Global Phase Behavior of Mixtures of Short and Long *n*-Alkanes

The perturbed-hard-chain model of Beret, Donohue, and Prausnitz, in the simplified version of Kim et al., is compared with recent VLE data on mixtures of ethane and *n*-alkanes with carbon numbers from 16 to 24. By using and extrapolating the linear relations between the three adjustable model parameters and the carbon number, as given by Kim et al., we find that the experimental isothermal bubble curves are well represented up to the critical pressure without the use of any adjustable parameters. Experimental Henry constants for ethane in eicosane are well predicted at all temperatures. We find this global model more accurate than the Soave-Redlich-Kwong equation, even if the latter is fitted isotherm-by-isotherm to individual mixtures with temperature-dependent mixing parameters.

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Introduction

The phase behavior of mixtures of long and short *n*-alkanes is of importance both from a scientific point of view and for its practical interest. These mixtures are members of the class of systems containing chain molecules, such as polymer solutions. Fundamental approaches based on lattice statistics, such as that of Flory and Huggins, have yielded useful models for the fluid state, due to the introduction of phenomenological concepts by Hijmans (1961), Prausnitz and collaborators (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978), and others. The phase behavior of these mixtures is complex, as is evident from the experiments of Rowlinson and Freeman (1961), Schneider (1976), Lee and Kohn (1969), Puri and Kohn (1970), and Specovius et al. (1981), to name only a few.

The practical implications are many. They include the retrograde condensation of heavy compounds when depressurizing natural gas; the solubility of polymers; supercritical solubility of chain molecules; and liquid-liquid demixing in oil wells.

Our interest in the modeling of these systems arose because of the recent acquisition of a large body of phase equilibrium data in binary mixtures of ethane and normal alkanes with carbon numbers C from 16 to 30, at the Delft University of Technology by Peters et al. (1986–1988) and by Glaser et al. (1985). The Soave-Redlich-Kwong (SRK) equation was used to model the individual mixtures. The results were not satisfactory. Two mixing parameters were required to fit individual P-x isotherms. These mixing parameters were strongly and unpredictably temperature-dependent. This is not really surprising. In the SRK equation, there are no provisions for taking into account the chainlike character of the molecules, and the excluded volume is grossly oversimplified. An additional problem with the original fits was that the global features that mark these systems as members of a family were ignored so that no predictive power resulted from the fits. In contrast, the carbon number was effectively incorporated as an additional variable in the van der Waals model developed by Pegg et al. (1983) for the vicinity of the tricritical point in the quasibinaries of ethane and *n*-alkanes. Although the van der Waals equation suffers from the same defects as the SRK equation, in a limited range around the tricritical point an accurate representation of the global phase behavior was obtained.

The perturbed-hard-chain (PHC) theory of Beret and Prausnitz (1975) and Donohue and Prausnitz (1978), in the simplified version of Kim et al. (1986), appeared to us an excellent alternative to the cubic equations mentioned, since it incorporates the chain interactions and the density dependence of some intramolecular degrees of freedom of long molecules while, in addition, it describes the repulsive interactions by the much more realistic expression of Carnahan and Starling (1972). Kim et al. fitted the model to vapor pressure and coexistence curves of mostly pure alkanes with carbon numbers up to $C = 20$. They also found that the three adjustable model parameters correlate linearly with the carbon number. In this paper, we extrapolate their correlation of these parameters to higher carbon numbers, up to $C = 24$, and compare the model with our mixture data for

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ethane–*n*-alkane systems. We also compare with more restricted data for the mixtures of methane with hexadecane and eicosane. After a brief introduction of the model, the comparisons with the experimental vapor-liquid equilibrium (VLE) curves are presented. We demonstrate that the model with the pure-component parameters extrapolated from the correlation of Kim et al. leads to predicted behavior that is more accurate for the mixtures than that of the original Soave-Redlich-Kwong fits. We also compare with Henry constant data for ethane-eicosane over a considerable temperature range and find the model satisfactory. The existence of a validated model for mixtures of chain molecules opens up possibilities for studying global phase behavior in a realistic way. That is, not only can the model be used to study how the different types of phase behavior evolve in parameter space, but also we may expect it to predict which real mixtures, and under what conditions, will show particular features such as liquid-liquid demixing and tricriticality.

