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## Lattice–fluid model for gas–liquid chromatography

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### Abstract

Lattice–fluid models describe molecular ensembles in terms of the number of lattice sites occupied by molecular species ( $r$ -mers) and the interactions between neighboring molecules. The lattice–fluid model proposed by Sanchez and Lacombe (Macromolecules, 1978;11:1145–1156) was used to model specific retention volume data for a series of  $n$ -alkane solutes with  $n$ -alkane, polystyrene, and poly(dimethylsiloxane) stationary liquid phases. Theoretical equations were derived for the specific retention volume and also for the temperature dependence and limiting (high temperature) values for the specific retention volume. The model was used to predict retention volumes within 10% for the  $n$ -alkanes phases; 22% for polystyrene; and from 20 to 70% for PDMS using no adjustable parameters. The temperature derivative (enthalpy) could be calculated within 5% for all of the solutes in nine stationary liquid phases. The limiting value for the specific retention volume at high temperature (entropy controlled state) could be calculated within 10% for all of the systems. The limiting data also provided a new chromatographic method to measure the size parameter,  $r$ , for any chromatographic solute using characteristic and size parameters for the stationary phase only. The calculated size parameters of the solutes were consistent, i.e. independent of the stationary phase and agreed within experimental error with the size parameters previously reported from saturated vapor pressure, latent heat of vaporization or density data. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Lattice–fluid models; Retention volume;  $n$ -Alkanes; Polystyrene; Poly(dimethylsiloxane)

### 1. Introduction

Lattice–fluid models have been used extensively to interpret and model solubility and swelling data for gases and supercritical fluids in polymers [1,2]. Similar models have been used to interpret chromatographic retention volume data obtained by elution GC for infinite dilution solutes [3,4]. Other authors have used the same theoretical foundation to model solute retention in supercritical fluid chromatography [5–7]. All of these theoretical treatments of chromatographic systems were based on the model proposed by Sanchez and Lacombe [8]. The lattice-

based constructs known variously as compressible-lattice, lattice–fluid, or Ising–fluid models represent the only molecular models which allow calculation of chromatographic retention volumes or partition coefficients directly rather than the pressure or temperature derivatives. Such models are a natural extension of the original Flory–Huggins treatment [9,10].

The basic concept of lattice–fluid models involves the description of the distribution of molecules, treated as  $r$ -mers, on a three-dimensional lattice with each site and each mer occupying a volume  $v^*$ . Each  $r$ -mer occupies  $r$  sites on the lattice, so the hard-core volume of each molecule or  $r$ -mer is  $rv^*$ . If there are  $N_i$  molecules of component  $i$  each occupying a

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volume of  $r_i v_i^*$ , the hard-core volume of component  $i$  would be  $N_i r_i v_i^*$ . If the total number of lattice sites is  $M$ , the total volume of a lattice would be  $M v^*$ . For mixtures, intermolecular interactions are described by an interaction parameter,  $\chi_{ij}$ , which is a function of the mer–mer interaction energies,  $\epsilon_{ii}$ ,  $\epsilon_{jj}$ , and  $\epsilon_{ij}$ .

One of the unique features of lattice–fluid models is the concept that not all of the lattice sites must be occupied even in a condensed phase. This allows for the incorporation of free volume in a polymer and compressibility of both the stationary and mobile phases. If the number of these unoccupied sites is represented as  $N_0$ , then  $M = N_0 + \sum_{i=1}^k r_i N_i$  for a system with  $k$  components. The thermodynamics of a given system can be described in terms of the Gibbs free energy,  $G = E + PV - TS$ , or Helmholtz free energy,  $A = G - PV$  depending upon the conditions, i.e. constant pressure or constant volume. Existing lattice–fluid models differ somewhat in their exact formulation of the energy, volume, and entropy terms; however, the basic structures are similar to that point.

Most lattice–fluid models yield an equation-of-state from the relation  $(\partial G / \partial V)_{T,P,\phi} = 0$  or  $(\partial A / \partial M)_{T,\phi} = -P v^*$ , where the subscript  $\phi$  represents constant composition. The most frequently used EOS was proposed by Sanchez and Lacombe [11].

$$\frac{\tilde{P}}{\tilde{T}} + \frac{\tilde{\rho}^2}{\tilde{T}} + \ln(1 - \tilde{\rho}) + \tilde{\rho} \left(1 - \frac{1}{r}\right) = 0 \quad (1)$$

where  $\tilde{P}$  and  $\tilde{T}$  are the reduced pressure and temperature, respectively.  $\tilde{\rho}$  is a concentration term representing the fraction of lattice sites that are occupied, i.e.

$$\tilde{\rho} = \frac{\sum_{j=1}^k N_j r_j}{N_0 + \sum_{j=1}^k N_j r_j}$$

The final step in the application of a lattice–fluid model is to invoke the equilibrium requirement that the chemical potential of any component distributed between two phases must be equal in both phases. The chemical potential can be derived from the free energy expression by the definition  $\mu_i \equiv (\partial G / \partial n_i)_{T,P,n_j}$  or  $\mu_i \equiv (\partial A / \partial n_i)_{T,M,n_j}$ . The equilibrium

condition can then be used to derive solubility isotherms for a solute component distributed between a compressible gas or supercritical fluid and a condensed liquid or polymer. The solubility isotherms, particularly with the solute at infinite dilution, lead to retention volume equations for chromatographic systems.

### 1.1. Partition coefficient (retention volume) equations

Sanchez and Rogers [3] derived a retention volume equation for an infinite dilution component,  $i$ , in gas chromatography using the relation that  $\mu_i^{MP} = \mu_i^{SP}$ . The general expression for the chemical potential of any component  $i$  in any phase is [12]:

$$\begin{aligned} \frac{\mu_i}{RT} = & \ln \phi_i \tilde{\rho} + 1 - r_i \sum_{j=1}^k \frac{\phi_j}{r_j} \\ & + r_i v_i^* \tilde{\rho} \left\{ \sum_{j=1}^k \phi_j \chi_{ij} - \sum_{j=1}^k \sum_{i=1}^{j-1} \phi_i \phi_j \chi_{ij} \right\} \\ & + r_i \left[ \frac{-\tilde{\rho}}{\tilde{T}_i} + \frac{\tilde{P}_i}{\tilde{T}_i \tilde{\rho}} + \left( \frac{1 - \tilde{\rho}}{\tilde{\rho}} \right) \ln(1 - \tilde{\rho}) \right] \end{aligned} \quad (2)$$

where  $\phi_i = (r_i N_i v_i^*) / (r N v^*)$  is the volume fraction of component  $i$ ,  $v_i^*$  represents the hard-core volume of a mer of component  $i$ , and  $\chi_{ij}$  is the interaction parameter which is defined to be pair-wise additive in energy density [8],  $\epsilon_{ij}^* / v_i^* = P_{ij}^*$  rather than energy.

This definition results in an interaction parameter,  $\chi$ , with dimensions of mol/l. This is in contrast with the dimensionless interaction parameter more commonly used to describe polymer solutions.

