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# Solute retention in gas and supercritical fluid chromatography versus pairwise interactions within the system: a numerical treatment in perturbations of molecular parameters

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## Abstract

A semi-quantitative outline of the effects of molecular parameters on retention properties in a chromatographic system was obtained by combining the classical and molecular thermodynamic approaches to the problem of solute distribution between the stationary and the mobile phase. The treatment deals with isotropic, nonelectrolyte systems containing an elastomer as a principal component of the stationary phase. The procedure consists in applying a mean-field lattice-fluid model to compute the sensitivities of the macroscopic properties to perturbations in the molecular parameters of a reference system in four representative regimes of mobile phase density. The reference system is typical of open-tubular, capillary supercritical fluid chromatography (SFC) and the four density regimes typify the operating conditions of gas chromatography, low-density SFC, near-critical SFC and high (liquid-like) density SFC. Swelling of the stationary polymer with the absorbed mobile phase fluid is included in the procedure. The density-dependent patterns of the molecular parameters relevant to the pertinent retention and thermodynamic properties are presented and discussed.

*Keywords:* Thermodynamic parameters; Solute distribution; Lattice-fluid models; Retention parameters; Molecular parameters

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## 1. Introduction

The effects of operating temperature, pressure and mobile phase composition on chromatographic retention in non-electrolyte systems have been described by employing both general concepts of classical thermodynamics and model-dependent treatments of molecular thermodynamics. In the particular case of supercritical fluid chromatography (SFC), for example, the classical concepts [1–7] resolved the effects of the above operating conditions on retention into

contributions from the partial molar properties of the solute in the mobile and the stationary phase, from the mechanical properties (i.e., compressibilities and thermal expansivities) of both phases and from the terms related to swelling of the stationary phase with the dissolved mobile phase fluid. In parallel, the molecular thermodynamic treatments [8–14] mostly employed various kinds of lattice-fluid models to express solute retention in terms of molecular-level descriptors of the chromatographic system.

In this paper, an attempt is made to combine

the classical and molecular approaches in order to quantify and rank the effects of molecular parameters on retention, on its changes with temperature ( $T$ ), pressure ( $P$ ) and mobile phase density ( $\rho_m$ ) and on their constituent thermodynamic properties. This covers the wide range between gas- and liquid-like densities of the mobile phase and, in this sense, provides a thermodynamic complement to the (mostly instrumental) concept of unified chromatography [15,16]. Particular attention is paid to the effect of stationary phase swelling that has been treated in earlier gas chromatographic (GC) studies [17,18] and gained new importance in SFC [6,7]. Rather than providing a rigorous analysis, this work was intended to result in an easily interpretable visualization of the effects of molecular parameters on the separate macroscopic properties. Naturally, the resultant picture depends on the particular composition of the chromatographic system as well as on  $T$ ,  $P$  and  $\rho_m$ . Therefore, in order to arrive at a “user-friendly” form of the results, a simple perturbation treatment of a well defined reference system is employed and the continuous range of mobile phase densities is replaced by four representative density regimes. It is assumed that both phases of the chromatographic system are isotropic, that the solute is retained in the column solely by bulk partitioning between the two phases and that the principal component of the stationary phase is a high-molecular-mass elastomer. The reference solute–polymer–mobile phase system considered is typical of open-tubular capillary SFC, namely naph-

thalene–poly(dimethylsiloxane)–carbon dioxide.

## 2. Theory

### 2.1. Representation of the effect of mobile phase density

The continuous  $P\rho_m T$  space of carbon dioxide above its critical temperature can be represented by four state points that are characterized in Table 1. The four state points will be referred to as the ultra-low, low, intermediate and high density regimes and, in practice, they typify the operating conditions of gas chromatography (GC), low-density SFC, near-critical SFC and high (liquid-like) density SFC, respectively. The values of density, fugacity coefficient, thermal pressure coefficient [ $= (\partial P/\partial T)_{\rho_m}$ ] and solubility parameter were calculated from a high-precision equation of state (EOS) for carbon dioxide [19].

### 2.2. Description of the method

The perturbation treatment below is based on the equilibrium distribution of a trace amount of solute between the mobile and the stationary phase of the chromatographic system. The solute is therefore assumed to be in a state of infinite dilution in both phases so that the solute–solute interactions are absent. The other assumptions involved have been mentioned above. The molecular model employed should be able to reproduce and/or predict not only the familiar

Table 1  
Characterization of the representative density regimes of CO<sub>2</sub>

Property	Density regime			
	Ultra-low	Low	Intermediate	High
Temperature (°C)	100	100	50	50
Pressure (bar)	2	75	100	200
Density (g cm <sup>-3</sup> ) <sup>a</sup>	0.00285	0.131	0.385	0.785
Fugacity coefficient <sup>a</sup>	0.995	0.835	0.638	0.410
Thermal pressure coefficient (bar K <sup>-1</sup> ) <sup>a</sup>	0.00542	0.319	1.37	4.77
Solubility parameter [(J cm <sup>-3</sup> ) <sup>1/2</sup> ] <sup>a</sup>	0.0481	2.15	6.50	12.3

<sup>a</sup> Calculated from the high-precision EOS for CO<sub>2</sub> published by Ely et al. [19].

chromatographic quantities, i.e., solute partition coefficient,  $K$ , solute capacity factor,  $k'$ , and phase ratio,  $V_s/V_m$ , but also the derivatives of  $\ln k'$  with respect to  $T$ ,  $P$  and  $\rho_m$  and the thermodynamic parameters that make up the derivatives. The isothermal pressure derivative and isobaric temperature derivative of  $\ln k'$  may be written as

$$(\partial \ln k' / \partial P)_T = p_\nu + p_\beta + p_s \quad (1)$$

and

$$(\partial \ln k' / \partial T)_P = t_h + t_\alpha + t_s \quad (2)$$

The quantities  $p_\nu$ ,  $p_\beta$ ,  $p_s$ ,  $t_h$ ,  $t_\alpha$  and  $t_s$  are termed “aggregate components of retention derivatives” and are given by [6,13]

$$p_\nu = -\Delta V_{1t} / (RT) \quad (3)$$

$$p_\beta = -\beta_{mT} - (V_s/V_m)\beta_{sT} \quad (4)$$

$$p_s = -[1/(RT)](\partial \mu_{1s}^\infty / \partial w_{3s})_{T,P}(\partial w_{3s} / \partial P)_{T,\sigma} \quad (5)$$

$$t_h = \Delta H_{1t} / (RT^2) \quad (6)$$

$$t_\alpha = \alpha_{mP} + (V_s/V_m)\alpha_{sP} \quad (7)$$

$$t_s = -[1/(RT)](\partial \mu_{1s}^\infty / \partial w_{3s})_{T,P}(\partial w_{3s} / \partial T)_{P,\sigma} \quad (8)$$

