Vapor-Liquid Equilibria from Perturbation Gas Chromatography

Part I: Multicomponent Parameter Estimation

Elution times determined from perturbation chromatography experiments are functions of all sorbing species isotherms through the concentration partial derivatives. Measurements at a sufficient number of appropriate compositions along with isotherm models and adjustable parameters allow reduction of the retention time data to VLE by a nonlinear parameter estimation procedure described in this paper. The method can be implemented for both empirical isotherm models, which can be used to minimize model deficiencies, and for theoretical thermodynamic models, which have extrapolation potential and may require fewer parameters.

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Introduction

The perturbation chromatography experiment (also called elution on a plateau, step and pulse, inverse chromatography) consists of observing the response peaks eluted from a column perturbed slightly from an initial steady state. The length of time required to elute each peak (in a multicomponent system multiple peaks will be produced from any input perturbation) depends upon the values of all of the sorption isotherm concentration partial derivatives for all the species in the system at the steady state operating conditions of temperature, pressure, and composition.

The dependence of each peak elution time upon all of the sorbing species equilibria has been termed interference (Helfferich and Klein, 1970) and complicates the extraction of individual species isotherms from multicomponent experimental chromatography data. Each peak is not associated with any single species, as is the case for traditional chromatography at infinite dilution or for perturbation with isotopic tracers of species that are at finite concentration. One must experimentally determine a number of elution times over a suitable composition grid and then fit these data with isotherm models through their derivatives.

In previous work the theoretical basis was presented for determining the isotherms of multiple sorbing species from perturbation chromatography retention times at constant temperature and pressure (Glover and Lau, 1983). The general result places no restrictions on the form of the isotherms and relates the retention times for each eluted peak in a multicomponent system to all of the isotherm concentration partial derivatives for all of the sorbing species. In this paper the computational details of extracting model parameters using nonlinear parameter estimation procedures is given. The method can be implemented for both empirical isotherm models, which can be used to lessen model deficiencies, and for theoretical thermodynamic models, which have extrapolation potential and may require fewer parameters. The technique is of value for determining VLE in systems where there is a nonvolatile stationary-phase component including polymers and zeolites and does not require isotopic tracers or sampling vapor or liquid phases for concentration measurements. Part II (Ruff et al., 1986) provides an experimental example with three flowing-phase species, one of which is nonsorbing.

Review of Perturbation Chromatography Results

In a previous paper Glover and Lau (1983) presented a theoretical basis for extracting the sorption isotherms for multiple species using perturbation gas chromatography. The end-use equation given for a general multicomponent system in principle allows this determination in spite of the component peak interferences that occur in multicomponent systems, and without the use of isotopic tracers, provided that the sorption (or lack thereof) of one of the species is known *a priori*.

The result is quite general in that it places no restrictions on the form of the sorption isotherms and applies both to nonstoi-

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chiometric as well as to stoichiometric sorption, provided that the restrictions of the theory are met, i.e., that the total flowing-phase concentration is constant, that the temperature is constant, that the perturbations are small enough to satisfy the linearization of the partial differential equations, and that flow rates are sufficiently low that equilibrium is achieved locally. Actually, this last condition may not be necessary provided that the perturbation response peaks reach asymptotic behavior and that the asymptotic velocity is measured, as opposed to a velocity that is the result of the transient behavior in the beginning of the column (Deans et al., 1970). Also, the result allows changes in the flowing phase velocity and the stationary phase cross-sectional areas due to the perturbation as well as the dependence of each species' isotherm on the concentrations of the other species in the system.

A unique feature of the development was the selection of a dry basis concentration for the species in the stationary phase as opposed to mole fractions. This enabled the actual end-use equation for a general multicomponent system to be obtained fairly easily and cleanly, as opposed to merely stating a procedure that one might follow to obtain the result for a specific situation. It requires that there be a component in the stationary phase that does not transfer to the flowing phase. All other species concentrations are expressed per mass of this component. This certainly is the normal situation in chromatography applications.

