

Relative Retention in Supercritical Fluid Chromatography as a Source of Partial Molar Properties

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In addition to its significance as an analytical tool, supercritical fluid chromatography also provides a useful technique for measurement of thermodynamic properties. The purpose of this contribution is to point out some advantages of using the *relative retention* of a pair of solutes to obtain the solute partial molar properties in supercritical solvents. First, the particular benefits of using the relative retention are shown at the general thermodynamic level of the problem. Next, the Flory–Huggins equation of state (EOS) is employed to derive the correction terms for the composition derivatives of the solute chemical potentials that can readily be used in reducing the experimental retention data to the partial molar properties. When the Flory–Huggins EOS is combined with the regular solution theory, the corrections require pure-component parameters only. Further, as thermodynamic data on *isomeric* solutes are often of interest in applications of supercritical solvents, the additional simplifications in the correction terms for isomeric solutes are explicitly included.

Introduction

Supercritical fluid chromatography (SFC) has often been employed to determine thermodynamic properties of a solute at infinite dilution in the mobile-phase fluid. Most applications have involved determination of the partial molar properties of solutes in carbon dioxide^{1–9} or determination of the partition coefficients of solutes between carbon dioxide and the stationary phase.^{4,5,10,11} Applications of SFC with binary (cosolvent-modified) mobile-phase fluids to study the cosolvent effects have so far been less frequent.^{12,13} The changes in operating conditions of SFC (temperature, pressure, composition of the mobile-phase fluid) result in the changes of equilibrium proportion(s) of the component(s) of the mobile-phase fluid in the stationary phase. With a few exceptions,^{4,5,13} however, the corrections for composition changes in the stationary phase have been omitted in reducing the SFC retention data to the partial molar properties, although thermodynamic models using various kinds of lattice fluid theory^{5,11,14–17} suggest that the corrections may amount to tens of percent. Apart from relative complexity of the corrections, the main reason for their omission has been the lack of necessary data on sorption of the mobile-phase fluid into the stationary phase. Fortunately, owing to noteworthy efforts by several groups, such data gradually become available, at least for the cross-linked poly(dimethyl siloxane) (PDMS)–pure CO₂ system^{5,10,18–21} and for systems comprising PDMS and cosolvent-modified CO₂.^{17,22}

The data on partial molar properties have mostly been obtained from retention data for a single solute, and consequently, the composition corrections have been worked out^{5,14,17,23,24} for that particular situation. As a separation method, however, chromatography makes it possible to handle several solutes within a single experimental run; therefore, it seems to be useful to use *relative retention* of a pair of solutes to obtain solute partial molar properties in a solute + mobile-phase fluid mixture. Although this suggestion appears to be trivial at first glance, it entails three important, beneficial consequences.

(i) The relative retention of two solutes, if obtained from a single injection, is less sensitive to uncertainties in the dead retention time (as compared to the individual retention factors of the two solutes).

(ii) The use of relative retention makes the chromatographic method comparative because one of the two solutes may serve as a reference, with the respective partial molar property known from an independent source.

(iii) As compared to the case of a single solute, the corrections for stationary-phase effects become simpler in the case of relative retention because, even at the model-independent level of general thermodynamics, certain hard-to-access parts of the corrections are eliminated.

The purpose of this work is to specify the corrections for composition changes in the stationary phase if the relative retention is to be used to obtain the solute partial molar properties in the mobile-phase fluid. The treatment below will concern the systems of open-tubular, capillary SFC; in these systems, the principal component of the stationary phase is a lightly cross-linked polymer so that the stationary phase may be treated as a bulk phase. After discussing the problem at the level of general thermodynamics, the Flory–Huggins equation of state (EOS) will be used to derive the correction terms for the composition derivatives of the solute chemical potentials that can readily be used in reducing the experimental retention data to the partial molar properties. Further, as thermodynamic data on *isomeric* solutes are often of interest in applications of supercritical solvents, the additional simplifications in the correction terms for isomeric solutes will be explicitly included. The common assumption of infinite dilution of the solute(s) in both phases of the chromatographic system has been retained in the present treatment. Liu and O'Connell²⁵ have recently used the fluctuation solution theory to model the effect of solute–solute interactions in the mobile phase on retention in SFC.

