclusion

Equations giving the pressure and temperature derivatives of retention in SFC have been modified to account for the pressure- or temperature-induced changes in composition and amount of the stationary phase ("swelling"). The major contributions to the

pressure and temperature derivatives of the solute retention may be expressed in terms of measurable quantities. To model these contributions, either direct experimental data or the results of reliable correlations may be employed. The contribution of the swelling of the stationary phase cannot be obtained by using classical thermodynamics only, so that a suitable concept from molecular thermodynamics is needed. In the specific case of capillary SFC with polymeric stationary phases, the semiempirical combination of the Scatchard-Hildebrand regular solution theory with the Flory-Huggins theory of athermal mixtures of chain molecules has been employed. In a particular model system close to the critical point of the mobile phase, the swelling's contribution to the pressure change of retention has been found to counter the contributions of the solute partial molar volumes and of the mobile-phase compressibility. The behavior of the density derivative of solute retention at high pressures has also been discussed, and a criterion for the occurrence of a minimum in  $\ln k_1$  as a function of the mobile-phase density has been obtained.

## Glossary

$f$	fugacity
$h$	molar enthalpy
$\bar{h}$	partial molar enthalpy
$k$	capacity ratio
$M$	molar mass
$\bar{M}_n$	number-average molar mass
$n$	mole number
$p_v, p_B, p_s$	terms defined by eqs 18, 19, and 20, respectively
$P$	pressure
$R$	molar gas constant
$S$	term defined by eq 30
$t_h, t_a, t_s$	terms defined by eqs 22, 23, and 24, respectively
$t_0$	retention time of a nonsorbed marker
$t_R$	retention time of the solute
$T$	thermodynamic temperature
$v$	molar volume
$\bar{v}$	partial molar volume
$V$	geometric volume
$w$	mass fraction
$x$	mole fraction

## Greek Letters

$\alpha$	expansivity
$\beta$	compressibility
$\gamma$	activity coefficient
$\delta$	solubility parameter
$\mu$	chemical potential
$\rho$	density
$\varphi$	fugacity coefficient
$\Phi$	volume fraction
$\chi$	Flory-type interaction parameter

## Principal Subscripts

1	solute
2	principal component of the stationary phase
3	mobile-phase fluid
4	second component of the mobile phase (modifier)
m	mobile phase
M	equilibrium mixture of the components 1, 2, and 3
n	constant mole number
P	constant pressure
s	stationary phase
T	constant temperature
x	constant composition

## Superscripts

+	perfect gas
$\infty$	infinite dilution

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