A more convenient form of the chemical potential equation can be formulated by incorporating the equation-of-state, Eq. (1) in the form:

$$\begin{aligned} \left( \frac{1 - \tilde{\rho}}{\tilde{\rho}} \right) \ln(1 - \tilde{\rho}) = \\ - (1 - \tilde{\rho}) \left[ \frac{\tilde{P}}{\tilde{T} \tilde{\rho}} + \frac{\tilde{\rho}}{\tilde{T}} + \left( 1 - \frac{1}{r} \right) \right] \end{aligned} \quad (3)$$

The chemical potential equation then becomes

$$\begin{aligned} \frac{\mu_i}{RT} = & \ln \phi_i \tilde{\rho} + 1 - r_i \sum_{j=1}^k \frac{\phi_j}{r_j} \\ & + r_i v_i^* \tilde{\rho} \left\{ \sum_{j=1}^k \phi_j \chi_{ij} - \sum_{j=1}^k \sum_{i=1}^{j-1} \phi_i \phi_j \chi_{ij} \right\} \\ & + r_i \left[ \frac{-\tilde{\rho}}{\tilde{T}_i} + \frac{\tilde{P}_i}{\tilde{T}_i \tilde{\rho}} - (1 - \tilde{\rho}) \left[ \frac{\tilde{P}}{\tilde{T}_i \tilde{\rho}} + \frac{\tilde{\rho}}{\tilde{T}} \right. \right. \\ & \left. \left. + \left(1 - \frac{1}{r}\right) \right] \right] \end{aligned} \quad (4)$$

In the classical GC example, the conditions assumed for the *mobile phase* in the model are  $\phi_{i(m)}$  and  $\rho_m \rightarrow 0$ . The reduced parameters for the system,  $\tilde{P}$ ,  $\tilde{T}$ ,  $\tilde{\rho}$  and  $r$  then become  $\tilde{P}_i$ ,  $\tilde{T}_i$ ,  $\tilde{\rho}_m$  and  $r_i$ , respectively. Then

$$\frac{\mu_{i(m)}}{RT} = \ln \phi_{i(m)} \tilde{\rho}_m - r_i \left(1 - \frac{1}{r_i}\right)$$

Some explanation or justification for the physically unrealistic assumption that the chromatographic mobile phase is composed of pure solute at zero pressure is necessary. In practical GC, the mobile phase consists of an inert carrier gas with a low, but finite, concentration of solute. This carrier gas is necessary to transport the solute through the column but does not influence the thermodynamic equilibrium requirements for the solute because of the very weak gas phase interactions between the solute and the inert carrier gas. Thus, it is reasonable to simply ignore the carrier gas in any theoretical model.

For the *stationary phase*, the model assumes that  $\phi_{i(s)} \rightarrow 0$  and thus,  $\tilde{\rho}_s = \tilde{\rho}_2$ .

Therefore

$$\begin{aligned} \frac{\mu_{i(s)}}{RT} = & \ln \phi_{i(s)} \tilde{\rho}_2 + 1 - \frac{r_i}{r_2} \\ & + r_i \left[ \frac{-\tilde{\rho}_2}{\tilde{T}_i} + \frac{\tilde{P}_i}{\tilde{T}_i \tilde{\rho}_2} - (1 - \tilde{\rho}_2) \left[ \frac{\tilde{P}_2}{\tilde{T}_2 \tilde{\rho}_2} + \frac{\tilde{\rho}_2}{\tilde{T}_2} \right. \right. \\ & \left. \left. + \left(1 - \frac{1}{r_2}\right) \right] + v_i^* \tilde{\rho}_2 \chi_{i2} \right] \end{aligned}$$

Under normal GC conditions  $\tilde{P}_i$  and  $\tilde{P}_2$  are both less than 0.001 and can be neglected.

$$\begin{aligned} \frac{\mu_{i(s)}}{RT} = & \ln \phi_{i(s)} \tilde{\rho}_2 + 1 - r_i + r_i \tilde{\rho}_2 \\ & \times \left[ \frac{-1}{\tilde{T}_i} - (1 - \tilde{\rho}_2) \frac{1}{\tilde{T}_2} + v_i^* \chi_{i2} + \left(1 - \frac{1}{r_2}\right) \right] \end{aligned}$$

Equating the chemical potential for component  $i$  in both phases gives

$$\begin{aligned} \ln \left( \frac{\phi_{i(s)} \tilde{\rho}_2}{\phi_{i(m)} \tilde{\rho}_m} \right) = & r_i \tilde{\rho}_2 \\ & \times \left[ \frac{1}{\tilde{T}_i} + \frac{1 - \tilde{\rho}_2}{\tilde{T}_2} - \left(1 - \frac{1}{r_2}\right) - v_i^* \chi_{i2} \right] \end{aligned} \quad (5)$$

The LHS of Eq. (5) can be related to the chromatographic partition coefficient by the relation  $\frac{\phi_{i(s)} \tilde{\rho}_2}{\phi_{i(m)} \tilde{\rho}_m} = \frac{N_{i(s)} M_m v_m^*}{M_s v_s^* N_{i(m)}} = K_i$ . The partition coefficient is related to the specific retention volume of a solute at the column temperature [13] by the relation  $K_i = V_{g(i)} \rho_2$ . Thus

$$\ln V_{g(i)} \rho_2 = r_i \tilde{\rho}_2 \left[ \frac{1}{\tilde{T}_i} + \frac{1 - \tilde{\rho}_2}{\tilde{T}_2} - \left(1 - \frac{1}{r_2}\right) - v_i^* \chi_{i2} \right] \quad (6)$$

Eq. (6) can be related to the expression originally derived by Sanchez and Rogers [3] by substitution of the EOS terms for the stationary phase which gives

$$\begin{aligned} \ln V_{g(i)} \rho_2 = & r_i \left\{ \frac{\tilde{\rho}_2}{\tilde{T}_i} - \left( \frac{1 - \tilde{\rho}_2}{\tilde{\rho}_2} \right) \ln(1 - \tilde{\rho}_2) \right. \\ & \left. - \left(1 - \frac{1}{r_2}\right) - v_i^* \tilde{\rho}_2 \chi_{i2} \right\} \end{aligned} \quad (7)$$

This equation is equivalent to Eq. (18a) of Ref. [3] if it is assumed that  $1 - 1/r_2 \approx 1$  and that the definition of  $v_i^*$  as the mer volume rather than the  $r$ -mer volume.

The interaction parameter term in Eq. (7) can be calculated using the hard-core volume of an  $r$ -mer which is given by the relation  $r_i v_i^* = (M_i)/(\rho_i^*)$ , thus

$$r_i v_i^* \chi_{i2} = \frac{M_i}{\rho_i^* RT} [P_i^* + P_2^* - 2P_{i2}^*]$$

Sanchez and Rogers [12] used four sets of literature data to test Eq. (7) for several solutes with different

liquid phases [14]. The results were satisfactory (average error less than 15%) for nonpolar systems. However, not surprisingly, for systems involving polar/nonpolar mixtures the partition coefficients were consistently overestimated by the lattice–fluid model. The results were quite striking, nevertheless, considering that only a geometric mean combining rule was used for  $P_{i2}^*$  and no other mixture or adjustable parameters were used in the model. The present investigation is designed to extend the evaluation of the lattice–fluid model to a broader range of chromatographic systems; to derive and assess theoretical expression for the temperature-dependence and limiting high-temperature values of the retention volume; finally to develop a novel chromatographic method for the determination of the characteristic size parameters of chromatographic solutes.

Martire and Boehm [5] derived a similar equation; however, the temperature-dependant parameters were written in terms of interaction energies using the relation  $1/\tilde{T}_i = \epsilon_{ii}^*/kT$ . Thus Eq. (7) can be recast as a partition coefficient equation with  $\epsilon^*$  values.

$$\ln K^\circ = -r_i \tilde{\rho}_2 \times \left\{ \frac{\epsilon_{ii}^*}{RT} + \left(1 - \frac{1}{r_2}\right) - \frac{\epsilon_{22}^*}{RT} \ln(1 - \tilde{\rho}_2) + v_i^* \chi_{i2} \right\} \quad (8)$$

The overall interaction energy,  $\epsilon_{ii}^*$ , for the interaction of a mer with  $z$  surrounding mers is related to the simple mer–mer interaction energy,  $\epsilon_{ii}$ , by the relation  $\epsilon_{ii}^* = -z\epsilon_{ii}/2$ . Martire and Boehm used the negative sign to indicate attractive forces. Thus, Eq. (9) can be written in terms of  $\epsilon$  values rather than  $\epsilon^*$  values as

$$\ln K^\circ = -r_i \tilde{\rho}_2 \left(1 - \frac{1}{r_2}\right) - r_i v_i^* \tilde{\rho}_2 \chi_{i2} - \frac{zr_i}{2RT} [\tilde{\rho}_2 \epsilon_{ii} + \tilde{\rho}_2 \epsilon_{22} - \tilde{\rho}_2^2 \epsilon_{22}] \quad (9)$$

The definition of  $\chi_{i2}$  in terms of  $\epsilon$  then becomes

$$\chi_{i2} = \frac{1}{RT} \left( -\frac{z\epsilon_{ii}}{2v_i^*} - \frac{z\epsilon_{22}}{2v_2^*} + \frac{z\epsilon_{i2}}{v^*} \right)$$

If it is assumed that the mer volumes of components  $i$  and  $2$  are equal, then

$$\ln K^\circ = -r_i \tilde{\rho}_2 \left(1 - \frac{1}{r_2}\right) - \frac{zr_i}{RT} \left[ \tilde{\rho}_2 \epsilon_{i2} - \frac{\tilde{\rho}_2^2 \epsilon_{22}}{2} \right] \quad (10)$$

This is Eq. (39) of Ref. [4] if it is recognized that  $\theta_{c(s)}^\circ = \tilde{\rho}_2$ .