General Relationships

In what follows, the solute will be identified by subscript 1, the principal component of the stationary phase by subscript 2,

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the principal component of the mobile phase by subscript 3, and the cosolvent (modifier) by subscript 4. When referring to the relative retention of a pair of solutes, the two solutes will be denoted by A and B. The quantities pertaining to the stationary and the mobile phases will be identified by subscripts s and m, respectively.

Systems without Cosolvent. Thermodynamic background of the effects of operating pressure and temperature on the retention factor, k_1 , of a single solute in a system of open-tubular column SFC without cosolvent has been discussed before.^{4,5,11,14,15,23} In the present context, the relationship between the isothermal pressure derivative of $\ln k_1$ and the thermodynamic properties may be written as

$$\frac{\bar{v}_{1m}^\infty}{RT} = \left(\frac{\partial \ln k_1}{\partial P} \right)_T + \frac{\bar{v}_{1s}^\infty}{RT} + \beta_{mT} + \frac{V_s}{V_m} \beta_{sT\sigma} + \frac{1}{RT} \left(\frac{\partial \mu_{1s}^\infty}{\partial w_{3s}} \right)_{T,P,n_{2s}} \left(\frac{\partial w_{3s}}{\partial P} \right)_{T,\sigma} \quad (1)$$

where R is the molar gas constant, T is the temperature, P is the pressure, \bar{v}_{1m}^∞ and \bar{v}_{1s}^∞ are the infinite-dilution partial molar volumes of the solute in the mobile and the stationary phase, respectively, β_{mT} is the isothermal compressibility of the pure mobile-phase fluid, $\beta_{sT\sigma}$ is the isothermal compressibility of the stationary phase at saturation with the mobile-phase fluid, V_s and V_m are the geometric volumes of the two phases in the column, μ_{1s}^∞ is the infinite-dilution chemical potential of the solute in the stationary phase, and w_{3s} is the mass fraction of the mobile-phase fluid in the stationary phase. Subscript n_{2s} refers to insolubility of component 2 in the mobile-phase fluid, and subscript σ stresses saturation of the stationary phase with the dissolved mobile-phase fluid. The reason for using mass fraction in the last term is that, in open-tubular column SFC, component 2 is a high molar mass polymer ($M_2 \rightarrow \infty$), which makes mole fraction an inconvenient composition variable for the stationary phase. For two solutes A and B, therefore, the link between the difference $\bar{v}_{Am}^\infty - \bar{v}_{Bm}^\infty$ and the pressure quotient of the relative retention, k_A/k_B , is given by

$$\bar{v}_{Am}^\infty - \bar{v}_{Bm}^\infty = RT \left(\frac{\partial \ln(k_A/k_B)}{\partial P} \right)_T + \bar{v}_{As}^\infty - \bar{v}_{Bs}^\infty + \left[\left(\frac{\partial \mu_{As}^\infty}{\partial w_{3s}} \right)_{T,P,n_{2s}} - \left(\frac{\partial \mu_{Bs}^\infty}{\partial w_{3s}} \right)_{T,P,n_{2s}} \right] \left(\frac{\partial w_{3s}}{\partial P} \right)_{T,\sigma} \quad (2)$$

In a similar way, the relationship between the isobaric temperature derivative of $\ln k_1$ for a single solute and the thermodynamic properties is

$$\frac{\bar{h}_{1m}^\infty}{RT^2} = \frac{\bar{h}_{1s}^\infty}{RT^2} - \left(\frac{\partial \ln k_1}{\partial T} \right)_P + \alpha_{mP} + \frac{V_s}{V_m} \alpha_{sP\sigma} - \frac{1}{RT} \left(\frac{\partial \mu_{1s}^\infty}{\partial w_{3s}} \right)_{T,P,n_{2s}} \left(\frac{\partial w_{3s}}{\partial T} \right)_{P,\sigma} \quad (3)$$

where \bar{h}_{1m}^∞ and \bar{h}_{1s}^∞ are the infinite-dilution partial molar enthalpies of the solute in the mobile and the stationary phase, respectively, α_{mP} is the isobaric expansivity of the pure mobile-phase fluid (3), and $\alpha_{sP\sigma}$ is the isobaric expansivity of the stationary phase at saturation with the mobile-phase fluid. Therefore, the difference $\bar{h}_{Am}^\infty - \bar{h}_{Bm}^\infty$ is related to the temper-