Perturbed-Hard-Chain Model

In the perturbed-hard-chain theory of Beret and Prausnitz (1975) and of Kim et al. (1986), those internal degrees of freedom of chain molecules that involve appreciable changes of conformation of the molecule, and that are therefore dependent on the density, are incorporated in the configurational partition function, according to an idea first developed by Prigogine (1957). The segments of each chain molecule are supposed to act like hard spheres of diameter σ. The repulsive part of the partition function is assumed to be of the form given by Carnahan and Starling (1972). In the present application, the diameter σ does not depend on temperature. Each segment is assigned an energy parameter ϵ representing the interaction energy with a segment of another molecule if it happens to be within the interaction range. The attractive interaction energy of the mixture is approximated by means of considerations that combine ingredients of the radial distribution function of square-well molecules with those of lattice statistics of chain molecules. For details, we refer to Kim et al. (1986).

In this model, a molecule with segments of species i is characterized by a chain length or number of segments s_i, a segment diameter σ_{ii}, an energy per unit surface area ϵ_{ii}, a total surface area q_i, and a number, $3c_i$, of density-dependent degrees of freedom. When the model is applied to a one-component fluid, only the products $T_i^* = \epsilon_{ii}q_i/c_ik$ and $v_{ii}^* = N_As_i\sigma_{ii}^3/\sqrt{2}$, with N_A = Avogadro's number, occur, together with c_i, as adjustable parameters. For a mixture of n different types of chain molecules, characterized by mole fractions x_i, $i = 1 - n$, the model parameters are obtained from those of the pure components by means of

$$\begin{aligned}\langle c\rangle &= \sum_i x_ic_i\\ \sigma_{ij} &= (\sigma_{ii} + \sigma_{jj})/2\\ \epsilon_{ij} &= \sqrt{\epsilon_{ii}\epsilon_{jj}}\,(1 - k_{ij})\\ \langle v^*\rangle &= \sum x_iv_{ii}^* = N_A\sum_i x_i\sigma_{ii}^3s_i/\sqrt{2}\\ v_{ij}^* &= N_A\sigma_{ij}^3s_j/\sqrt{2}\end{aligned} \tag{1}$$

In our application, $\sigma_{ij} = \sigma_{ii} = \sigma_{jj}$, $\epsilon_{ii} = \epsilon_{jj}$, and the mixture parameter k_{ij} is either set equal to zero or to a small, temperature-independent value.

The compressibility factor Pv/RT of the mixture is calculated from

$$Pv/RT = 1 + \langle c\rangle z^{rep} - \frac{Z_M\langle cv^*Y\rangle}{v + \langle cv^*Y\rangle/\langle c\rangle} \tag{2}$$

and with Z_M a constant set equal to 36 in this application. Also, in accordance with Carnahan and Starling (1972):

$$z^{rep} = \frac{4\tau\tilde{\rho} - 2(\tau\tilde{\rho})^2}{(1 - \tau\tilde{\rho})^3} \tag{3}$$

where

$$\tilde{\rho} = \langle v^*\rangle/v \qquad \text{and} \qquad \tau = 0.7405 \tag{4}$$

while

$$\langle cv^*Y\rangle = \sum_{ij} x_ix_jc_iv_{ji}^*\left(\exp\frac{\epsilon_{ij}q_i}{2c_ikT} - 1\right) \tag{5}$$

The corresponding expression for the fugacity coefficient can be found in the paper by Kim et al. These authors also list the pure-component parameters T_i^*, v_{ii}^*, and c_i for *n*-alkanes up to eicosane, which parameters were obtained by fitting coexistence curve and vapor pressure data. They showed that the model, thus defined by means of pure-component data only, represented the K values of the systems methane-propane, ethane-hexane, and Henry's constant for ethane-hexadecane without the need for introducing the mixture parameter k_{ij}.