In Eqs. 3–8, subscripts 1, 2 and 3 identify the solute, stationary polymer and mobile phase fluid, respectively.  $R$  is the gas constant,  $\Delta V_{1t}$  and  $\Delta H_{1t}$  are the molar volume and molar enthalpy of solute transfer from the mobile to the stationary phase, respectively,  $\mu_{1s}^\infty$  is the chemical potential of the solute at infinite dilution in the stationary phase,  $w_{3s}$  is the mass fraction of the mobile phase fluid in the stationary phase and the subscript  $\sigma$  indicates saturation of the stationary phase with the dissolved mobile phase fluid. The symbols  $\beta_{mT}$  and  $\beta_{sT}$  refer to isothermal compressibilities of the mobile and the stationary phase, respectively, and  $\alpha_{mP}$  and  $\alpha_{sP}$  are isobaric expansivities of the mobile and the stationary phase, respectively. The quantities  $\beta_{sT}$  and  $\alpha_{sP}$  are those along the line of saturation of the stationary phase with the mobile phase fluid.

Statistical thermodynamic treatment of the chromatographic systems specified above poses stringent demands on the molecular model em-

ployed because the model has to handle diverse media – dilute (low-pressure) gas, supercritical fluid and amorphous polymer – and their interactions with reasonable accuracy and with a single set of parameters. The treatment employed here is a modified version of the mean-field lattice model described by Panayiotou and Vera [20] and later extended to multi-component mixtures and applied to polymer–supercritical fluid systems [21]. The molecules comprising the mixture are assumed to be distributed on a lattice formed by sites of constant volume. A site may be occupied by a molecular segment or it may remain empty. A molecule of component  $i$  is assumed to consist of  $r_i$  segments and the segments of components  $i$  and  $j$  interact with a characteristic energy  $\varepsilon_{ij}$ . Application of the model to an  $n$ -component mixture requires  $n$  size parameters  $r_i$ ,  $n$  energy parameters  $\varepsilon_{ii}$  for interaction between segments of the same kind and  $n(n-1)/2$  unlike-interaction energy parameters  $\varepsilon_{ij}$  ( $j \neq i$ ). The pure-component parameters  $r_i$  and  $\varepsilon_{ii}$  are obtained by fitting the model to experimental  $P\rho T$  data for the respective component  $i$ . The unlike-interaction energy parameters  $\varepsilon_{ij}$  are related to  $\varepsilon_{ii}$  and  $\varepsilon_{jj}$  by a modified geometric-mean rule:

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1 - \delta_{ij}) \quad (9)$$

where the binary parameter  $\delta_{ij}$  has to be obtained from suitable experimental data. The parametrization of the model for the particular reference system has been described before [14]. From the model's EOS and the relationship for a component's chemical potential [20,21], expressions have been obtained [13] for all thermodynamic properties appearing in Eqs. 3–8. A reference value of the phase ratio has been set by assuming that, at a given temperature (cf., Table 1) and very low pressure (i.e., no swelling),  $V_s/V_m = 0.016$ , which corresponds to a 0.2- $\mu\text{m}$  thick polymer film in a 50  $\mu\text{m}$  I.D. capillary column. The model thus provides a tool for translating non-chromatographic experimental information used to obtain the parameters into predictions and/or correlations of quantities of chromatographic interest.

In a selected density regime (cf., Table 1), the effects of a molecular parameter on the retention-related macroscopic properties can be probed by changing slightly the particular parameter while keeping temperature, pressure and the remaining molecular parameters constant. The sensitivity  $S$  of a macroscopic property  $X$  to a molecular parameter  $y$  may be expressed as

$$S = \frac{X_{\text{pert}} - X_{\text{ref}}}{X_{\text{ref}}} \cdot \frac{y_{\text{ref}}}{y_{\text{pert}} - y_{\text{ref}}} \quad (10)$$

where  $X_{\text{ref}}$  is the value of the macroscopic property in the reference system and  $X_{\text{pert}}$  is the perturbed value obtained by replacing the reference value of the molecular parameter,  $y_{\text{ref}}$ , with a perturbed value,  $y_{\text{pert}}$ . A positive value of  $S$  means that an increase in the molecular parameter leads to an increase in magnitude of the macroscopic property. The resultant sensitivity  $S$  varies with the relative perturbation in the molecular parameter,  $(y_{\text{pert}} - y_{\text{ref}})/y_{\text{ref}}$ , unless the property  $X$  is linear in the parameter  $y$ . The variations in  $S$  decrease with decreasing relative perturbation in the molecular parameter provided that the effects of round-off errors are negligible. In the most demanding cases, a relative perturbation as low as  $10^{-6}$  in the molecular parameter has been required to make  $S$  stable to 0.1% or better.

Naturally, questions arise regarding the reliability and validity of the model predictions. Several measures have been taken in order to make the resultant sensitivities credible.

First, the  $P\rho_m T$  region very close to the critical point of the mobile phase fluid has been avoided in selecting the representative density regimes because all analytical EOS, including mean-field lattice models, perform poorly in that region. Nevertheless, the essential features of a supercritical fluid have been retained in the particular choice of the intermediate density regime (cf., the supercritical enhancements in  $\alpha_{mP}$  and  $\beta_{mT}$  in Table 2).

Second, parametrization of the model for the reference system [14] has been derived from pertinent experimental data. In particular, this concerns the  $\delta_{ij}$  values (Eq. 9) because the

Table 2  
Model predictions of relevant thermodynamic properties not used to obtain the parameters

Property	Density regime			
	Ultra-low	Low	Intermediate	High
$w_{3s}^a$	–	0.06	0.24	0.38
$w_{3s}^c$	0.0027	0.11	0.28	0.38
$\alpha_{mP} (\text{K}^{-1})^b$	0.00272	0.00525	0.0427	0.00736
$\alpha_{mP} (\text{K}^{-1})^c$	0.00271	0.00472	0.0379	0.00579
$\beta_{mT} (\text{bar}^{-1})^b$	0.502	0.0164	0.0311	0.00155
$\beta_{mT} (\text{bar}^{-1})^c$	0.502	0.0159	0.0346	0.00142

<sup>a</sup> Experimental values [22].

<sup>b</sup> Calculated from the high-precision EOS for  $\text{CO}_2$  published by Ely et al. [19].

<sup>c</sup> Calculated from the lattice-fluid model.

predictions of mixtures properties by lattice-fluid models are usually sensitive to unlike-interaction energy parameters.