ature quotient of the relative retention of solutes A and B, k_A/k_B , by

$$\bar{h}_{Am}^\infty - \bar{h}_{Bm}^\infty = \bar{h}_{As}^\infty - \bar{h}_{Bs}^\infty - RT^2 \left(\frac{\partial \ln(k_A/k_B)}{\partial T} \right)_P - T \left[\left(\frac{\partial \mu_{As}^\infty}{\partial w_{3s}} \right)_{T,P,n_{2s}} - \left(\frac{\partial \mu_{Bs}^\infty}{\partial w_{3s}} \right)_{T,P,n_{2s}} \right] \left(\frac{\partial w_{3s}}{\partial T} \right)_{P,\sigma} \quad (4)$$

Systems with Cosolvent. The quantities underlying the isothermal, isobaric shift in the retention factor of a single solute with composition of a binary mobile-phase fluid in a system of open-tubular column SFC have been identified before²⁴ to yield

$$\left(\frac{\partial \ln \varphi_{1m}^\infty}{\partial x_{4m}} \right)_{T,P} = \left(\frac{\partial \ln k_1}{\partial x_{4m}} \right)_{T,P,n_{2s}} + \zeta_{4m} + \frac{V_s}{V_m} \zeta_{4s} \left(\frac{\partial x_{4s}}{\partial x_{4m}} \right)_{T,P,n_{2s},\sigma} + \frac{1}{RT} \left(\frac{\partial \mu_{1s}^\infty}{\partial x_{4s}} \right)_{T,P,n_{2s}} \left(\frac{\partial x_{4s}}{\partial x_{4m}} \right)_{T,P,n_{2s},\sigma} \quad (5)$$

where φ_{1m}^∞ is the infinite-dilution fugacity coefficient of the solute in the binary mobile-phase fluid, ζ_{4m} is the mixing expansivity of the mobile-phase fluid,

$$\zeta_{4m} = - \frac{1}{\nu_m} \left(\frac{\partial \nu_m}{\partial x_{4m}} \right)_{T,P} \quad (6)$$

with ν_m being the molar volume of the binary mobile-phase fluid, and the quantity ζ_{4s} is given by

$$\zeta_{4s} = - \frac{1}{V_s} \left(\frac{\partial V_s}{\partial x_{4s}} \right)_{T,P,n_{2s}} \quad (7)$$

Equation 5 applies to the case that the principal component of the stationary phase is a polymer of very high molar mass ($M_2 \rightarrow \infty$). For two solutes A and B, one obtains, in an analogy to eqs 2 and 4,

$$\left(\frac{\partial \ln \varphi_{Am}^\infty}{\partial x_{4m}} \right)_{T,P} - \left(\frac{\partial \ln \varphi_{Bm}^\infty}{\partial x_{4m}} \right)_{T,P} = \left(\frac{\partial \ln(k_A/k_B)}{\partial x_{4m}} \right)_{T,P,n_{2s}} - \frac{1}{RT} \left[\left(\frac{\partial \mu_{As}^\infty}{\partial x_{4s}} \right)_{T,P,n_{2s}} - \left(\frac{\partial \mu_{Bs}^\infty}{\partial x_{4s}} \right)_{T,P,n_{2s}} \right] \left(\frac{\partial x_{4s}}{\partial x_{4m}} \right)_{T,P,n_{2s},\sigma} \quad (8)$$

Benefits of the Use of Relative Retention. The above links between the retention data and the thermodynamic properties indicate that, as compared to the use of the retention factor of a single solute (eqs 1, 3, and 5), the use of relative retention of two solutes (eqs 2, 4, and 8) is somewhat less demanding as regards the auxiliary information needed to reduce the retention data to the properties desired. First, the properties of the mobile-phase fluid, β_{mT} , α_{mP} , and ζ_{4m} , are not needed in reducing the data on relative retention. Second, and more important, the hard-to-model properties $\beta_{sT\sigma}$, $\alpha_{sP\sigma}$, and ζ_{4s} of the stationary phase are also eliminated, and the ratio of volumes of both phases, V_s/V_m , does not appear in the relationships involving the relative retention. Therefore, information needed to reduce the relative retention to the partial molar properties includes only the solute-independent composition data for the stationary phase and the composition derivatives of the infinite-dilution chemical potential of the solute in the stationary phase. While the composition data may be obtained from independent measurements of the distribution of the mobile-phase component(s) between the

mobile and the stationary phase,^{5,10,17–22} a suitable thermodynamic model is required to evaluate the derivatives of the chemical potential of the solute; below, the Flory–Huggins EOS will be used for that purpose. Because all the composition derivatives given below are to be taken at constant T , P , and n_{2s} , the respective subscripts in the derivatives will be dropped to simplify notation. Further, the subscript s will also be dropped as all the properties mentioned below refer to the stationary phase.