The key result from the perturbation chromatography theory required for extracting isotherm information is the equation for individual response peak elution times in terms of the isotherm derivatives:

$$\left| \frac{N}{M_s} t_r \mathbf{I} + (\mathbf{Y}^* - \mathbf{I}) \cdot \boldsymbol{\beta}^* + \mathbf{y}^* \mathbf{b}_n \right| = 0 \qquad (1)$$

This equation allows for sorption of all of the flowing-phase species, but to be applicable one must know independently the complete isotherm for the nth species in the multicomponent environment. The easiest way to accomplish this is to use a species that is nonsorbing, in which case $\mathbf{b}_n = \mathbf{0}$. This also requires that a nonsorbing species be available for determining the column void volume and hence the inert peak elution time, a condition that may pose difficulties at high pressures or for certain stationary phases (e.g., zeolites).

At each steady state composition this equation is an nth-order polynomial with $(n - 1)$ net retention time roots, which are the times associated with the $(n - 1)$ peaks that would be observed experimentally. With the $(n - 1)$ times for which this equation holds determined experimentally, it becomes a set of $(n - 1)$ simultaneous equations in terms of the $(n - 1)^2$ unknown composition partial derivatives (the β's).

As a specific example, the result for sorption of a single species from a flowing phase with a nonsorbing species ($n = 2$ so that only one equation is obtained from the general result) is

$$\left(\frac{\partial g_1}{\partial y_1}\right)^* = \frac{N}{M_s} \frac{t_{r_1}}{(1 - y_1)} \qquad (2)$$

This is a particularly simple result in that the isotherm derivative for this species can be evaluated at each steady state composition independent of other experimental observations. This finite concentration result and its infinite dilution simplification have been used many times for experimental determinations of phase equilibrium. Another result, for two sorbing species at finite concentration with one nonsorbing species ($n = 3$ so that there are two simultaneous equations in terms of the four isotherm partial derivatives), is

$$\left(\frac{\partial g_1}{\partial y_1}\right)^* \left(\frac{\partial g_2}{\partial y_2}\right)^* - \left(\frac{\partial g_1}{\partial y_2}\right)^* \left(\frac{\partial g_2}{\partial y_1}\right)^* = \left(\frac{N}{M_s}\right)^2 \frac{t_{ra} t_{rb}}{(1 - y_1^* - y_2^*)}$$

and

$$(1 - y_1^*) \left(\frac{\partial g_1}{\partial y_1}\right)^* + (1 - y_2^*) \left(\frac{\partial g_2}{\partial y_2}\right)^* - y_1^* \left(\frac{\partial g_2}{\partial y_1}\right)^* - y_2^* \left(\frac{\partial g_1}{\partial y_2}\right)^* = \frac{N}{M_s} (t_{ra} + t_{rb}) \qquad (3)$$

Note that the form of Eq. 1 would give two equations, each of which is second-degree in one of the net retention times t_{ra} or t_{rb}. This alternate form is selected for easy comparison with the single-component case, Eq. 2. This specific case illustrates the isotherm coupling of the peaks that exists. These two equations are not sufficient by themselves to determine either of the species isotherms or even their derivatives at the steady state composition, (unless one of the species is at infinite dilution, in which case the isotherms decouple and there are only two isotherm partial derivatives). Retention times from a number of compositions can be sufficient, however, to obtain the individual isotherms, as discussed in this paper.

Determination of Sorption Isotherms

General outline of procedure

In general terms, the procedure for extracting isotherms from a set of peak net retention times is easily stated. It first requires selecting an appropriate isotherm model either that relates the stationary-phase concentrations for each species to the flowing-phase set of concentrations (one isotherm for each sorbing component) or, vice versa, that relates the flowing-phase concentration for each species to the stationary-phase set of concentrations. The model for each component will contain adjustable parameters and may be based in theory or may be entirely empirical.