Therefore, Eqs. (6), (7) and (10) are all similar expressions for the partition coefficient or specific retention volume. Eq. (7), however, contains a rather unwieldy logarithm term and Eq. (10) is based on the assumption that the mer volumes of the solute and solvent are equal and this is a questionable assumption for typical GC systems. For these reasons, Eq. (6) will be used to model the data for gas chromatographic systems in this investigation.

## 1.2. Temperature effects on retention

One method of evaluating Eq. (6) is to derive an expression to model the temperature dependence of chromatographic retention volume data. The stationary phase density can be calculated at any temperature from the EOS, so the temperature dependence of the retention volume can be expressed as:

$$\begin{aligned} & \frac{\partial}{\partial(1/T)} \left\{ \frac{1}{\tilde{\rho}_2} \ln V_{g(i)} \rho_2 \right\} \\ & = r_i \left[ T_i^* + T_2^* - \frac{\partial}{\partial(1/T)} \left( \frac{\tilde{\rho}_2}{\tilde{T}_2} \right) - v_i^* \frac{\partial \chi_{i2}}{\partial(1/T)} \right] \end{aligned} \quad (12)$$

However, the derivative of the interaction parameter can be written as:

$$\begin{aligned} -v_i^* \frac{\partial \chi_{i2}}{\partial(1/T)} & = -v_i^* \left[ \frac{T_i^*}{v_i^*} + \frac{T_2^*}{v_2^*} - 2\sqrt{\frac{T_i^*}{v_i^*}} \sqrt{\frac{T_2^*}{v_2^*}} \right] \\ & \frac{\partial}{\partial(1/T)} \left\{ \frac{1}{\tilde{\rho}_2} \ln V_{g(i)} \rho_2 \right\} \\ & = r_i \left[ T_2^* \left(1 - \frac{v_i^*}{v_2^*}\right) + 2T_{i2}^* \sqrt{\frac{v_i^*}{v_2^*}} - \frac{\partial}{\partial(1/T)} \left( \frac{\tilde{\rho}_2}{T_2} \right) \right] \end{aligned}$$

Expressing the temperature derivatives in a different form gives

$$\begin{aligned} & \frac{\partial}{\partial(1/T)} \left\{ \frac{1}{\tilde{\rho}_2} \ln V_{g(i)} \rho_2 \right\} \\ &= r_i \left[ T_2^* \left( 1 - \frac{v_i^*}{v_2^*} \right) + 2T_{i2}^* \sqrt{\frac{v_i^*}{v_2^*}} - \tilde{\rho}_2 T_2^* \right. \\ & \quad \left. - T \tilde{\rho}_2 \frac{\partial \ln \tilde{\rho}_2}{\partial \tilde{T}_2} \right] \end{aligned} \quad (13)$$

The last term of Eq. (13) is proportional to the isobaric thermal expansion coefficient,  $\alpha_2$ , of the stationary phase which is defined as  $\alpha_2 \equiv 1/V(\partial V/\partial T)_p$ . In terms of reduced parameters, the relation is  $\alpha_2 T_2^* = -(\partial \ln \tilde{\rho}_2/\partial \tilde{T}_2)_p$ . Thus, the slope of the van't Hoff-type plot for solute  $i$  can be expressed in terms of the isobaric thermal expansion coefficient, characteristic temperature, and density of a stationary liquid phase. The only solute parameters required are the size parameter,  $r_i$ , the mer volume,  $v_i^*$ , and the characteristic temperature,  $T_i^*$ .

$$\begin{aligned} & \frac{\partial}{\partial(1/T)} \left\{ \frac{1}{\tilde{\rho}_2} \ln V_{g(i)} \rho_2 \right\} = r_i \\ & \quad \times \left[ T_2^* \left( 1 - \frac{v_i^*}{v_2^*} \right) + 2T_{i2}^* \sqrt{\frac{v_i^*}{v_2^*}} - \tilde{\rho}_2 T_2^* (1 + \alpha_2 T) \right] \end{aligned} \quad (14)$$

Likewise, the lattice–fluid model can be used to predict the limiting values for the retention volumes of chromatographic solute at very high temperatures, i.e. at  $1/T \rightarrow 0$ .

### 1.3. Limiting retention at high temperature

The intercept of a van't Hoff-type plot of  $1/\tilde{\rho}_2 \ln V_{g(i)} \rho_2$  vs.  $1/T$  can be derived from Eq. (6) by

$$\begin{aligned} & \text{Lim}_{1/T \rightarrow 0} \left\{ \frac{1}{\tilde{\rho}_2} \ln V_{g(i)} \rho_2 \right\} \\ &= -r_i \left[ (1 - 1/r_2) + \text{Lim}_{1/T \rightarrow 0} (\tilde{\rho}_2/\tilde{T}_2) \right] \end{aligned} \quad (15)$$

Evaluation of the  $\text{Lim}_{1/T \rightarrow 0} (\tilde{\rho}_2/\tilde{T}_2)$  term of Eq. (15) must be empirical because the true limit of the ratio  $\tilde{\rho}_2/\tilde{T}_2$  is zero as shown in Fig. 1. Moreover, the equation-of-state is not well behaved at high temperatures. However, in the temperature range  $T \leq T_2^*$ ,  $\tilde{\rho}_2/\tilde{T}_2$  is approximately a linear function of

$1/\tilde{T}_2$ . There is some temperature dependence, however, because the slope in the practical temperature region is equal to  $\tilde{\rho}_2(1 + \alpha_2 T)$  and the intercept extrapolated from the linear region is  $-\tilde{\rho}_2 \alpha_2 T_2^*$ . This gives an empirical relation for the intercept of a van't Hoff plot

$$\text{Lim}_{1/T \rightarrow 0} \left\{ \frac{1}{\tilde{\rho}_2} \ln V_{g(i)} \rho_2 \right\} = -r_i [(1 - 1/r_2) - \tilde{\rho}_2 \alpha_2 \tilde{T}_2^*] \quad (16)$$

In Eq. (16), the only solute parameter is  $r_i$ . Thus,  $r_i$  can be determined from the intercept of a van't Hoff plot if the stationary phase parameters,  $r_2$ ,  $\tilde{\rho}_2$ ,  $\alpha_2$ , and  $T_2^*$  are known. The applicable values of the reduced density and thermal expansion coefficient are the average values over the experimental temperature range.

## 2. Results and discussion

### 2.1. *n*-Alkane stationary phases

In order to evaluate the specific retention volume equation as well as the derived equations for the temperature dependence (enthalpy) and limiting values at high temperature (entropy) of the specific retention volumes, specific retention volume data were required for a given set of solutes and solvents over a range of temperatures. The most fundamentally significant systems would be the *n*-alkanes. Such a data set has been reported [15] for the  $C_4$  to  $C_{10}$  *n*-alkanes in the  $C_{22}$  to  $C_{36}$  *n*-alkanes at 80, 100, and 120°C.