Chemical Potential Derivatives from the Flory–Huggins EOS

Mixing vs Elastic Contributions to the Gibbs Free Energy. According to the Flory–Huggins theory,²⁶ the Gibbs free energy of mixing in a multicomponent system is given by

$$\Delta G_{\text{mix}} = RT \left(\sum_i \sum_{j>i} n_i \phi_j \chi_{ij} + \sum_i n_i \ln \phi_i \right) \quad (9)$$

where n_i is the amount of substance (mole number) of component i , ϕ_i is the volume fraction of component i in the mixture, and χ_{ij} is the Flory–Huggins interaction parameter for components i and j . Since component 2 of the system is a cross-linked polymer in the present application of the theory, the total Gibbs free energy contains an elastic contribution,^{27–29}

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{el}} \quad (10)$$

Within the frame of the affine network model,^{28,29} the elastic contribution may be written as

$$\Delta G_{\text{el}} = \frac{3}{2} \nu RT (\phi_2^{-2/3} - 1) + \gamma RT \ln \phi_2 \quad (11)$$

where ν is the number of network chains and γ the number of junctions in the network; both quantities are expressed in mole number units, and they are related by $\gamma = 2\nu/\Lambda$, with Λ being the average functionality of the network. Alternatively, in the frame of the phantom network model,^{28,29} the elastic contribution is given by

$$\Delta G_{\text{el}} = \frac{3}{2} \xi RT (\phi^{-2/3} - 1) \quad (12)$$

where the cycle rank of the network, ξ , is related to ν and Λ by $\xi = (1 - 2/\Lambda)\nu$.

Systems without Cosolvent. It follows from eq 10 that the composition derivative of the infinite-dilution chemical potential of the solute will be obtained by superposing the mixing and the elastic contributions,

$$\left(\frac{\partial \mu_1^\infty}{\partial w_3} \right) = \left(\frac{\partial \mu_1^\infty}{\partial w_3} \right)_{\text{mix}} + \left(\frac{\partial \mu_1^\infty}{\partial w_3} \right)_{\text{el}} \quad (13)$$

Mixing Contribution. Assuming composition-independent values of χ_{ij} , one obtains from eq 9 that

$$\frac{1}{RT} \left(\frac{\partial \mu_1^\infty}{\partial w_3} \right)_{\text{mix}} = \frac{\phi_2 \phi_3}{w_2 w_3} \left[\chi_{13} - \chi_{12} - \frac{\nu_1}{\nu_2} (\phi_2 - \phi_3) \chi_{23} - \frac{1}{\phi_2} + \frac{\nu_1}{\nu_2} - \frac{\nu_1}{\nu_3} \right] \quad (14)$$

where w_i is the mass fraction of component i in the mixture and ν_i is the molar volume of component i as a measure of the molecular size of component i . Further, the interaction parameter χ_{ij} may be interpreted in terms of the regular solution theory as^{10,30}

$$\chi_{ij} = \frac{\nu_i}{RT} (\delta_i - \delta_j)^2 \quad (15)$$

where δ_i is the solubility parameter of component i . Substitution from eq 15 into eq 14 yields

$$\left(\frac{\partial \mu_1^\infty}{\partial w_3} \right)_{\text{mix}} = \nu_1 \frac{\phi_2 \phi_3}{w_2 w_3} \left[(\delta_1 - \delta_3)^2 - (\delta_1 - \delta_2)^2 - (\phi_2 - \phi_3)(\delta_2 - \delta_3)^2 - RT \left(\frac{1}{\nu_1 \phi_2} - \frac{1}{\nu_2} + \frac{1}{\nu_3} \right) \right] \quad (16)$$