Comparison with New VLE Data

We calculated the two-phase equilibrium for several mixtures at some of the experimental isotherms by equating fugacities of each component in the two phases. In Figures 1–4 we compare isothermal *P-x* data for the vapor-liquid equilibrium of the systems ethane-C_{16}, C_{20}, C_{22}, and C_{24}, respectively, where C_s denotes

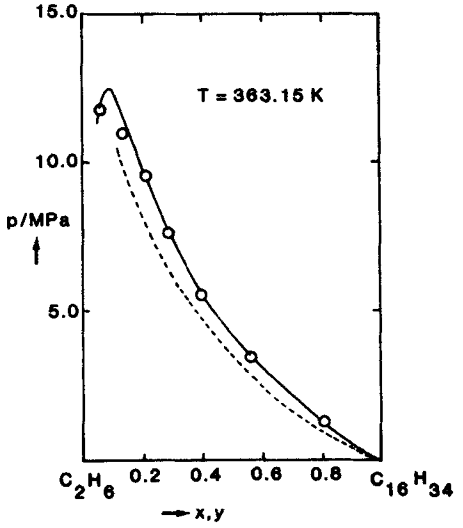

Figure 1. Comparison of VLE data for ethane-hexadecane at 363.15 K with PHC model.

○ exp. data, Peters et al. (1988a); ---- model, k_{12} = 0.000; —— model, k_{12} = 0.025

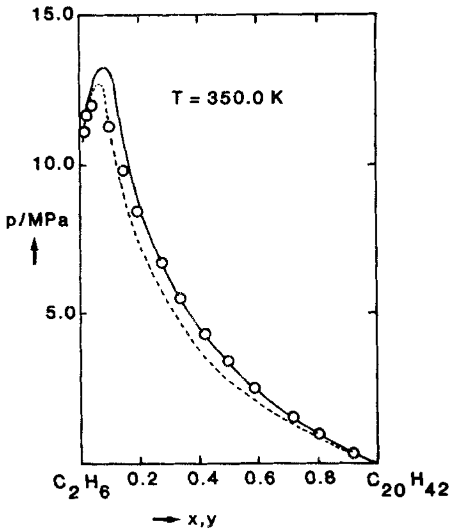

Figure 2. Comparison of VLE data for ethane-eicosane at 350.0 K with PHC model.

O exp. data, Peters et al. (1987b); ---- model, k_{12} = 0.000; —— model, k_{12} = 0.020

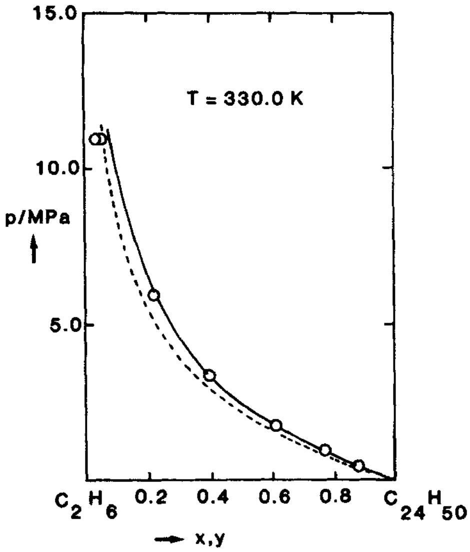

Figure 4. Comparison of VLE data for ethane-tetracosane at 330.0 K with PHC model.

O exp. data, Peters et al. (1987a); ---- model, k_{12} = 0.000; —— model, k_{12} = 0.020

an *n*-alkane with carbon number *s*. The data are mostly on the bubble side of the vapor-liquid loop. For the systems ethane-C_{22} and C_{24}, the pure-component parameters were obtained by linearly extrapolating the parameter vs. carbon number plots of Kim et al. With pure-component parameters only, the model predicts the steep rise of the *P-x* curve to better than 5% in pressure.

We have made no attempt to optimize k_{12} other than assigning it some small temperature-independent values. The model predictions with k_{12} = 0.02 for the system ethane-C_{24} are compared at several temperatures, 330 K (Figure 4), 340 K (Figure 5), and 350 K (Figure 6), and are all found to be accurate. Similarly, for the system ethane-C_{20}, the model, with the same value k_{12} = 0.02, predicts the VLE data at 350 K (Figure 2) and at 450 K (Figure 7) equally well.

In Figures 6 and 7 we compare the predictions of the perturbed-hard-chain model with constant k_{12} = 0.02 with those of the Soave-Redlich-Kwong equation. The pure-component parameters were taken from Reid et al., (1977) and Prausnitz et al., (1985). The k_{12} values were optimized for each individual isotherm, and found to be strongly temperature-dependent. The PHC model predicts the data for ethane-eicosane and ethane-tetracosane while the SRK equation, tailored to the individual isotherms, does not give adequate results with one mixing parameter; Peters (1986) obtained satisfactory results with two adjustable, temperature-dependent mixing parameters.