In order to calculate the partition coefficients, retention volumes, and density of the stationary phase, a set of three characteristic parameters ( $P^*$ ,  $T^*$ , and  $\rho^*$ ) is required for each component. Sanchez and Panayiotou [12] reported such data for the normal alkanes up to  $n$ - $C_{17}H_{36}$  along with polystyrene, polyethylene, and PDMS. These parameters are given in Tables 1 and 2. The size parameter,  $r$ , was calculated from the relation for those components with determinate molecular weights,  $M$ . Likewise, the mer volume for each component was determined from the relation  $v_i^* = 10^3 RT_i^*/P_i^*$  or  $v_i^* = M_i/r_i \rho_i^*$ . The characteristic parameters for the

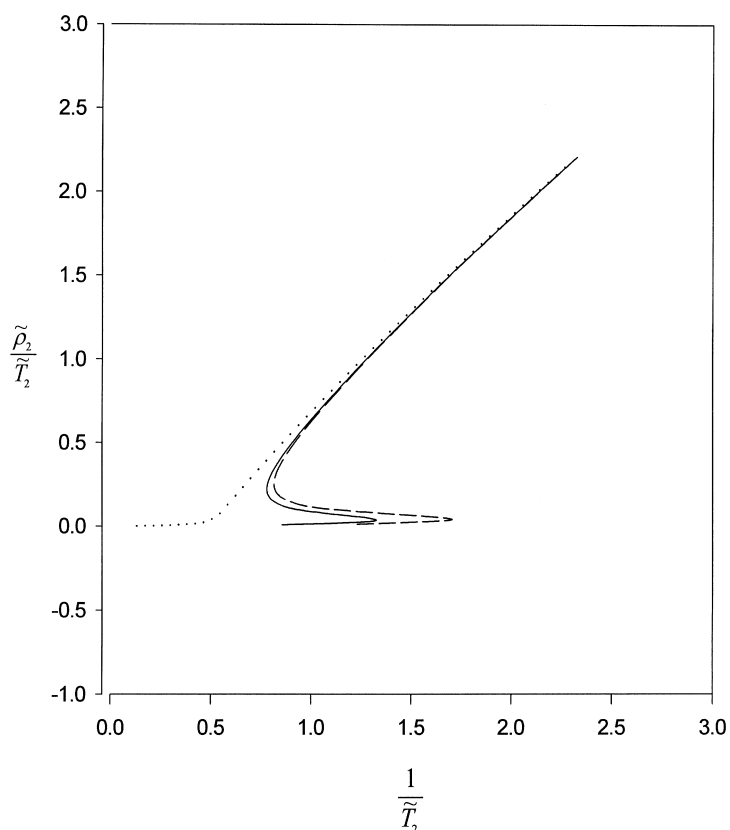


Fig. 1. Variation of  $\tilde{\rho}_2/\tilde{T}_2$  with  $1/\tilde{T}_2$  for polymers with different size parameters. Assuming  $\tilde{P}_2 \leq 0.001$  ( $\cdots$ )  $r \leq 100$ , (—)  $r = 20$ , (---)  $r = 10$ .

higher molecular weight *n*-alkane stationary phases were estimated by extrapolation of the published data for lower *n*-alkanes [12]. For example, Fig. 2 shows the carbon number dependence of  $T^*$  and  $\rho^*$  for the *n*-alkanes, and the extrapolated data for *n*-C<sub>22</sub>H<sub>46</sub> to *n*-C<sub>36</sub>H<sub>74</sub> which are also given in Table 2. The

values for  $\rho_2^*$  were also determined from an extrapolation of the mer volume,  $r_i v_i^* = M_i/\rho_i^*$ , which is a linear function of carbon number for the *n*-alkanes. The results from this extrapolation agreed within 1–2% of the values obtained from the extrapolation of  $\rho^*$  data for the lower *n*-alkanes.

Table 1  
Characteristic parameters of the chromatographic solutes [12]

Solute	$T^*$ (K)	$P^*$ (Atm)	$\rho^*$ (g/ml)	$r = \frac{MP^*}{10^3 RT^* \rho^*}$	$v^* = \frac{10^3 RT^*}{P^*}$
Propane	371	3089	0.690	6.48	9.83
<i>n</i> -Butane	403	3178	0.736	7.58	10.4
<i>n</i> -Pentane	441	3059	0.755	8.08	11.8
<i>n</i> -Hexane	476	2941	0.775	8.37	13.3
<i>n</i> -Heptane	487	3050	0.800	9.57	13.1
<i>n</i> -Octane	502	3039	0.810	10.34	13.6
<i>n</i> -Decane	530	3000	0.837	11.75	14.5

Table 2  
Characteristic parameters for the stationary liquid phases

Liquid phase	$T^*$ (K)	$P^*$ (atm)	$\rho^*$ (g/ml)	$r$	$v^* = \frac{10^3 RT^*}{P^*}$	$10^4 \alpha$ ( $K^{-1}$ )
$n\text{-C}_{22}\text{H}_{46}$	607	2484	0.008	17.6	20.1	9.3
$n\text{-C}_{24}\text{H}_{50}$	613	2406	0.890	18.2	20.9	9.4
$n\text{-C}_{28}\text{H}_{58}$	623	2259	0.890	19.6	22.6	8.6
$n\text{-C}_{30}\text{H}_{62}$	627	2201	0.900	20.1	23.4	8.4
$n\text{-C}_{32}\text{H}_{66}$	630	2125	0.900	20.6	24.3	8.3
$n\text{-C}_{34}\text{H}_{70}$	633	2050	0.900	21.0	25.3	8.3
$n\text{-C}_{36}\text{H}_{74}$	636	1992	0.900	21.5	26.1	8.1
Polyethylene [12]	649	4194	0.904	$\infty$	12.7	4.7 [16]
Polystyrene [12]	735	3523	1.11	$\infty$	17.1	6.9 [17]
Poly(dimethyl siloxane) [12]	476	2980	1.10	$\infty$	13.1	10.3 [17]
	577 <sup>a</sup>		1.04 <sup>a</sup>		15.9	

<sup>a</sup> Calculated from density data.

Estimation of the size parameters for the stationary phases was necessary because the usual assumption that  $1 - 1/r_2 \approx 1$  resulted in significant errors. It was observed empirically that a plot of  $r_i \sqrt{T_1^*}$  vs.  $r_i$  was linear ( $R^2 = 0.9995$ ) for the  $n$ -alkanes from  $C_1$  to  $C_{17}$ . The  $r$  values given in Table 2 were calculated from a linear extrapolation for the  $n$ -alkanes from

$C_{22}$  to  $C_{36}$ . The characteristic pressures were calculated from the  $r$ ,  $T^*$  and  $\rho^*$  values.

The specific retention volumes for the  $n$ -alkane solutes were calculated from the characteristic parameters using Eq. (6). The interaction parameter was calculated from the characteristic pressure using only the geometric mean assumption for  $P_{12}^*$ , i.e.

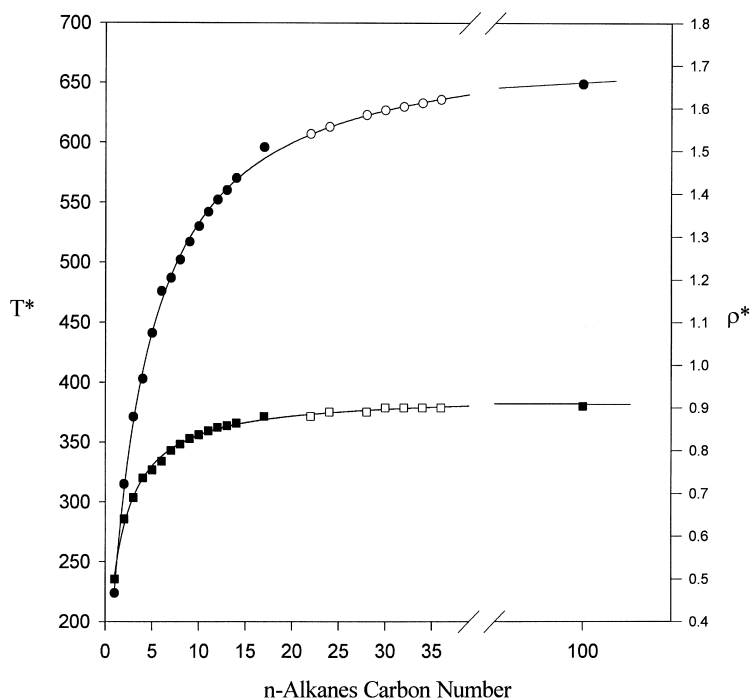


Fig. 2. Characteristic parameters of  $n$ -alkanes. Sanchez and Panayiotou [3]: (●)  $T^*$ , (■)  $\rho^*$ ; this work: (○)  $T^*$ , (□)  $\rho^*$ .