To illustrate the predictive power of the Panayiotou–Vera model, Table 2 shows the calculated values of several quantities that were not used to obtain the model parameters. The predictions are tested either against experimental data or against reliable results obtained from a high-precision EOS for carbon dioxide [19]. The fair agreement in most values shown in Table 2 indicates that a semi-quantitative significance can be assigned to the model predictions of the effects of molecular parameters. In other words, if Eq. 10 suggests a strong sensitivity of a macroscopic property to a model parameter, a reasonable probability exists that the result is not an artifact of the model but that the property is indeed sensitive to the true molecular-level feature reflected in the particular parameter (cf., Section 2.4).

### 2.3. Characteristics of the reference system

Figs. 1–4 present the most important properties of the reference system as calculated from the lattice model. In Fig. 1, retention quantities  $K$  and  $k'$  display the expected decrease with increasing density and solvating power of the mobile phase fluid. However, the relative drops

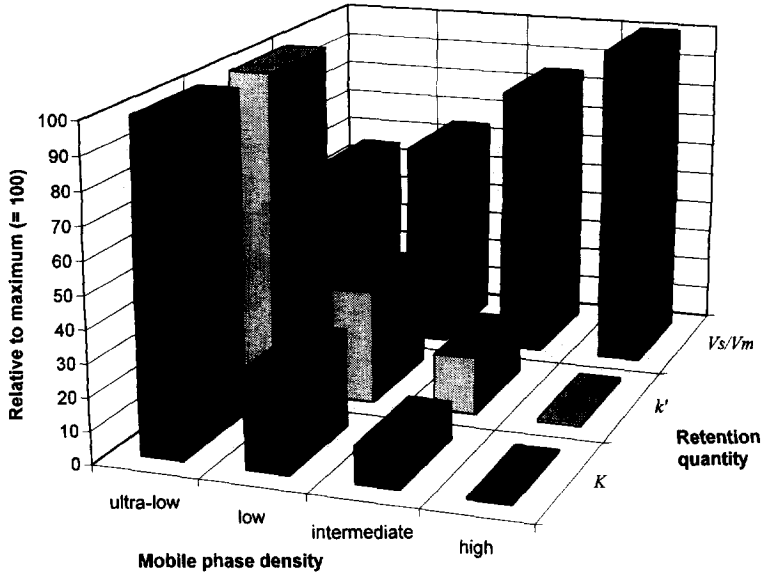


Fig. 1. Relative values of the retention quantities and phase ratio in the reference system. Maximum values (=100%) are  $K = 209$ ,  $k' = 3.36$  and  $V_s/V_m = 0.0293$ .

in both quantities differ because the phase ratio increases from the ultra-low to high density regimes ( $k' = KV_s/V_m$ ). Fig. 2 shows the varia-

tions in the derivatives of  $\ln k'$  with respect to  $T$ ,  $P$  and  $\rho_m$ ; the derivatives  $(\partial \ln k' / \partial \ln \rho_m)_T$  and  $[\partial \ln k' / \partial (1/T)]_{\rho_m}$  are related to those given by

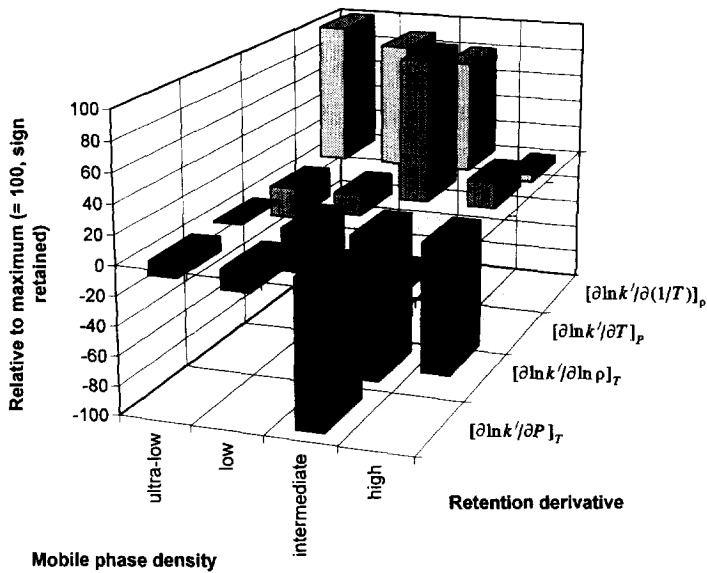


Fig. 2. Relative values of the derivatives of  $\ln k'$  with respect to  $T$ ,  $P$  and  $\rho_m$  in the reference system. Maximum values ( $= \pm 100\%$ ) are  $(\partial \ln k' / \partial P)_T = -0.128 \text{ bar}^{-1}$ ,  $(\partial \ln k' / \partial \ln \rho_m)_T = -3.71$ ,  $[\partial \ln k' / \partial (1/T)]_{\rho_m} = 3430 \text{ K}$  and  $(\partial \ln k' / \partial T)_P = 0.114 \text{ K}^{-1}$ .

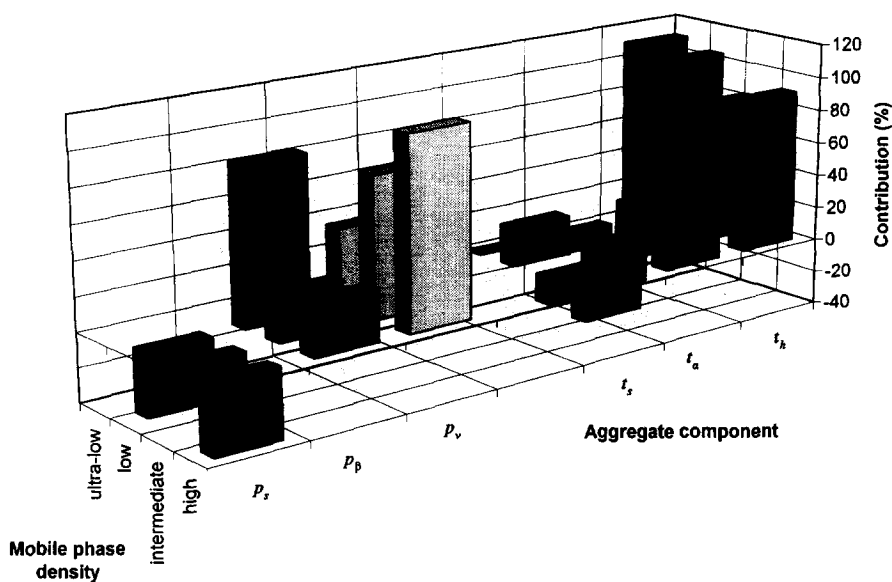


Fig. 3. Relative contributions of the aggregate components to the pressure and temperature derivatives of  $\ln k'$  in the reference system (see text for the reasons for the absence of the  $p_s$ ,  $p_\beta$  and  $p_\nu$  values at ultra-low density).