When initial values for the various parameters are chosen, the isotherm partial derivatives required in Eq. 1 for a given steady state composition can be evaluated and the $(n - 1)$ polynomial equations solved for the $(n - 1)$ retention times. These can be compared to experimental times and subsequent iterations used to improve the agreement. Comparison of the experimental and calculated net retention times is a least-squares optimization procedure that requires evaluating a set of residuals at each composition. For a specific peak net retention time of t_{ra}, an appropriate residual is simply the difference between the experimental and calculated net retention times:

$$r_a = (t_{ra,\mathrm{exp}} - t_{ra,\mathrm{calc}}) \qquad (4)$$

where $t_{ra,\mathrm{calc}}$ is calculated as one of the roots of Eq. 1, given the isotherm model and parameters. Only if the isotherm parameters are correctly chosen, the model is correct, and the data are exact will all residuals be identically zero for a set of data. The optimization procedure requires calculation of an objective function J as a weighted sum of the squares of the residuals, over all compositions and over all retention times at each composition.

$$J = \sum_{i=1}^{N} \sum_{j=1}^{(n-1)} (w_{ij} r_{ij}^2) \tag{5}$$

For specific values of experimentally known flowing-phase concentrations and for a particular set of isotherm functions, J can be considered to be a function of the m isotherm fit parameters as the only unknowns.

Minimizing with respect to the various isotherm parameters gives a number of simultaneous equations equal to the number of fit parameters, i.e.,

$$\left(\frac{\partial J}{\partial \alpha_k}\right)_{\alpha_i} = 0 \tag{6}$$

If the number of compositions is sufficient and they are appropriately chosen, then the equations are independent and can be solved simultaneously using an appropriate numerical solution technique.

The basic procedure outlined to this point, while not the typical parameter estimation procedure in that it works with residuals calculated from the function derivatives rather than the function itself, still is fairly straightforward in concept. The actual implementation, however, can be quite involved due to the variety of models that might be selected. Two general forms are considered below: dry-basis empirical functions, which conform to the form of the equations derived in the chromatography theory, and implicit models, which may be implicit functions of the dry-basis concentrations themselves or may involve concentrations other than the dry-basis concentrations. Models based in theory, the statistical-mechanical polymer solution theories for example, are of the latter type and hence are highly implicit. Theoretical models have the distinct advantage of requiring relatively few parameters and being capable of reasonable extrapolation. Empirical models can be used to remove or lessen the model dependence of the isotherm determination.

Dry-basis models

If models are chosen that express the various stationary-phase dry-basis concentrations as explicit functions of the $(n - 1)$ independent flowing phase mole fractions and the m fit parameters, i.e.,

$$X_i = g_i(y_1, y_2, \ldots, y_{n-1}, \alpha) \tag{7}$$

then analytical expressions for the partial derivatives required in Eq. 1 for the calculation of the net retention times can be obtained and the iterations to obtain the minimum objective function are very straightforward. In order to find accurate representations of a sorption isotherm, it is generally necessary to choose different candidate functional representations, determine the parameters α for each candidate by minimization of Eq. 5, and then use statistical measures to choose the most appropriate representation among the candidates.

A natural choice for the representation of Eq. 7 is through polynomial expressions in the flowing-phase mole fractions. In general, Eq. 7 may be represented as the product of $n - 1$ polynomials, each of its own chosen degree in the mole fraction y_i. Each term in that product will have a parameter associated with it, the collection of which is represented by the vector α. Values for the parameters are to be determined by the solution of Eq. 6, or by numerical minimization of Eq. 5. Examination of the resulting residuals (Draper and Smith, 1981, Ch. 3) may be used to help determine the appropriate order of the polynomials, as well as to eliminate insignificant polynomial terms from the isotherm model. It is desirable to retain as candidates only the polynomial terms that contain y_i so that X_i will vanish when $y_i = 0$.

Since the ith isotherm is expected to be a much stronger function of y_i than the other flowing-phase mole fractions, a simplification of the above procedure is appropriate. Binary data first may be used to model the primary isotherm behavior, and then the multicomponent data may be used to determine the secondary effects of the other species.