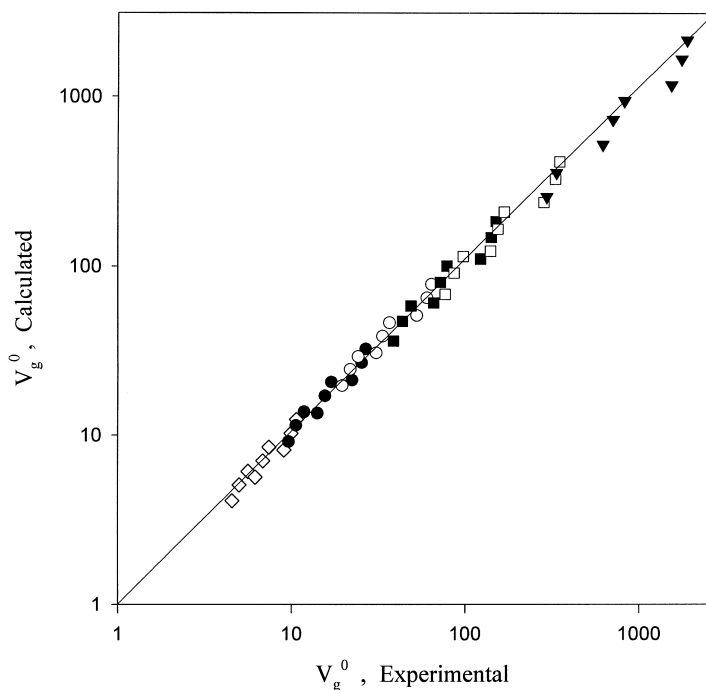


Fig. 3. Comparison of calculated and experimental specific retention volumes for *n*-alkanes solutes in *n*-C<sub>22</sub>H<sub>46</sub>, *n*-C<sub>28</sub>H<sub>58</sub>, and *n*-C<sub>36</sub>H<sub>74</sub>. (◇) Butane, (●) pentane, (○) hexane, (■) heptane, (□) octane, (▼) decane.

$P_{i2}^* = \sqrt{P_i^* P_2^*}$ . The results are shown in Fig. 3 in the form of a plot of calculated versus experimental specific retention volumes. The average relative error of the calculated data for all of the solutes and stationary phases was less than 10%. This is a satisfactory result in view of the fact that no adjustable (mixture) parameters were used. The temperature dependence of the retention volume data was calculated from Eq. (14) using the isobaric thermal expansion coefficient for the stationary phases given in Table 2. Likewise, the limiting (high temperature) values of the specific retention volume were calculated from Eq. (16) using the size parameters for the solutes given in Table 1. The results are shown in Fig. 4 in the form of a van't Hoff plot of  $1/\bar{\rho}_s \ln V_g^0$  vs.  $1/T$  in which a very unique intersection pattern is observed for the extrapolated lines which pass through a common point at about 900 °K. Such an extensive extrapolation to  $1/T=0$  is physically unrealistic, but the pattern is intriguing because the high temperature extrapolation would represent an

entropy dominated regime in which only the size parameter  $r_1$  would determine the retention volume of a solute. In this entropy-driven domain, the largest solute with the highest  $r_1$  value would be retained less than solutes with smaller  $r_1$  values in a given stationary phase due to the unfavorable entropy change for the larger solutes.

Although Eq. (16) is empirical, it provides a completely independent method for calculation of the size parameter for any solute from the limiting value of the specific retention volume for any stationary phase with known characteristic and size parameters. Table 3 shows the results for such calculations for the *n*-alkane systems. This method for the evaluation of lattice–fluid size parameters is unique due to the infinite dilution and the limiting high temperature condition of the solutes which means that no equation-of-state parameters are required for the evaluation of the size parameters for the solutes. The reversal of elution order of the solutes at high temperature is predicted by Eq. (16). The term in



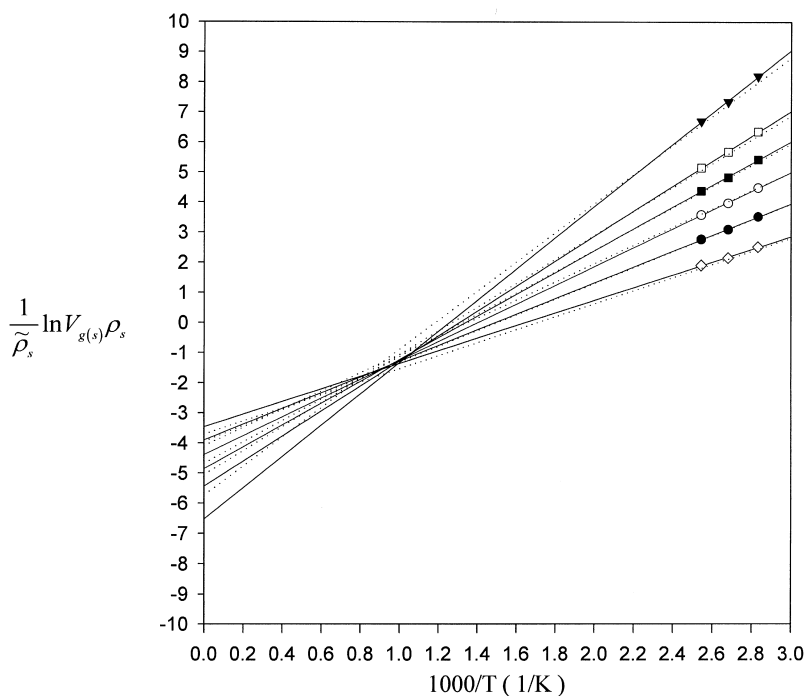


Fig. 4. van't Hoff plots for *n*-alkanes in  $n\text{-C}_{34}\text{H}_{70}$ . ( $\diamond$ ) Butane, ( $\bullet$ ) pentane, ( $\circ$ ) hexane, ( $\blacksquare$ ) heptane, ( $\square$ ) octane, ( $\blacktriangledown$ ) decane. Solid lines: regression of experimental data; dotted lines: calculated from Eqs. (14) and (15).

square brackets is always positive because  $\alpha_2$  is about  $10^{-4} \text{ K}^{-1}$  for most polymers. Thus, increasing  $r$  values for the solutes result in decreasing specific retention volumes as shown in Fig. 4.

With the exception of docosane, the calculated size parameters for a given solute are surprisingly independent of the stationary phase and reasonable close to the literature values determined by non-chromatographic experimental methods. The agreement is excellent considering the extended extrapolation to  $1/T \rightarrow 0$  to required for the chromatographic data.