Eqs. 1 and 2 by simple general relationships [23–25]. The conspicuous maxima in  $(\partial \ln k' / \partial P)_T$  and  $(\partial \ln k' / \partial T)_P$  at the intermediate density as compared with the other densities indicate that the two derivatives diverge at the critical point of the mobile phase fluid. Relative contributions of the aggregate components to  $(\partial \ln k' / \partial P)_T$  and  $(\partial \ln k' / \partial T)_P$  are displayed in Fig. 3. The most important feature of Fig. 3 is that the

contributions from swelling-related aggregates  $p_s$  and  $t_s$  are never negligible, with the possible exception of  $t_s$  in the GC limit (ultra-low density). The chart does not show the large contributions of  $p_\beta$  and  $p_\nu$  to  $(\partial \ln k' / \partial P)_T$  in the ultra-low density regime (4150% and –3995%, respectively); however, as the two large values nearly compensate for each other, the contribution of  $p_s$  (–55%) is still important even in the GC limit.

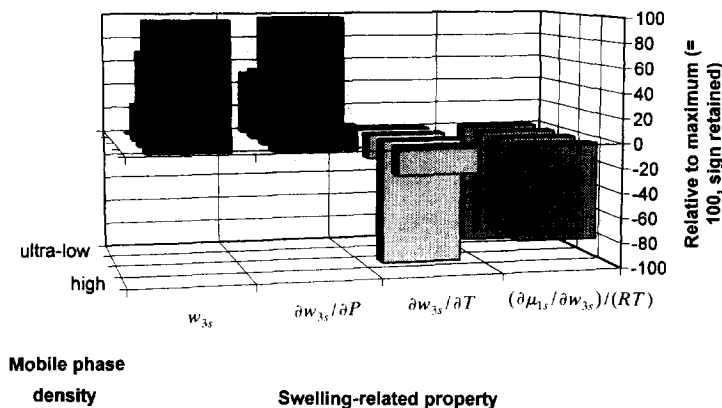


Fig. 4. Relative values of the swelling-related properties in the reference system. Maximum values ( $= \pm 100\%$ ) are  $w_{3s} = 0.385$ ,  $(\partial w_{3s} / \partial P)_{T,\sigma} = 0.00276 \text{ bar}^{-1}$ ,  $(\partial w_{3s} / \partial T)_{P,\sigma} = -0.00482 \text{ K}^{-1}$  and  $(\partial \mu_{1s}^* / \partial w_{3s})_{T,P} / (RT) = -4.88$ .

Among the swelling-related properties in Fig. 4,  $w_{3s}$  and  $(\partial\mu_{1s}^\infty/\partial w_{3s})_{T,P}/(RT)$  display smooth variations from the GC to high-density SFC limits while  $(\partial w_{3s}/\partial P)_{T,\sigma}$  and  $(\partial w_{3s}/\partial T)_{P,\sigma}$  exhibit marked maxima in the intermediate density regime (near-critical SFC). The variations shown in Figs. 1–4 agree with experimentally observed trends in all cases in which experimental information is available.

#### 2.4. Macroscopic significance of perturbations in molecular parameters

In a chromatographic system with a neat (single-component) mobile phase fluid there are nine molecular parameters characterizing the (1 + 2 + 3) system within the lattice model employed here, namely, size parameters  $r_1, r_2, r_3$  and segment interaction-energy parameters  $\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{12}, \varepsilon_{13}$  and  $\varepsilon_{23}$ . Because of the assumption of infinite dilution of the solute, segmental solute–solute interactions are absent and the parameter  $\varepsilon_{11}$  does not affect any macroscopic property of interest here. Further, the assumption of a very high molecular mass of the stationary polymer ( $M_2 \rightarrow \infty, r_2 \rightarrow \infty$ ) means that the parameter  $r_2$  also does not affect the retention properties. What remains then is to assign macroscopic interpretations to perturbations in the other seven parameters.

A change in solute molecular size  $r_1$  at constant interaction-energy parameters corresponds to a shift from one solute to another in a homologous series of solutes. In a similar way, a sole change in  $r_3$  would mimic a shift in a homologous series of mobile phase fluids which is a situation with no currently practised parallel. It should be noted, however, that properly weighted, simultaneous variations in  $r_3$  and  $\varepsilon_{33}$  could serve as a primitive representation of adding a modifier to the mobile phase fluid although a rigorous treatment of the effect of modifier on solute retention has to be based on a separate thermodynamic analysis [26]. Within the lattice model employed, segment–segment interaction energy parameters  $\varepsilon_{ij}$  are positive and increase with increasing strength of the  $i$ – $j$  interaction. An increase in  $\varepsilon_{ii}$  therefore reflects an

increase in polarizability and/or polarity of component  $i$ . Typical fitted values of  $\varepsilon_{ii}$  [21] range from ca. 100  $k_B$  for  $n$ -alkanes through ca. 140  $k_B$  for aromatic hydrocarbons and ca. 190  $k_B$  for methanol to ca. 400  $k_B$  for water, where  $k_B$  is the Boltzmann constant. In an analogous manner, an augmented value of  $\varepsilon_{ij}$  indicates a stronger and/or more specific  $i$ – $j$  interaction.

### 3. Results and discussion

#### 3.1. Primary thermodynamic properties of the system

Prior to discussing the sensitivities of retention quantities to molecular-level features of the chromatographic system, the disparate effects of molecular parameters on essential thermodynamic properties of the system will be demonstrated in a few examples.

Fig. 5 shows that, in the particular reference system, there are clear trends in the effects of molecular parameters on  $(\partial\mu_{1s}^\infty/\partial w_{3s})_{T,P}/(RT)$  at all densities and that the sensitivities to a particular parameter do not change significantly from one density regime to another. Considering the low sensitivities to size parameters, the alternating signs of sensitivities to interaction energies suggest that  $(\partial\mu_{1s}^\infty/\partial w_{3s})_{T,P}/(RT)$  remains relatively stable when a component of the system is changed. This is because changing a component affects two or three interaction energies, e.g., replacing poly(dimethylsiloxane) with a poly(methylphenylsiloxane) affects the parameters  $\varepsilon_{12}, \varepsilon_{22}$  and  $\varepsilon_{23}$ . Since the parameters usually vary in the same direction upon such a change, a tendency to mutual offset of the separate effects on  $(\partial\mu_{1s}^\infty/\partial w_{3s})_{T,P}/(RT)$  results.