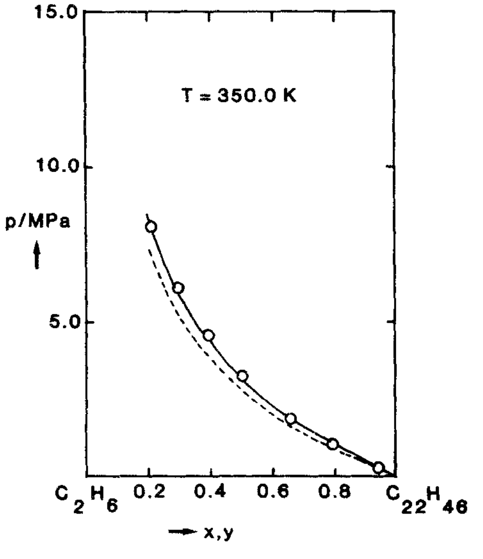

Figure 3. Comparison of VLE data for ethane-docosane at 350.0 K with PHC model.

O exp. data, Peters et al. (1988b); ---- model, k_{12} = 0.000; —— model, k_{12} = 0.015

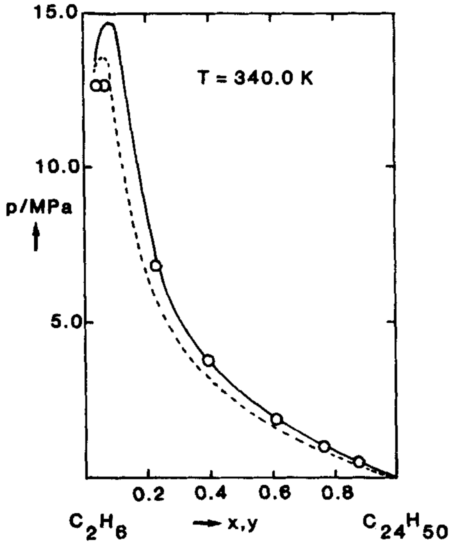

Figure 5. Comparison of VLE data for ethane-tetracosane at 340.0 K with PHC model.

O exp. data, Peters et al. (1987a); ---- model, k_{12} = 0.000; —— model, k_{12} = 0.020

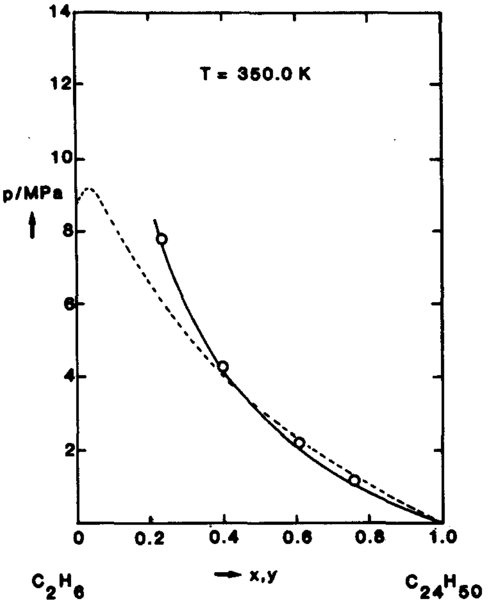

Figure 6. Comparison of predictive power of PHC model with k_{12} fixed at 0.020, with SRK equation with k_{12} optimized for the individual isotherm.

Data for ethane-tetracosane at 350.0 K

O exp. data, Peters et al. (1987a); ---- SRK, $k_{12} = -0.0204$; —— PHC, $k_{12} = 0.020$

Even though, in the comparisons in Figures 1–10, we have used several choices for k_{12} ranging from 0 to 0.025, it is obvious that the model is not very sensitive to the choice of k_{12}. A value of 0.02 for the mixture parameter for the interaction energy of unlike pairs k_{12}, the same in all cases and at all temperatures, leads to a good representation of the data over the entire composition range. Although quantitative agreement with the data near the critical point cannot be expected from a classical equation, the model appears to represent the top of the dew-bubble curve adequately.