## 2.2. Polystyrene stationary phase

In their original study, Sanchez and Rogers [3] analyzed their model using a portion of the retention volume data of Stiel and Harnish [14]. In the present investigation, the entire data set was used to evaluate Eq. (6) for the *n*-alkane solutes and the results are shown in Fig. 5. In this case, the theoretical line is plotted over the full temperature range and the theoretical lines for all the solutes converge at high temperature because of the unrealistic values of  $\tilde{\rho}_2$

Table 3  
Lattice–fluid model size parameters calculated from Eq. (16)

Solute	Stationary liquid phase						$r$		
	$n\text{-C}_{22}\text{H}_{46}$	$n\text{-C}_{24}\text{H}_{50}$	$n\text{-C}_{28}\text{H}_{58}$	$n\text{-C}_{30}\text{H}_{62}$	$n\text{-C}_{32}\text{H}_{66}$	$n\text{-C}_{34}\text{H}_{70}$	$n\text{-C}_{36}\text{H}_{74}$	Avg.	Lit. [12]
$n\text{-C}_4\text{H}_{10}$	5.6	–	6.6	6.0	6.7	6.4	6.6	6.3	7.6
$n\text{-C}_5\text{H}_{12}$	6.8	7.2	7.9	7.4	8.2	7.2	7.4	7.4	8.1
$n\text{-C}_6\text{H}_{14}$	7.7	8.3	8.6	8.2	9.1	8.1	8.1	8.3	8.4
$n\text{-C}_7\text{H}_{16}$	8.6	9.2	9.6	9.2	9.9	9.0	9.2	9.2	9.6
$n\text{-C}_8\text{H}_{18}$	9.4	10.4	10.7	10.2	10.9	10.1	10.1	10.3	10.3
$n\text{-C}_{10}\text{H}_{22}$	10.5	12.0	12.6	12.7	12.7	12.1	12.6	12.1	11.8

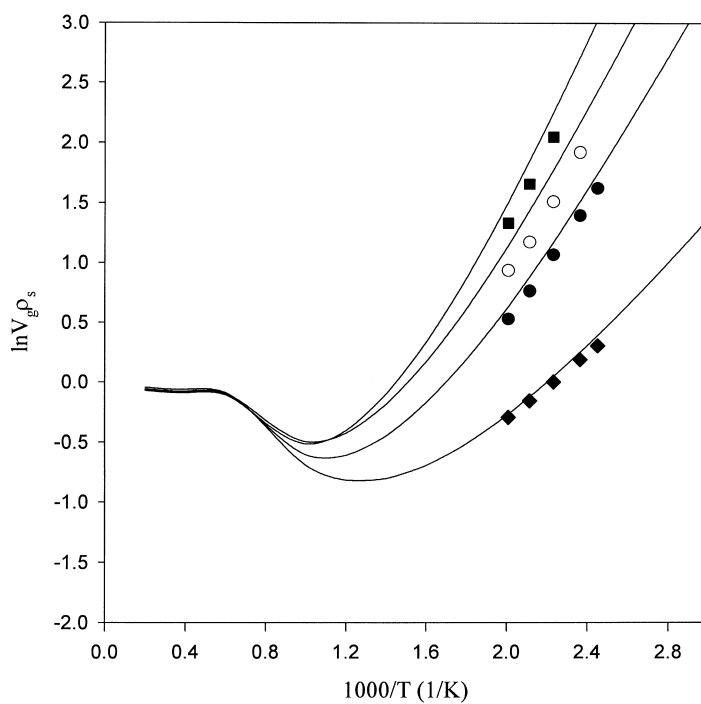


Fig. 5. Theoretical model, Eq. (6), for *n*-alkanes in polystyrene. (◆) Propane, (●) *n*-pentane, (○) *n*-hexane, (■) *n*-heptane.

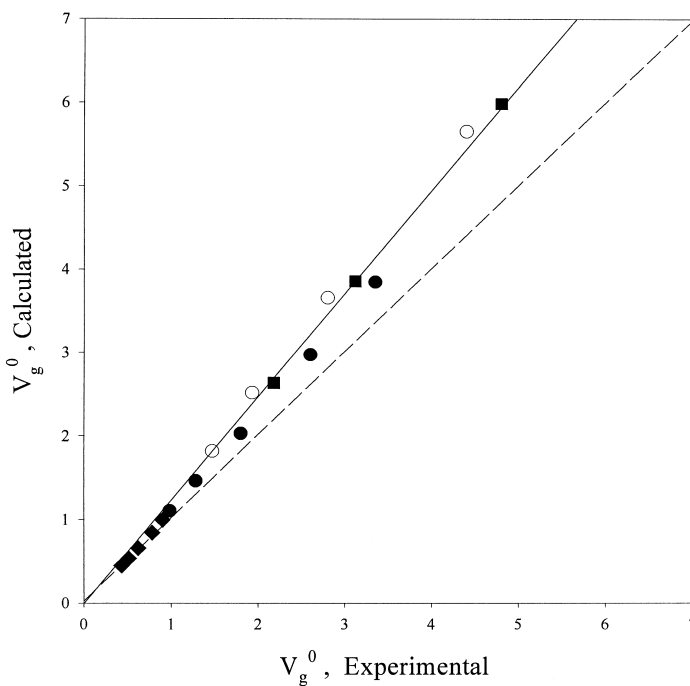


Fig. 6. Comparison of calculated and experimental [9] specific retention volumes for *n*-alkane solutes in polystyrene at 408, 423, 448, 473, and 498 K. (◆) Propane, (●) *n*-pentane, (○) *n*-hexane, (■) *n*-heptane, (---) ideal conditions.

predicted from the EOS at very high pressures. At the experimental temperatures, however, the model is reasonably accurate. The comparison of experimental and calculated specific retention volumes is illustrated in Fig. 6. The model consistently overestimates the retention volume by about 25%. This is comparable to Sanchez and Roger's reported maximum error of 30% for *n*-hexane in polystyrene [3]. The linear van't Hoff plots extrapolated from experiments to very high temperatures shown in Fig. 7 display the same intersection pattern as was observed with the *n*-alkane solutes. The size parameters calculated from Eq. (16) were 5.9, 8.1, 8.3, and 9.0 for propane, pentane, hexane, and heptane, respectively. The corresponding literature [12] values are 6.5, 8.1, 8.4, and 9.6.

### 2.3. Poly(dimethylsiloxane) stationary phases

Laub and co-workers have published an extensive collection of specific retention volume data for various poly (dimethylsiloxane) phases [18–21]. A preliminary investigation of this system, however, revealed a deficiency in the published [12] characteristic parameters for this stationary phase. The published characteristic parameters did not produce the correct density values over the experimental temperature range. Shih and Flory [22] measured the density of PDMS over a wide temperature range. The experimental data along with the density calculated from the published characteristic parameters are shown in Fig. 8. New values of the characteristic temperature and density were calculated from the

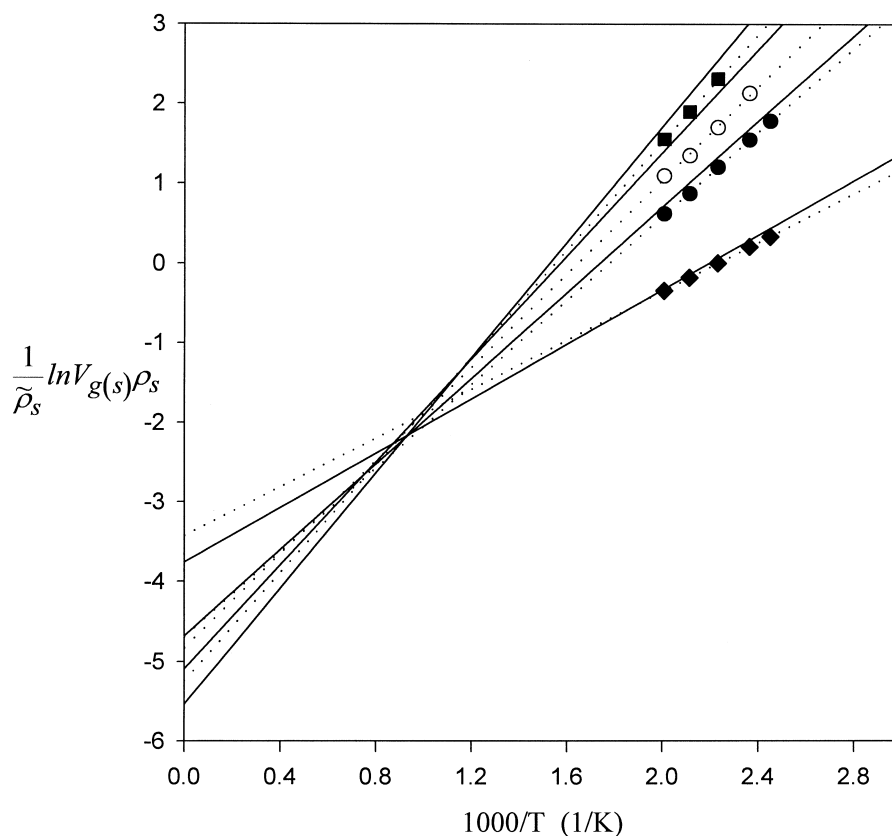


Fig. 7. van't Hoff plots for *n*-alkanes in polystyrene. (◆) Propane, (●) *n*-pentane, (○) *n*-hexane, (■) *n*-heptane. Solid lines: regression of experimental data; dotted lines: calculated from Eqs. (14) and (16).