Negative values of the sensitivity of  $w_{3s}$  to  $\varepsilon_{22}$  (Fig. 6) indicate that a stronger polymer–polymer interaction tends to expel the dissolved mobile phase fluid from the stationary phase. In turn, a stronger polymer–fluid interaction promotes the fluid’s solubility in the polymer, as expected. Both effects become more important as the density of the fluid increases.

As the isobaric expansivity of the mobile

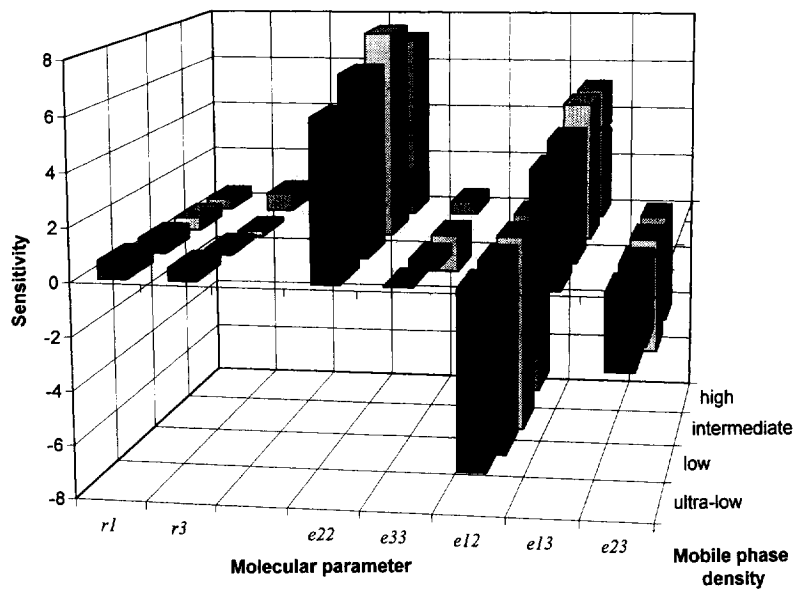


Fig. 5. Sensitivity of  $(\partial\mu_{3s}^x / \partial w_{3s})_{T,P} / (RT)$  to perturbations in molecular parameters.

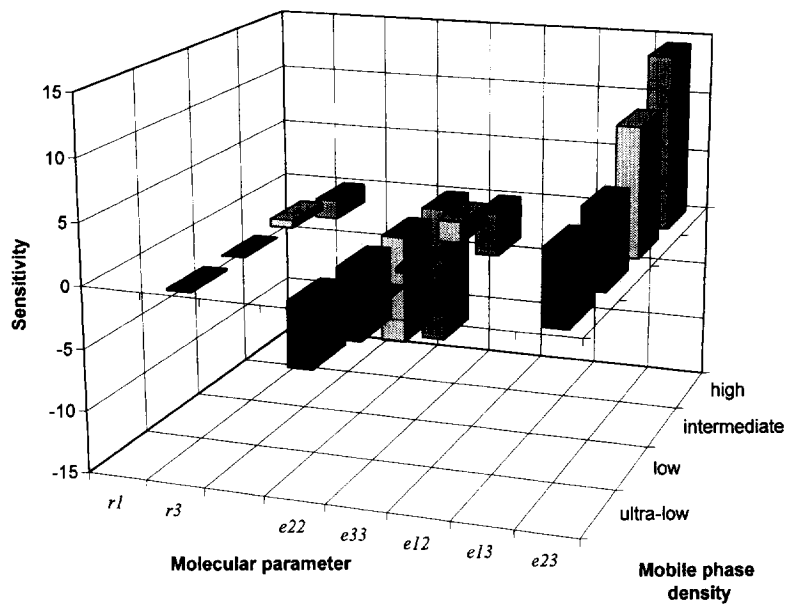


Fig. 6. Sensitivity of  $w_{3s}$  to perturbations in molecular parameters.



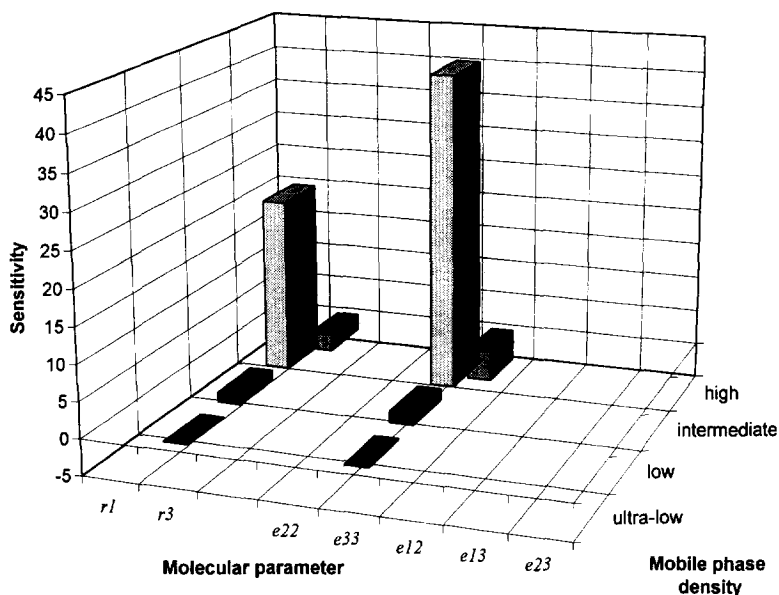


Fig. 7. Sensitivity of  $\alpha_{mP}$  to perturbations in molecular parameters.

phase fluid is a pure-component property, it varies only with  $r_3$  and  $\epsilon_{33}$  (Fig. 7). The strong sensitivities to both molecular parameters in the intermediate density regime reflect the relative proximity of the regime to the fluid's critical point ( $\alpha_{mP}$  diverges at the critical point). In the high-density limit, both increased molecular size and a stronger fluid–fluid interaction appear to decrease  $\alpha_{mP}$ .

The isothermal compressibility of the stationary phase along the line of saturation of the stationary phase with the mobile phase fluid,  $\beta_{sT}$ , is very difficult to visualize. Interaction energies  $\epsilon_{22}$  and  $\epsilon_{23}$  are predicted to be the most important molecular parameters here (Fig. 8), especially at high densities of the fluid.

Except in the high-density regime, the sensitivities of the molar volume of solute transfer to interactions involving the stationary polymer (2) are relatively low (Fig. 9). This is because  $\Delta V_{1t}$  equals the difference between solute partial molar volumes in the stationary and the mobile phase,  $\bar{v}_{1s}^\infty - \bar{v}_{1m}^\infty$ . At low densities, the polymer-independent  $\bar{v}_{1m}^\infty$  is the dominant term. Likewise as with  $\alpha_{mP}$ , the augmented sensitivities of  $\Delta V_{1t}$  to  $r_3$  and  $\epsilon_{33}$  in the intermediate density regime

remind of the divergence of  $\bar{v}_{1m}^\infty$  at the fluid's critical point.