Elastic Contribution. From the affine network model (eq 11), the following relationship results:

$$\frac{1}{RT} \left(\frac{\partial \mu_1^\infty}{\partial w_3} \right)_{\text{el}} = \frac{\phi_2 \phi_3}{w_2 w_3} \frac{\nu_1}{V_0} \left[\gamma - \frac{1}{3} \nu \phi_2^{-2/3} \right] \quad (17)$$

where V_0 is the volume of the stationary polymer (component 2) in an unswollen state. The alternative, phantom network model gives

$$\frac{1}{RT} \left(\frac{\partial \mu_1^\infty}{\partial w_3} \right)_{\text{el}} = - \frac{1}{3} \frac{\phi_2^{1/3} \phi_3}{w_2 w_3} \frac{\nu_1}{V_0} \xi \quad (18)$$

Isomeric Solutes. The mixing and the elastic contributions are substituted into eq 13 to obtain the total value of $(\partial \mu_1^\infty / \partial w_3)$, and the resultant expression may then be used in eqs 2 or 4, with $1 = A$ and $1 = B$, respectively. If the solutes A and B are isomers, their molecular volumes are the same, and the equality $\nu_A = \nu_B$ may be assumed to apply; this results in some simplifications. First, according to both affine network and phantom network models, the elastic contribution to $(\partial \mu_1^\infty / \partial w_3)$ is proportional to the molar volume of the solute (eqs 17 and 18). For isomeric solutes A and B, therefore, the elastic contributions offset each other (provided that the same network model has been used for both solutes) so that, employing eq 16, the difference in the chemical potential derivatives is

$$\left(\frac{\partial \mu_A^\infty}{\partial w_3} \right) - \left(\frac{\partial \mu_B^\infty}{\partial w_3} \right) = 2 \frac{\phi_2 \phi_3}{w_2 w_3} \nu_A (\delta_A - \delta_B) (\delta_2 - \delta_3) \quad (19)$$

Systems with Cosolvent. Again, the composition derivative of the infinite-dilution chemical potential of the solute includes the mixing and the elastic contributions,

$$\left(\frac{\partial \mu_1^\infty}{\partial x_4} \right) = \left(\frac{\partial \mu_1^\infty}{\partial x_4} \right)_{\text{mix}} + \left(\frac{\partial \mu_1^\infty}{\partial x_4} \right)_{\text{el}} \quad (20)$$

Mixing Contribution. In a four-component system with $M_2 \rightarrow \infty$ and with the interaction parameters independent of

composition, eq 9 yields

$$\frac{1}{RT} \left(\frac{\partial \mu_1^\infty}{\partial x_4} \right)_{\text{mix}} = \frac{1}{\nu_M} \left\{ (\nu_3 - \nu_4) \phi_2 \chi_{12} + [(\nu_3 - \nu_4) \phi_3 - \nu_3] \chi_{13} + [(\nu_3 - \nu_4) \phi_4 + \nu_4] \chi_{14} - \frac{\nu_1}{\nu_2} \phi_2 [2(\nu_3 - \nu_4) \phi_3 - \nu_3] \chi_{23} - \frac{\nu_1}{\nu_2} \phi_2 [2(\nu_3 - \nu_4) \phi_4 + \nu_4] \chi_{24} - \frac{\nu_1}{\nu_3} [2(\nu_3 - \nu_4) \phi_3 \phi_4 - \nu_3 \phi_4 + \nu_4 \phi_3] \chi_{34} + \nu_3 - \nu_4 - \frac{\nu_1}{\nu_2} (\nu_3 - \nu_4) \phi_2 + \nu_1 \left(\frac{\nu_4}{\nu_3} - 1 \right) \phi_3 + \nu_1 \left(1 - \frac{\nu_3}{\nu_4} \right) \phi_4 \right\} \quad (21)$$