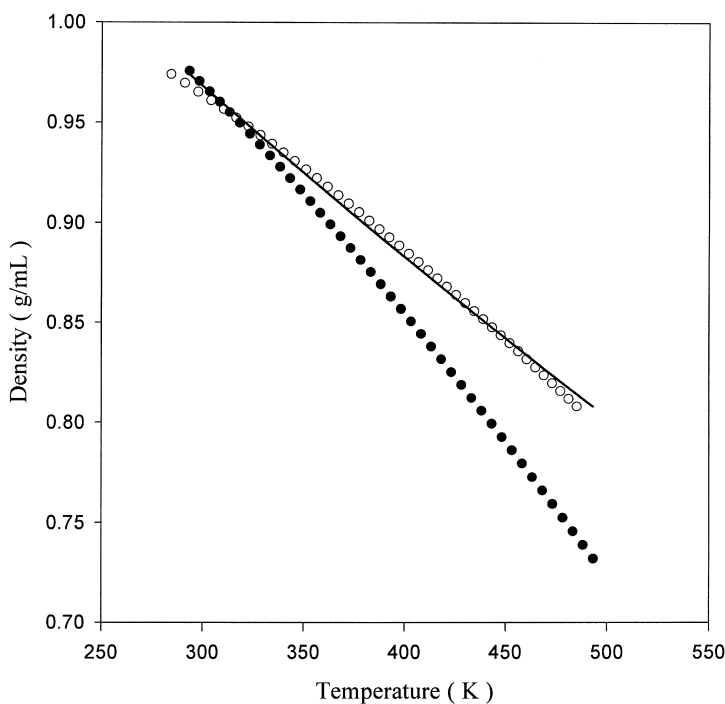


Fig. 8. Density calculated from Flory's polynomial [22]. (○) Density calculated from EOS using  $T^* = 577$  K,  $\rho^* = 1.04$  g/ml; (●) density calculated from EOS using  $T^* = 476$  K,  $\rho^* = 1.10$  g/ml.

experimental density data and the results are also illustrated in the figure. The revised characteristic temperature and density were used to calculate the specific retention volumes of six *n*-alkanes from 30 to 80°C. The results are shown in Fig. 9. In this case, the error increases with increasing size of the solute. The average error for *n*-pentane was 22% (comparable with polystyrene) but almost 70% for *n*-decane.

The temperature dependence of the specific retention volume for each solute is illustrated in Fig. 10. The common crossover phenomenon is again observed at high temperatures ( $\approx 650^\circ\text{C}$ .)

### 3. Conclusions

The lattice–fluid model proposed by Sanchez and Lacombe [8] provides a method to calculate absolute retention volumes for gas chromatographic systems using published characteristic constants for the solute and stationary phase and a geometric mean approximation for the mixture parameter  $P^*$ . The accuracy

of the model is excellent for *n*-alkane systems but less satisfactory for *n*-alkane solutes in polystyrene and poly(dimethylsiloxane). Nevertheless, the lattice–fluid model is one of the few available models that can be used to calculate specific retention volumes and partition coefficients for volatile solutes in liquids or polymers.

The equations are simple and tractable because no adjustable parameters are required. The energy density or characteristic pressure *for the mixture* is calculated using geometric mean approximation, i.e.  $P_{ij}^* = \sqrt{P_i^* P_j^*}$ . Thus, the retention volume equations should be accurate for systems in which the geometric mean approximation is accurate. That is, the model should be most accurate for systems in which the mer components of the solute and stationary phase are chemically similar. Thus it was observed that the alkane–alkane systems were accurately modeled; however, the results were less satisfactory for the stationary phases containing phenyl or siloxane moieties. The model can be made to fit experimental retention volumes for both the poly-

styrene and poly(dimethylsiloxane) systems by using an empirical correction to the interaction parameter as suggested by Rogers and Sanchez [4]; however, the integrity and elegance of the original model must be sacrificed.

If the isobaric thermal expansion coefficient of the stationary phase is known or can be calculated from the equation-of-state, the lattice–fluid model provides a foundation, Eq. (14), for calculating the slope of van't Hoff-type plots of  $1/\bar{\rho}_s \ln K^\circ$  vs.  $1/T$ , i.e. the enthalpy of transfer of the solute from the mobile to the stationary phases. Fig. 11 shows a comparison of the calculated and observed slopes for all of the systems investigated in this study. The agreement between the model and experimental data is good

even for the systems in which the calculated retention volume data were not satisfactory.

Finally, the model also provides a method, Eq. (16), to calculate the limiting value of the retention volume of chromatographic solutes at very high temperatures if the characteristic parameters for the stationary phase along with the size parameter of the solute are known. More interestingly, however, the measured limiting data can be used with Eq. (16) to calculate the size parameter for a chromatographic solute. The results of such calculations for all of the applicable system are illustrated in Fig. 12.

The Sanchez–Lacombe lattice–fluid model provides a theoretical foundation for the prediction and interpretation of gas chromatographic retention data

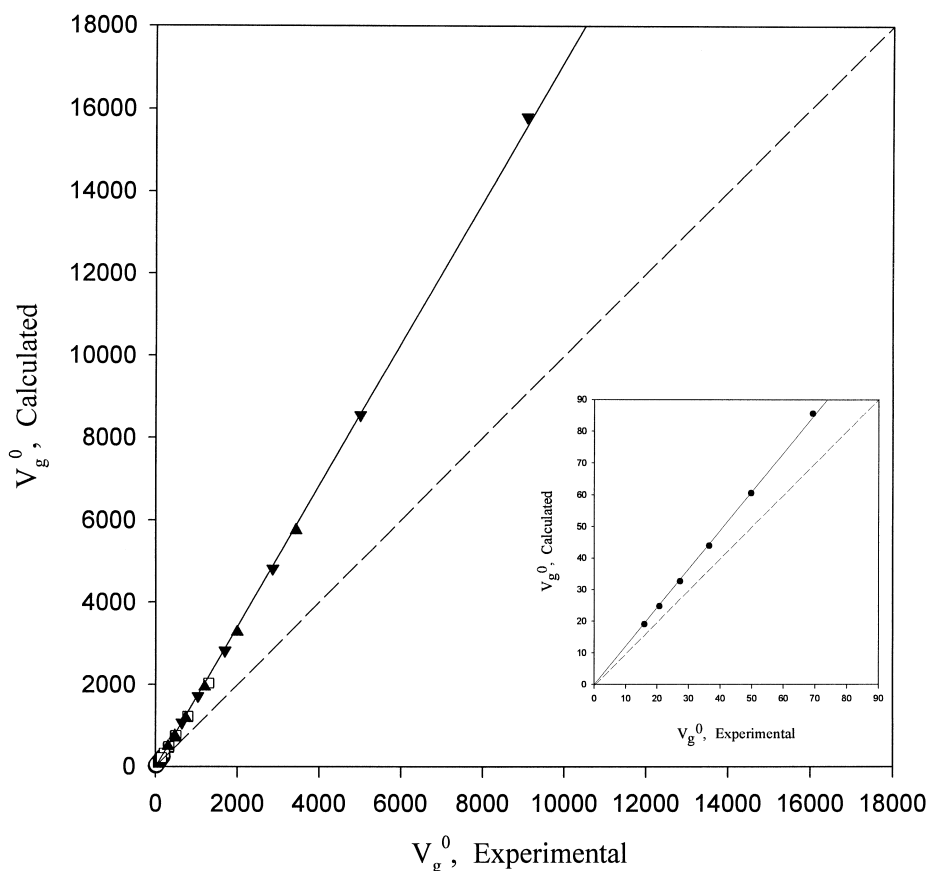


Fig. 9. Comparison of specific retention volumes of *n*-alkanes in PDMS. (●) Pentane, (○) hexane, (■) heptane, (□) octane, (▲) nonane, (▼) decane, (---) ideal conditions.