Following this approach, we write Eq. 7 as:

$$X_i = g_{bi}(y_i, \alpha_b) f_i(y_1, \ldots, y_{i-1}, y_{i+1}, \ldots, y_{n-1}, \alpha) \tag{8}$$

We first determine the function $g_{bi}(y_i, \alpha_b)$ by reduction of the binary data. Again, candidate functional forms are to be specified. The general approach is identical to that associated with Eq. 7. In this case, however, the procedure is greatly simplified if candidate functions are chosen for which the derivative $\partial g_{bi}/\partial y_i$ is linear in the parameters. Since the peak time is linear with respect to the isotherm derivative, see Eq. 2, the estimation of g_{bi} is a linear regression problem. Thus, the normal equations represented by Eq. 6 are linear in the parameters, enabling them to be calculated explicitly. Furthermore, linear regression theory (Draper and Smith, 1981) may be used to decide among the candidate functional representations. Polynomials and polynomial splines are suitable functions since they are linear in the parameters. Functions that are not linear in the parameters may be desirable should fewer parameters be required to obtain an accurate fit of the binary data. For example, an exponential functional may be appropriate for many isotherms. The parameters would then be determined by the solution of the set of nonlinear algebraic equations represented by Eq. 6, or by numerical minimization of Eq. 5.

Once the binary isotherms are determined, the secondary effects may be estimated by using the multicomponent data to determine the functions f_i set of parameters α in Eq. 8. The product of polynomial representations for each mole fraction y_i may again be used. Note, however, that the number of parameters to be determined in Eq. 8 will generally be greatly reduced compared to those that would be determined when using the general procedure discussed with Eq. 7.

Consider, as an illustration, a ternary situation. Assume that the primary isotherm behavior can be accurately modeled by a cubic polynomial (constrained to have zero sorption at the origin), and also that the secondary effects can be represented by a quadratic polynomial. Using the simplified approach, one would determine three fit parameters from the binary data and three fit parameters with the multicomponent data. If Eq. 7 were to be used, we would form a candidate as the product of the cubic and quadratic polynomials. This product would have nine, rather than six, fit parameters to be determined. Of course, by setting certain fit parameters to zero, the candidate functional representations given by Eqs. 7 and 8 would be the same. Even in this case, the computational requirements are different. In the simplified approach, three of the parameters are determined by linear regression, whereas nonlinear minimization is used to determine the remaining three. In the other approach, the six fit parameters are to be obtained by nonlinear minimization.

Implicit models

Usually models that are based in theory are not consistent with the dry-basis formulation of the chromatographic relations above. Rather the stationary-phase concentrations are fractional concentrations that include the immobile species and, furthermore, the complete set of concentrations may appear rather than just the $(n - 1)$ independent concentrations for both the flowing and stationary phases. Hence, calculation of the partial derivatives for Eq. 1 is considerably more complicated.

The theoretical models are obtained from expressions for the fugacity of each species in both the flowing and stationary phases. The flowing-phase fugacity of each species will be expressed as an explicit function of all of the fractional concentrations of the flowing phase

$$\hat{f}_i^v = \hat{f}_i^v(y_1, y_2, \ldots, y_n) = \hat{f}_i^v(y) \tag{9}$$

and similarly the stationary-phase fugacity of each species will be expressed as an explicit function of all of the stationary-phase fractional concentrations

$$\hat{f}_i^s = \hat{f}_i^s(\xi_1, \xi_2, \ldots, \xi_n) \tag{10}$$

Note that in Eq. 7 only $(n - 1)$ independent concentrations are used in the variable set, whereas in Eq. 9 all n concentrations are included. The fractional concentrations for the stationary phase may be mole fractions, as is typical for VLE calculations, or they may be segment fractions or volume fractions, as appear in the polymer solution theories. At equilibrium, the fugacity for each species will be the same in both phases:

$$\hat{f}_i^v = \hat{f}_i^s,\ i = 1, 2, \ldots, (n - 1) \tag{11}$$

or, if the same reference fugacity is used for both phases then $\hat{a}_i^v = \hat{a}_i^s$, which gives an equilibrium relation for each sorbing species.