The molar volume of the mixture, ν_M , is given by

$$\nu_M = (w_2 \nu_2^{\text{sp}} + w_3 \nu_3^{\text{sp}} + w_4 \nu_4^{\text{sp}}) \left(\frac{w_3}{M_3} + \frac{w_4}{M_4} \right) \quad (22)$$

where ν_i^{sp} is the specific volume of component i in the mixture (volume/mass) and M_i is the molar mass of component i . Substituting from eq 15 into eq 21, one obtains

$$\left(\frac{\partial \mu_1^\infty}{\partial x_4} \right)_{\text{mix}} = \frac{\nu_1}{\nu_M} \left\{ (\nu_3 - \nu_4) \phi_2 (\delta_1 - \delta_2)^2 + [(\nu_3 - \nu_4) \phi_3 - \nu_3] (\delta_1 - \delta_3)^2 + [(\nu_3 - \nu_4) \phi_4 + \nu_4] \times (\delta_1 - \delta_4)^2 - \phi_2 [2(\nu_3 - \nu_4) \phi_3 - \nu_3] (\delta_2 - \delta_3)^2 - \phi_2 [2(\nu_3 - \nu_4) \phi_4 + \nu_4] (\delta_2 - \delta_4)^2 - [2(\nu_3 - \nu_4) \phi_3 \phi_4 - \nu_3 \phi_4 + \nu_4 \phi_3] (\delta_2 - \delta_3)^2 + RT \left[\frac{\nu_3 - \nu_4}{\nu_1} - \frac{\nu_3 - \nu_4}{\nu_2} \phi_2 + \left(\frac{\nu_4}{\nu_3} - 1 \right) \phi_3 + \left(1 - \frac{\nu_3}{\nu_4} \right) \phi_4 \right] \right\} \quad (23)$$

Elastic Contribution. The affine network model gives

$$\frac{1}{RT} \left(\frac{\partial \mu_1^\infty}{\partial x_4} \right)_{\text{el}} = \frac{1}{3} \frac{\nu_3 - \nu_4}{\nu_M} \frac{\nu_1}{V_0} (\nu \phi_2^{1/3} - \gamma \phi_2) \quad (24)$$

while the following relationship results from the phantom network model:

$$\frac{1}{RT} \left(\frac{\partial \mu_1^\infty}{\partial x_4} \right)_{\text{el}} = \frac{1}{3} \frac{\nu_3 - \nu_4}{\nu_M} \frac{\nu_1}{V_0} \xi \phi_2^{1/3} \quad (25)$$

Isomeric Solutes. In a pair of isomeric solutes A and B ($\nu_A = \nu_B$), the elastic contributions to the difference between the chemical potential derivatives in eq 8 cancel so that the difference is entirely due to the mixing contributions,

$$\left(\frac{\partial \mu_A^\infty}{\partial x_4} \right) - \left(\frac{\partial \mu_B^\infty}{\partial x_4} \right) = \frac{\nu_A}{\nu_M} (\delta_A - \delta_B) \{ (\nu_3 - \nu_4) \phi_2 (\delta_A + \delta_B - 2\delta_2) + [(\nu_3 - \nu_4) \phi_3 - \nu_3] (\delta_A + \delta_B - 2\delta_3) + [(\nu_3 - \nu_4) \phi_4 + \nu_4] (\delta_A + \delta_B - 2\delta_4) \} \quad (26)$$

Discussion

When using relative retention to obtain the partial molar properties, the corrections for composition changes in the stationary phase include (a) composition data on equilibrium

partitioning of the mobile-phase components into the stationary phase and (b) composition derivatives of the infinite-dilution chemical potentials of the solutes in the stationary phase. The present work only deals with the derivatives of the solute chemical potentials (b). The composition data (a) have to be obtained from an independent source; however, once known for a given combination of the stationary and the mobile phase, they can be applied with any solute. It seems to be expedient, therefore, to model the solute chemical potential derivatives (b) using the simple Flory–Huggins EOS combined with the elastic contribution.

The mixing contributions to the composition derivatives of the solute chemical potential have been derived assuming that the interaction parameters χ_{ij} do not vary with composition. This assumption is certainly questionable, especially for the χ_{ij} 's involving the principal component of the mobile-phase fluid.^{10,17,21} However, even the more recent lattice–fluid models applied to systems of interest in SFC^{11,15,31,32} do not reflect the composition variation of the interaction parameters. If the Flory–Huggins interaction parameters χ_{ij} are expressed from the regular solution theory, the equations for the solute chemical potential derivatives require pure-component parameters only. Therefore, the working equations given above provide for an approximate correction of the resultant partial molar properties for composition changes in the stationary phase without the need for binary interaction energy parameters between the solute and the other components. Feasibility and performance of this approach when applied to experimental data will be tested in a subsequent paper.

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