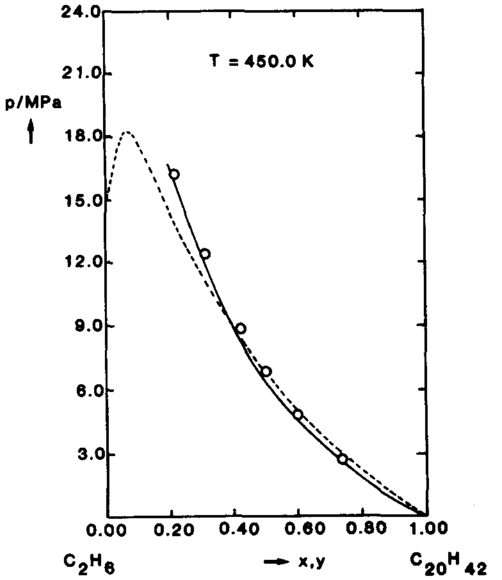

Figure 7. Comparison of predictive power of PHC model with k_{12} fixed at 0.020, with SRK equation with k_{12} optimized for the individual isotherm.

Data for ethane-eicosane at 450 K.

O exp. data, Peters et al. (1987b); ---- SRK, $k_{12} = -0.0077$; —— PHC, $k_{12} = 0.0200$

We have stretched the model to the limit by applying it to more restricted data sets for the system methane–*n*-alkane, knowing full well that methane does not fit in all that well with the other *n*-alkanes. In Figure 8, we compare with data for the system methane-hexadecane (Glaser et al., 1985). With the mixing parameter equal to zero, the model follows the top of the *P*-*x* curve accurately, but it is somewhat low in the range of intermediate pressures. Without adjustable mixing parameters, the SRK equation, however, misses the top of the *P*-*x* curve by 30% in pressure. Two adjustable mixing parameters, one for the interaction energy, one for the diameter of unlike pairs, are required to get an acceptable representation. In Figure 9 we show similar results for the system methane-C_{20} (van der Kooi, 1981).

Comparison with Experimental Henry Coefficients

Literature values of Henry's constants for ethane in eicosane are available from two sources, Ng et al. (1969) and Chappelow and Prausnitz (1974).

We have used the perturbed-hard-chain model to calculate the fugacity as a function of pressure. From the intercept of f/x vs. pressure, we obtained the model value of Henry's constant at each temperature. In Figure 10 we show the comparison of theory and experiment in the range 300–450 K. We also plot the calculated Henry's constant values at the measured pressures of Peters et al. (1987b). Although the predicted curve departs systematically from the experimental data at all temperatures, the average departures are of the same order as the scatter between the data set. This implies that the dilute mixture, near the pure-eicosane end, is well described by the perturbed-hard-chain theory, not only at 350 K (Figure 2) but over a large temperature range.

Discussion

We have applied a stringent test to the PHC model by comparing it with data for *n*-alkane mixtures with carbon numbers

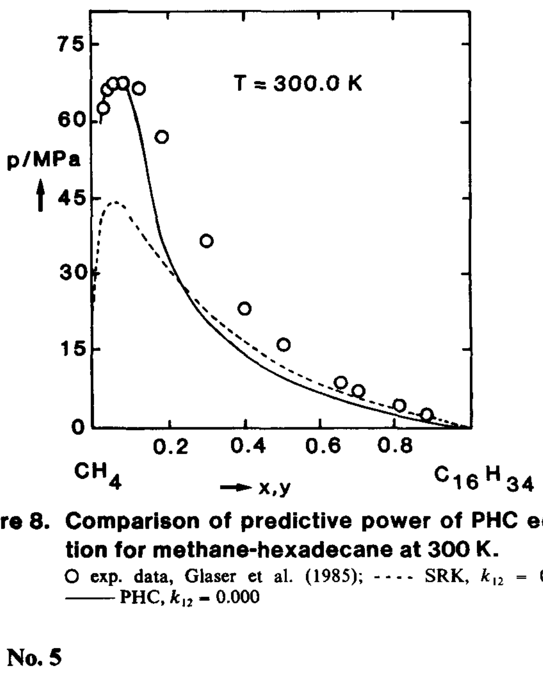

Figure 8. Comparison of predictive power of PHC equation for methane-hexadecane at 300 K.