These equations relate the stationary-phase concentrations to the flowing-phase concentrations from which the desired dry-basis isotherm partial derivatives can be obtained for the parameter estimation procedure. Specifying these sets of relations for all of the species (i.e., selecting isotherm models and parameters) establishes the equilibrium isotherms. Then, given all of the concentrations in the flowing phase, the concentrations in the stationary phase can be calculated iteratively. From them each of the dry-basis concentrations can be evaluated:

$$X_i = \lambda_i \frac{\xi_i}{\xi_s} \tag{12}$$

where λ_i is an appropriate composition independent conversion factor for each species. Hence, determining the set of implicit functions, Eq. 10, is equivalent in principle to selecting the explicit relations, Eq. 7.

However, using the implicit relations to calculate the net retention times is considerably more involved than using the explicit relations. For each sorbing species i the dry-basis concentration is expressed in terms of its fractional concentration and the stationary species fractional concentration, both of which in turn may be considered to be functions of the independent variable set of the $(n - 1)$ independent flowing-phase fractional concentrations

$$X = g(y^I) = \lambda \cdot \frac{\xi^I(y^I)}{\xi_s(y^I)} \tag{13}$$

Here and in subsequent equations the I superscript is used to distinguish the independent set of $(n - 1)$ concentrations from the complete set of n concentrations. The vector y^I has $(n - 1)$ elements whereas y has n. Then the isotherm partial derivatives in terms of the fractional concentrations and their partial derivatives are

$$\frac{\partial g}{\partial y^I} = \frac{\lambda}{\xi_s^2} \cdot [(1 - v^T \cdot \xi^I)I + \xi^I v^T] \cdot \frac{\partial \xi^I}{\partial y^I} \tag{14}$$

where the ij components of $\partial g/\partial y^I$, $\partial \xi^I/\partial y^I$, and the dyad $(\xi^I v^T)$ are

$$\left(\frac{\partial g_i}{\partial y_j^I}\right)_{y_k^I}, \left(\frac{\partial \xi_i^I}{\partial y_j^I}\right)_{y_k^I}, \xi_i^I$$

The stationary-phase partial derivatives with respect to the $(n - 1)$ independent flowing-phase concentrations that appear in this equation can be expressed in terms of the $(n - 1)$ isotherm relations, Eq. 11. Since $d\hat{a}_i^v = d\hat{a}_i^s$ then in terms of the n flowing- and stationary-phase concentrations ($\hat{a}_i^v$ and $\hat{a}_i^s$ are formulated as functions of all n concentrations):

$$\left(\frac{\partial \hat{a}^v}{\partial y}\right) \cdot \left(\frac{\partial y}{\partial y^I}\right) \cdot dy^I = \left(\frac{\partial \hat{a}^s}{\partial \xi}\right) \cdot \left(\frac{\partial \xi}{\partial \xi^I}\right) \cdot \left(\frac{\partial \xi^I}{\partial y^I}\right) \cdot dy^I \tag{15}$$

Here $\partial y/\partial y^I$ and $\partial \xi/\partial \xi^I$ are $n \times (n - 1)$ matrices with the upper $(n - 1) \times (n - 1)$ submatrix equal to the identity and with each element in the last row equal to -1.

The required $(n - 1)^2$ dry-basis partial derivatives now can be expressed in terms of the appropriate partial derivatives of the flowing- and stationary-phase functions in the isotherm models:

$$\frac{\partial g}{\partial y^I} = \frac{\lambda}{\xi_s^2} \cdot [(1 - v^T \cdot \xi^I)I + \xi^I v^T] \cdot \left[\left(\frac{\partial \hat{a}^s}{\partial \xi}\right) \cdot \left(\frac{\partial \xi}{\partial \xi^I}\right)\right]^{-1} \cdot \left(\frac{\partial \hat{a}^v}{\partial y}\right) \cdot \left(\frac{\partial y}{\partial y^I}\right) \tag{16}$$

This relation is the basis of the calculational procedure for fitting gas chromatographic data to implicit sorption models. Given the equilibrium models for the sorbing species (the $\hat{a}^s$ and the $\hat{a}^v$ functions) and the model parameters and the flowing-phase compositions, one can calculate the stationary-phase concentrations from Eq. 11 and the set of dry-basis partial derivatives from Eq. 16. These derivatives can be used to calculate net retention times, Eq. 1, to compare with the experimental times, Eq. 4. Determining the model fit parameters that minimize the objective function, Eq. 6, produces the estimated parameters.