### 3.2. Retention derivatives

The sensitivities  $S$  of the separate derivatives of  $\ln k'$  to the seven pertinent molecular parameters are compiled in Table 3. In each density regime, the molecular parameters are ordered according to their decreasing relevance to the particular macroscopic property. As a whole, the table confirms the expected overall increase in sensitivities to molecular parameters with increasing density of the mobile phase fluid. Since

$$(\partial \ln k' / \partial P)_T / (\partial \ln k' / \partial \ln \rho_m)_T = \beta_{mT} \quad (11)$$

the sensitivities of  $(\partial \ln k' / \partial P)_T$  and  $(\partial \ln k' / \partial \ln \rho_m)_T$  to any molecular parameter except those characterizing the pure mobile phase fluid,  $r_3$  and  $\epsilon_{33}$ , are identical. For all four derivatives of  $\ln k'$ , the size of the solute molecule ( $r_1$ ) exhibits a clearly discernible decrease in importance with increasing density of the mobile phase fluid. The molecular size of the fluid ( $r_3$ ) is relatively unimportant in the high-density limit

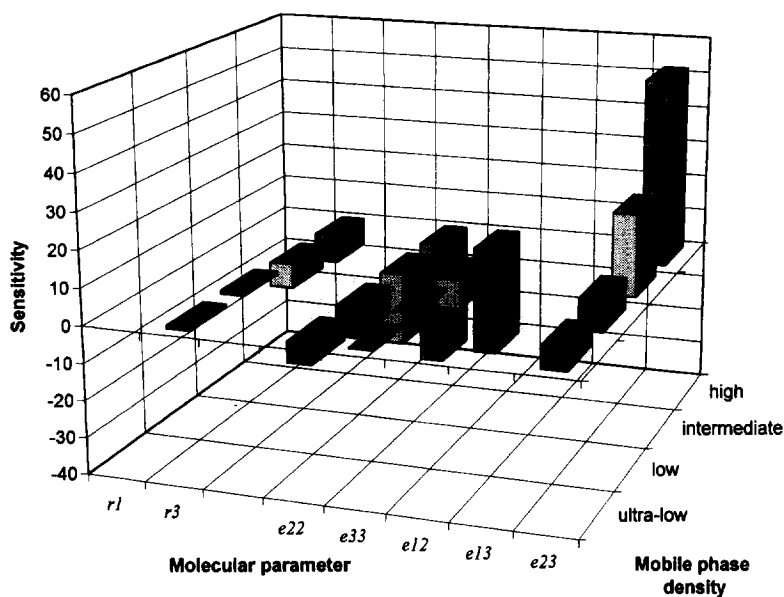


Fig. 8. Sensitivity of  $\beta_{57}$  to perturbations in molecular parameters.

but becomes very significant in the intermediate density regime because of the proximity to the fluid's critical point. Increasing the density brings about a relative decline in the sensitivity to

solute-polymer interaction energy ( $\epsilon_{12}$ ) in all four derivatives, and a less apparent enhancement in the sensitivity to solute-fluid interaction energy ( $\epsilon_{13}$ ) in all derivatives except the con-

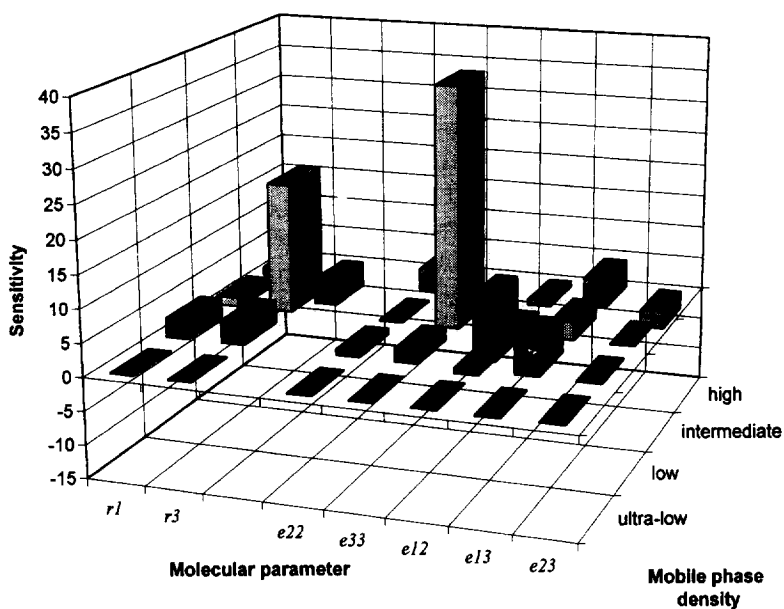


Fig. 9. Sensitivity of  $\Delta V_{11}$  to perturbations in molecular parameters.

Table 3  
Sensitivities of derivatives of  $\ln k'$  to perturbations in molecular parameters