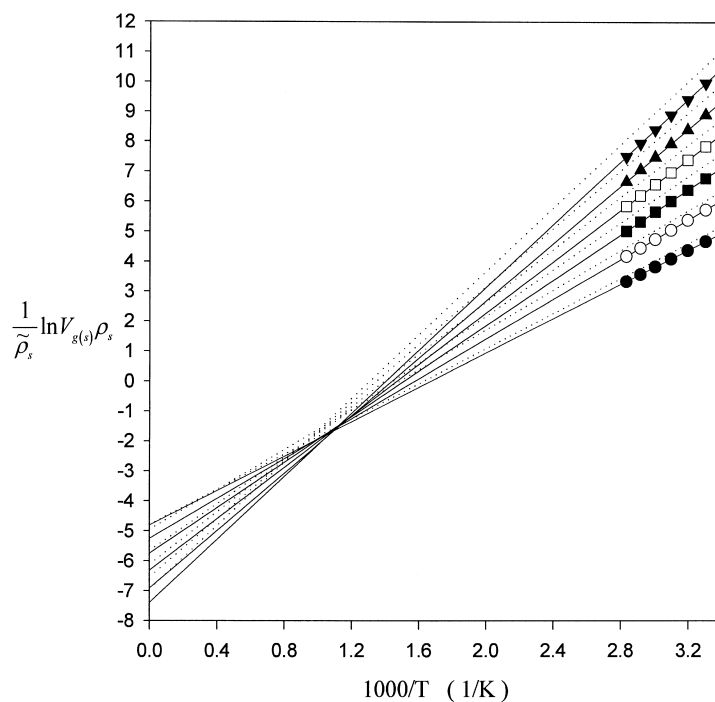


Fig. 10. van't Hoff plots for *n*-alkanes in PDMS. (●) Pentane, (○) hexane, (■) heptane, (□) octane, (▲) nonane, (▼) decane. Solid lines: regression of experimental data; dotted lines: calculated from Eqs. (14) and (16).

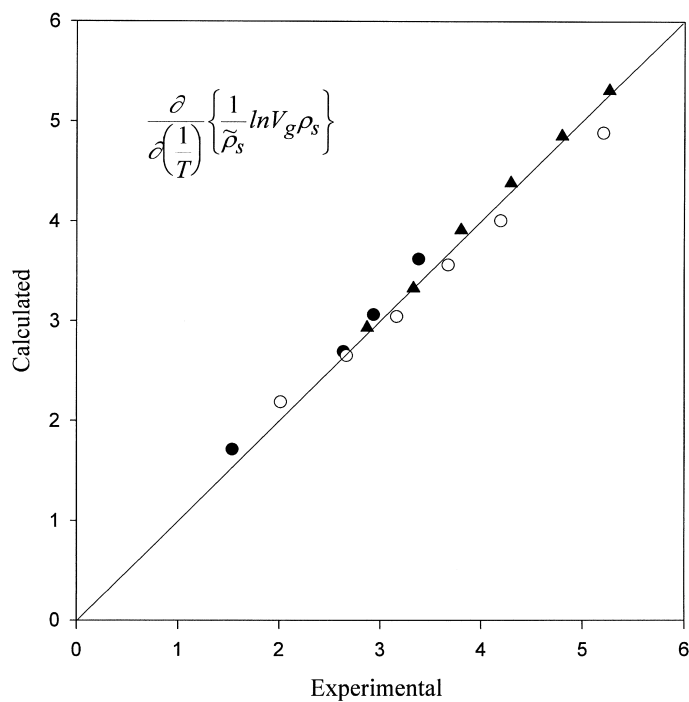


Fig. 11. Comparison of the slopes of *n*-alkanes in PDMS, polystyrene, and *n*-C<sub>22</sub>H<sub>46</sub>-*n*-C<sub>36</sub>H<sub>74</sub>. (▲) PDMS, (●) polystyrene, (○) *n*-C<sub>22</sub>H<sub>46</sub>-*n*-C<sub>36</sub>H<sub>74</sub>.

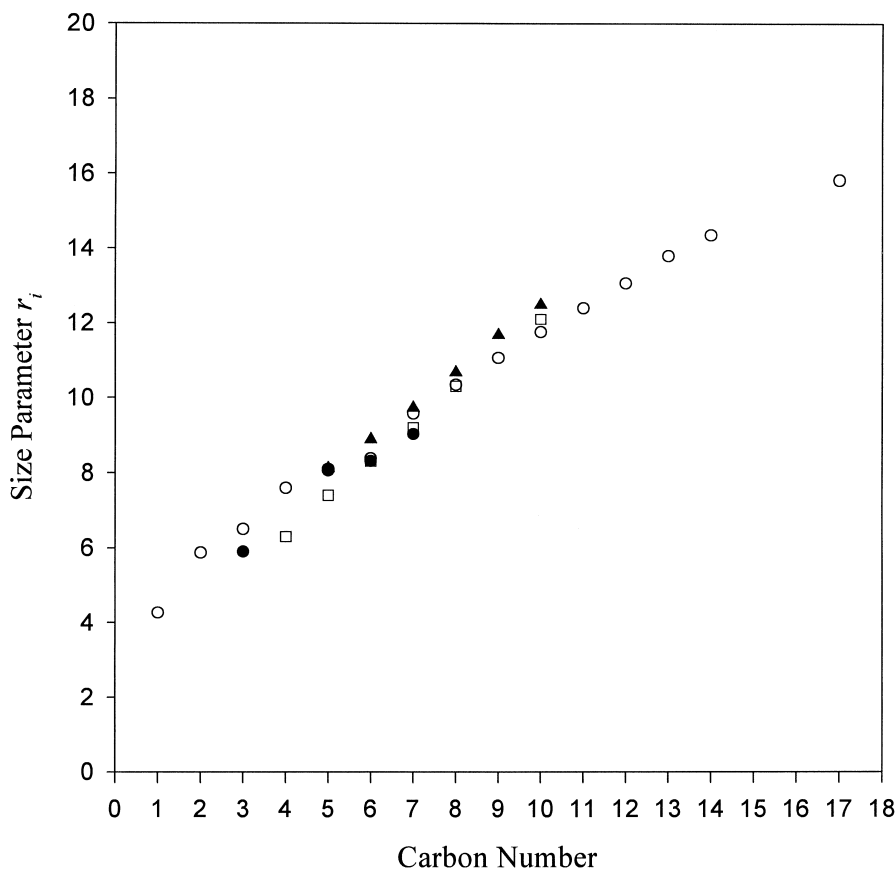


Fig. 12. Comparison of size parameters. (○) Sanchez and Panayiotou [12], (●) polystyrene, (□)  $n\text{-C}_{22}\text{H}_{46}\text{-}n\text{-C}_{36}\text{H}_{74}$ , (▲) PDMS.

as well as the effect of temperature on such chromatographic data. The next logical step will be to apply the same model to the much more complex systems encountered in supercritical fluid chromatographic systems.

### Acknowledgements

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