Example equations for a polymer solution model

The perturbation chromatography technique is convenient for determining polymer equilibrium with multiple solvents, and the theoretical solution models are examples of implicit equations. There are $(n - 1)$ sorbing species (solvents), the nth vapor phase component is helium, which is nonsorbing at low pressure, and the nth stationary phase component is polymer. Appropriate stationary-phase dry-basis concentrations are moles of solvent per mass of polymer (mass rather than moles of polymer is convenient to use since the polymer molecular weight usually is not known accurately) and appropriate vapor phase concentrations are mole fractions.

As a simple example of a set of implicit isotherm equations that are based in theory, the classical Flory-Huggins (Flory, 1942, 1953; Huggins, 1942) segment fraction solution model for this system is

$$\hat{a}_i^s = \Psi_i \exp\left\{\boldsymbol{\Psi}^T \cdot (\upsilon - \boldsymbol{r}^i) + \frac{1}{2}\left[(2\boldsymbol{u}_i^T - \boldsymbol{\Psi}^T) \cdot \pi \cdot \boldsymbol{\Psi}\right]\right\} = \Psi_i \Gamma_i \qquad i = 1, 2, \ldots, (n - 1) \quad (17)$$

where $\pi_{jk} = \pi_{kj} = (r_i/r_j)\chi_{jk}$, χ_{jk} being the usual Flory-Huggins binary interaction parameter for the jk pair. The π's, or equivalently the χ's, are the fit parameters. In this equation there is one parameter for each binary pair so that for n components in solution there are $n(n - 1)/2$ parameters. Additionally, the vapor phase relation based on a two-term pressure virial expansion is (Van Ness and Abbott, 1982)

$$\hat{a}_i^v = \frac{y_i P}{P_i^{\text{sat}}} \exp\left\{\frac{P}{RT}\left[(2\boldsymbol{u}_i^T - \boldsymbol{y}^T) \cdot \boldsymbol{B} \cdot \boldsymbol{y}\right] - \frac{B_{ii} P_i^{\text{sat}}}{RT}\right\} = y_i \gamma_i \qquad i = 1, 2, \ldots, (n - 1) \quad (18)$$

At low pressures the exponential term is close to unity. In the Flory-Huggins relation, the stationary-phase fractional concentrations are segment fractions (Ψ_i), which can be converted to dry-basis concentrations by the known characteristic hard-core specific volumes

$$g_i = \frac{v_{psp}^* \Psi_i}{M_i v_{isp}^* \Psi_p} = \lambda_i \frac{\Psi_i}{\Psi_p}, \quad i = 1, 2, \ldots, (n - 1) \quad (19)$$

and subsequently to weight fractions. Note that the concentrations of all n species present in the polymer solution including that of the polymer appear explicitly in Eq. 17. Also, all n vapor phase mole fractions appear explicitly in Eq. 18.

Analytical expressions for the partial derivatives necessary for Eq. 16 are

$$\left(\frac{\partial \hat{\boldsymbol{a}}^s}{\partial \boldsymbol{\Psi}}\right)_{ij} = \delta_{ij}\Gamma_i + \hat{a}_i^v\left(1 - \frac{r_i}{r_j} + \pi_{ij} - \boldsymbol{\Psi}^T \cdot \boldsymbol{\pi} \cdot \boldsymbol{u}_j\right) \quad (20)$$

and

$$\left(\frac{\partial \hat{\boldsymbol{a}}^v}{\partial \boldsymbol{y}}\right)_{ij} = \delta_{ij}\gamma_i + 2\frac{\hat{a}_i^v P}{RT}(B_{ij} - \boldsymbol{y}^T \cdot \boldsymbol{B} \cdot \boldsymbol{u}_j) \quad (21)$$

Some more recent polymer solution models, which incorporate an equation of state for the solution as an additional equation to be satisfied, are considered in the accompanying paper.