Derivative	Density regime							
	Ultra-low		Low		Intermediate		High	
	Parameter	S	Parameter	S	Parameter	S	Parameter	S
$(\partial \ln k'/\partial P)_T$	$\epsilon_{12}$	3.2	$\epsilon_{12}$	2.4	$\epsilon_{33}$	39	$\epsilon_{23}$	-14
	$\epsilon_{23}$	-1.7	$r_3$	1.9	$r_3$	21	$\epsilon_{22}$	9.8
	$r_1$	1.1	$\epsilon_{23}$	-1.6	$\epsilon_{13}$	1.7	$\epsilon_{33}$	-6.1
	$r_3$	1.0	$\epsilon_{33}$	1.5	$\epsilon_{23}$	-1.2	$r_3$	-3.2
	$\epsilon_{22}$	-0.066	$r_1$	1.1	$r_1$	1.0	$\epsilon_{13}$	2.6
	$\epsilon_{13}$	-0.034	$\epsilon_{13}$	0.62	$\epsilon_{22}$	0.77	$\epsilon_{12}$	2.1
	$\epsilon_{33}$	0.018	$\epsilon_{22}$	0.36	$\epsilon_{12}$	0.60	$r_1$	1.1
$(\partial \ln k'/\partial \ln \rho_m)_T$	$\epsilon_{12}$	3.2	$\epsilon_{12}$	2.4	$\epsilon_{33}$	9.4	$\epsilon_{23}$	-14
	$\epsilon_{23}$	-1.7	$\epsilon_{23}$	-1.6	$r_3$	6.4	$\epsilon_{22}$	9.8
	$r_1$	1.1	$r_3$	1.5	$\epsilon_{13}$	1.7	$\epsilon_{13}$	2.6
	$r_3$	0.99	$r_1$	1.1	$\epsilon_{23}$	-1.2	$\epsilon_{12}$	2.1
	$\epsilon_{22}$	-0.066	$\epsilon_{33}$	0.68	$r_1$	1.0	$\epsilon_{33}$	2.0
	$\epsilon_{13}$	-0.034	$\epsilon_{13}$	0.62	$\epsilon_{22}$	0.77	$r_1$	1.1
	$\epsilon_{33}$	0.0091	$\epsilon_{22}$	0.36	$\epsilon_{12}$	0.60	$r_3$	0.13
$[\partial \ln k'/\partial(1/T)]_{\rho_m}$	$\epsilon_{12}$	3.1	$\epsilon_{12}$	2.5	$\epsilon_{33}$	-10	$\epsilon_{33}$	46
	$\epsilon_{22}$	-1.3	$\epsilon_{22}$	-1.7	$r_3$	-7.5	$\epsilon_{12}$	-44
	$r_1$	1.0	$\epsilon_{23}$	1.1	$\epsilon_{23}$	7.3	$\epsilon_{22}$	28
	$\epsilon_{23}$	0.022	$r_1$	1.0	$\epsilon_{22}$	-5.6	$\epsilon_{23}$	-27
	$\epsilon_{13}$	0.014	$\epsilon_{13}$	0.54	$\epsilon_{13}$	1.7	$\epsilon_{13}$	22
	$r_3$	-0.00086	$r_3$	-0.20	$r_1$	0.90	$r_3$	13
	$\epsilon_{33}$	0.000016	$\epsilon_{33}$	-0.059	$\epsilon_{12}$	0.56	$r_1$	-0.61
$(\partial \ln k'/\partial T)_p$	$\epsilon_{12}$	3.1	$\epsilon_{12}$	2.5	$\epsilon_{33}$	67	$\epsilon_{23}$	-15
	$\epsilon_{22}$	-1.3	$\epsilon_{22}$	-2.3	$r_3$	39	$\epsilon_{22}$	11
	$r_1$	1.0	$\epsilon_{23}$	1.9	$\epsilon_{23}$	-3.1	$\epsilon_{13}$	4.2
	$\epsilon_{23}$	0.027	$r_3$	-1.1	$\epsilon_{22}$	2.2	$\epsilon_{12}$	-1.6
	$\epsilon_{13}$	0.014	$r_1$	0.96	$\epsilon_{13}$	1.7	$\epsilon_{33}$	1.6
	$r_3$	-0.0036	$\epsilon_{33}$	-0.75	$r_1$	1.0	$r_3$	-1.0
	$\epsilon_{33}$	-0.000057	$\epsilon_{13}$	0.51	$\epsilon_{12}$	0.61	$r_1$	1.0

stant-density one,  $[\partial \ln k'/\partial(1/T)]_{\rho_m}$ . The patterns in  $\epsilon_{12}$  and  $\epsilon_{13}$  may be explained by an increase in equilibrium mass fraction of the mobile phase fluid in the stationary phase from the ultra-low to high density regime (cf.,  $w_{3s}$  in Table 2). With increasing density, the polymer–fluid interaction energy ( $\epsilon_{23}$ ) displays varying position within the importance sequence; in the high-density limit, it is the most significant molecular parameter in all derivatives except  $[\partial \ln k'/\partial(1/T)]_{\rho_m}$ . The fluid–fluid interaction energy ( $\epsilon_{33}$ ) exhibits the largest fluctuations in importance within the four density regimes. In all four

derivatives, it is the least significant parameter in the ideal-gas limit (ultra-low density) and the most significant one near the critical point of the fluid (intermediate density). The polymer–polymer interaction energy ( $\epsilon_{22}$ ) shows two distinct patterns of behaviour. In the temperature derivatives,  $\epsilon_{22}$  ranks at a constant position throughout the density range while in  $(\partial \ln k'/\partial P)_T$  and  $(\partial \ln k'/\partial \ln \rho_m)_T$  its importance passes through a minimum in the low-density regime.

Further, in the derivatives with respect to temperature at the ultra-low density (GC limit), the sensitivity values warrant the separation of

the molecular parameters into two distinct groups because the sensitivities to  $\epsilon_{12}$ ,  $\epsilon_{22}$  and  $r_1$  are at least 40 times higher than those to the other parameters. Therefore, in accordance with experimental GC experience, the solute–polymer and polymer–polymer interaction energies and the size of solute molecule are predicted to be the decisive molecular parameters for the two derivatives in the ultra-low density regime. At elevated densities, any similar distinction among the various parameters is no longer justified.

### 3.3. Retention quantities and phase ratio

Table 4 illustrates the effects of perturbations in the seven molecular parameters on retention quantities and phase ratio. Again, an overall increase in the sensitivities with increasing density of the mobile phase fluid is apparent. The sensitivities of  $K$  and  $k'$  to the solute-related parameters  $r_1$ ,  $\epsilon_{12}$  and  $\epsilon_{13}$  are the same because the phase ratio is invariant to these parameters.

Some trends in  $K$  and  $k'$  are similar to those noted in the derivatives of  $\ln k'$ .

In  $K$  and  $k'$ , the decrease in importance of the size of solute molecule ( $r_1$ ) with increasing density of the mobile phase fluid is more marked than in retention derivatives (cf., Table 3). The size of the molecule of mobile phase fluid ( $r_3$ ) shows relatively little effect on both  $K$  and  $k'$  except in the intermediate density regime. For  $K$ , the solute–polymer interaction energy ( $\epsilon_{12}$ ) is the most important molecular parameter although it is suspended by  $\epsilon_{33}$  and  $r_3$  in the near-critical region. For  $k'$  at high densities,  $\epsilon_{12}$  loses some of its significance to  $\epsilon_{22}$  and  $\epsilon_{23}$  because of their effects on the phase ratio. The solute–fluid interaction energy ( $\epsilon_{13}$ ) displays a marginal or low relevance to both  $K$  and  $k'$  except in the high-density regime where the solvating power of the mobile phase fluid is sufficient to make  $\epsilon_{13}$  an important parameter. At high densities,  $\epsilon_{13}$  has a lower relevance to  $k'$  than to  $K$  because of the effects of  $\epsilon_{23}$  and  $\epsilon_{33}$  on

Table 4  
Sensitivities of retention quantities and phase ratio to perturbations in molecular parameters