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Notation

$\hat{a}_i$ = activity of component i in solution
$\boldsymbol{B}$ = $(n \times n)$ matrix of second virial coefficients
$\boldsymbol{b}_n$ = $1 \times (n - 1)$ vector of sorption derivatives for component n
$\hat{f}_i$ = fugacity of component i in solution
$\boldsymbol{g}$ = $(n - 1) \times 1$ vector of sorption isotherms; $(\boldsymbol{g})_i = g_i$
$\boldsymbol{I}$ = identity matrix
J = objective function
M_i = molecular mass of species i
M_s = total mass of dry stationary phase in column
N = vapor phase molar flow rate or the number of composition data points
n = total number of components in the flowing (or vapor) phase
P = pressure
P_i^{sat} = saturation pressure for component i
R = universal gas constant
$\boldsymbol{r}^i$ = $n \times 1$ vector of segment ratios, $(\boldsymbol{r}^i)_j = r_i/r_j$
r_j = number of segments per molecule for component j
r_{ij} = $(t_{r,\text{exp}} - t_{r,\text{calc}})$ for peak j at composition i
T = absolute temperature
t = time
t_r = net retention time of peak
$\boldsymbol{u}_i$ = $n \times 1$ unit vector whose only nonzero element is a value of unity in the ith position
$\boldsymbol{U}_i$ = $n \times n$ matrix whose only nonzero element is a value of unity in the iith position
v_{sp}^* = characteristic close-packed volume per unit mass
w_{ij} = weight factor for residual ij
$\boldsymbol{X}$ = $(n - 1) \times 1$ vector of dry-basis concentrations
$\boldsymbol{Y}$ = $(n - 1) \times (n - 1)$ matrix of independent vapor phase mole fractions, $Y_{ij} = y_i$
$\boldsymbol{y}$ = $n \times 1$ vector of vapor phase mole fractions, Eq. 9
$\boldsymbol{y}^*$ = $(n - 1) \times 1$ vector of vapor-independent phase mole fractions, Eq. 1

Greek letters

$\boldsymbol{\alpha}$ = vector of m fit parameters
$\boldsymbol{\beta}$ = matrix of sorption derivatives for components 1 through $(n - 1)$ $\beta_{ij} = (\partial g_i/\partial y_j)_{T,P,y_k}$
Γ_i = stationary-phase segment fraction activity coefficient of component i
γ_i = vapor phase mole fraction activity coefficient of component i
δ_{ij} = Kronecker delta; $\delta_{ij} = 0$ for $i \neq j$, $= 1$ for $i = j$
$\boldsymbol{\lambda}$ = $(n - 1) \times (n - 1)$ diagonal matrix of constants
$\boldsymbol{\xi}$ = $n \times 1$ vector of stationary-phase concentration fractions $(\boldsymbol{\xi})_i = \xi_i$
$\boldsymbol{\Psi}$ = $n \times 1$ vector of stationary-phase segment fractions, $(\boldsymbol{\Psi})_i = \Psi_i$
$\boldsymbol{\pi}$ = $n \times n$ matrix of binary interaction parameters
υ = column vector with each element equal to unity
χ_{jk} = Flory-Huggins interaction parameter for jk binary pair.

Superscripts

I = set of $(n - 1)$ independent concentration fractions
s = stationary phase
T = transpose
v = vapor phase
$*$ = steady state

Subscripts

$1, 2, \ldots, n$ = species $1, 2, \ldots, n$
exp = experimental value
calc = calculated value from model
a, b = response peak a or b, for a single composition
i = species i
p = polymer
s = nonvolatile stationary-phase component

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