Quantity	Density regime							
	Ultra-low		Low		Intermediate		High	
	Parameter	S	Parameter	S	Parameter	S	Parameter	S
$K$	$\epsilon_{12}$	20	$\epsilon_{12}$	17	$\epsilon_{33}$	-34	$\epsilon_{12}$	12
	$\epsilon_{22}$	-6.8	$\epsilon_{22}$	-5.9	$r_3$	-25	$\epsilon_{22}$	-8.6
	$r_1$	5.2	$r_1$	4.0	$\epsilon_{12}$	15	$\epsilon_{13}$	-7.4
	$r_3$	-0.022	$r_3$	-1.7	$\epsilon_{22}$	-7.2	$\epsilon_{33}$	-7.2
	$\epsilon_{23}$	0.017	$\epsilon_{33}$	-0.73	$\epsilon_{23}$	3.6	$\epsilon_{23}$	6.2
	$\epsilon_{33}$	0.0056	$\epsilon_{23}$	0.64	$r_1$	3.1	$r_3$	-2.3
	$\epsilon_{13}$	$<10^{-8}$	$\epsilon_{13}$	-0.30	$\epsilon_{13}$	-1.1	$r_1$	0.12
$k'$	$\epsilon_{12}$	20	$\epsilon_{12}$	17	$\epsilon_{33}$	-33	$\epsilon_{22}$	-18
	$\epsilon_{22}$	-6.8	$\epsilon_{22}$	-7.0	$r_3$	-24	$\epsilon_{23}$	17
	$r_1$	5.2	$r_1$	4.0	$\epsilon_{12}$	15	$\epsilon_{12}$	12
	$\epsilon_{23}$	0.039	$\epsilon_{23}$	1.8	$\epsilon_{22}$	-12	$\epsilon_{33}$	-10
	$r_3$	-0.019	$r_3$	-1.5	$\epsilon_{23}$	9.0	$\epsilon_{13}$	-7.4
	$\epsilon_{33}$	0.0056	$\epsilon_{33}$	-0.66	$r_1$	3.1	$r_3$	-3.2
	$\epsilon_{13}$	$<10^{-8}$	$\epsilon_{13}$	-0.30	$\epsilon_{13}$	-1.1	$r_1$	0.12
$V_s/V_m$	$\epsilon_{23}$	0.022	$\epsilon_{23}$	1.1	$\epsilon_{23}$	5.4	$\epsilon_{23}$	11
	$\epsilon_{22}$	-0.022	$\epsilon_{22}$	-1.0	$\epsilon_{22}$	-4.6	$\epsilon_{22}$	-9.1
	$r_3$	0.0032	$r_3$	0.15	$\epsilon_{33}$	0.89	$\epsilon_{33}$	-3.0
	$\epsilon_{33}$	0.000036	$\epsilon_{33}$	0.065	$r_3$	0.67	$r_3$	-0.84

the phase ratio. The polymer–fluid interaction energy ( $\epsilon_{23}$ ) shows a relatively small effect on  $K$  and a stable position in the importance sequence. For  $k'$ ,  $\epsilon_{23}$  is more important because of its bearing on the phase ratio. In the ultra-low and low density regimes, the fluid–fluid interaction energy ( $\epsilon_{33}$ ) has little influence on both  $K$  and  $k'$ . High sensitivities of both retention quantities to  $\epsilon_{33}$  near the fluid's critical point (intermediate density regime) contrast sharply with the small effect of  $\epsilon_{33}$  on the phase ratio. The contrast confirms that the high sensitivities of retention quantities and retention derivatives to  $\epsilon_{33}$  (and to  $r_3$ ) in the intermediate density regime arise in the mobile phase, i.e., they result from effects of  $\epsilon_{33}$  and  $r_3$  on the solvating power of the mobile phase fluid rather than from effects of  $\epsilon_{33}$  and  $r_3$  on the phase ratio. Except in the intermediate density regime, the polymer–polymer interaction energy ( $\epsilon_{22}$ ) is a very significant parameter in both  $K$  and  $k'$ . The effects of  $\epsilon_{22}$  on  $K$  and on  $V_s/V_m$  combine to make  $k'$  more sensitive to  $\epsilon_{22}$  as compared with  $K$ , especially in the high-density limit.

Similarly as for the retention derivatives, the sensitivities of  $K$  and  $k'$  to molecular parameters in the ultra-low density limit warrant the separation of the molecular parameters into two distinct groups. Compared with the retention derivatives, the distinction is more justified here because the sensitivities of  $K$  and  $k'$  to  $\epsilon_{12}$ ,  $\epsilon_{22}$  and  $r_1$  exceed those to the other parameters by more than two orders of magnitude. This finding coincides with ample experimental indications of the decisive role of the solute–polymer and polymer–polymer interaction energies and the solute molecular size in determining solute retention in GC.

For the phase ratio,  $V_s/V_m$ , the sequence of importance of the four pertinent parameters is relatively stable throughout the density range with the polymer–fluid and polymer–polymer interaction energies ranking as the most important molecular-level features of the system. The signs of the sensitivities confirm that, compared with the reference system, a stronger polymer–fluid interaction tends to increase the phase ratio whereas a stronger polymer–polymer interaction

results in a decrease. This result reflects the effects of both interaction energies on the equilibrium composition of the stationary phase (cf.,  $w_{3s}$  in Fig. 6).

#### 4. Conclusion

The classical and molecular thermodynamic approaches have been combined to yield a semi-quantitative picture of the effects of molecular parameters on retention properties in isotropic, non-electrolyte chromatographic systems with a polymer as a principal component of the stationary phase. The molecular parameters characterize the size of molecules and energy of their pairwise interactions. The treatment is based on the application of a mean-field lattice-fluid model to probe the macroscopic effects of small perturbations in the molecular parameters of a reference system. The reference system is typical of open-tubular capillary SFC and the continuous  $P\rho_m T$  space of the mobile phase fluid is reduced to four density regimes that represent the operating conditions of GC, low-density SFC, near-critical SFC and high (liquid-like) density SFC. The treatment results in semi-quantitative, density-dependent arrangements of molecular-level features of the chromatographic system according to their respective bearings on the separate macroscopic properties of the system. The macroscopic properties comprise retention quantities, their changes with the operating conditions and their constituent thermodynamic properties including those related to swelling of the stationary polymer with the mobile phase fluid. The following trends are apparent from the sensitivities of macroscopic properties to molecular parameters:

There is an overall increase in the sensitivities with increasing density of the mobile phase fluid.

With the increasing density, molecular-size parameters become less important than interaction energies.

For the retention quantities and retention derivatives near the critical point of the mobile phase fluid, characteristics of the pure fluid are predicted to be the most significant molecular

parameters. This result indicates that the relative importance of solute identity is suppressed near the fluid's critical point.

For the retention quantities and retention derivatives within the operating range of GC, the solute–polymer and polymer–polymer segmental interaction energies and the size of solute molecule are predicted to be the decisive molecular parameters. At higher densities, such a clear distinction among the molecular parameters according to their significance is no longer possible.

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