O exp. data, Glaser et al. (1985); ---- SRK, $k_{12} = 0.000$; —— PHC, $k_{12} = 0.000$

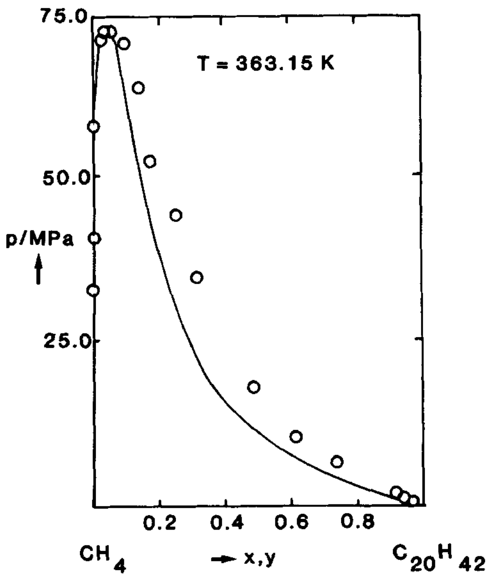

Figure 9. Comparison of predictive power of PHC equation for methane-eicosane at 363.15 K.

O exp. data, Kooi (1981); —— PHC eq.

outside the range to which the model had been fitted. Without any adjustable parameters, the model performs better than the SRK equation with one mixing parameter fitted isotherm-by-isotherm to the individual mixtures. Because of scarcity of data we have not tested the model on the dew side. Also, it is to be expected that the linear extrapolation of the model parameters may not be valid for arbitrarily high carbon number (G. Jin, private communication, 1987).

The model is ideally suited for studying global phase behavior, that is, the changes in the topology of phase diagrams as the interaction parameters, here determined by the carbon number, are varied. An example of such a study is the work of van Konynenburg and Scott (1980) for the van der Waals equation. We expect the present model to be considerably more realistic and therefore a better predictor for the phase behavior, three-phase split, or tricriticality of real systems. In order to determine the global behavior, it is necessary to find the critical lines and three-phase regions of binary mixtures. We have started this work.

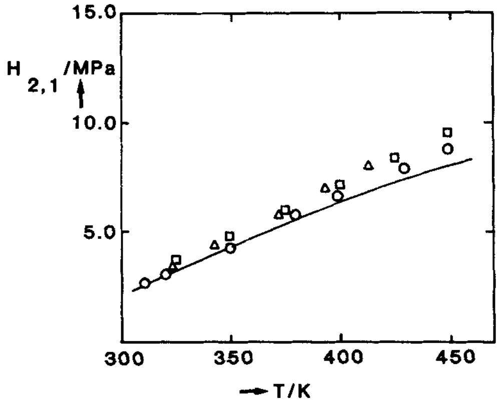

Figure 10. Comparison of experimental Henry constants for ethane in eicosane in the range 300–450 K with PHC model.

△ Ng et al (1969); □ Chappelow et al. (1974); O model at experimental pressures of Peters (1986); —— model, k_{12} = 0.025

The success the model has shown in describing the bubble curves of methane–*n*-alkane mixtures makes us hopeful that it can be used for describing retrograde condensation of natural gas. We are investigating this possibility.

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A NATO grant for collaborative research at the Department of Chemistry, Delft University of Technology, and the Thermophysics Division, National Bureau of Standards, enabled this work. We received generous advice, help and computer software from M. Donohue and G. D. Ikonomou at Johns Hopkins University and from R. A. Heidemann at the University of Calgary. We have profited from discussions with I. L. Pegg, G. Morrison and J. F. Ely at NBS.

Notation

C = carbon number
$3c_i$ = number of density-dependent degrees of freedom of molecules of species i
k = Boltzmann's constant
k_{ij} = mixture parameter for the interaction energy of unlike pairs
N_A = Avogadro's number
P = pressure
T = temperature
T_i^* = characteristic temperature for intersegmental interactions of type $i - i$
v = molar volume
v_{ii}^* = volume excluded by molecule of species i to segments of molecules of same species
v_{ij}^* = volume excluded by molecule of species j to segments of molecule of species i
q_i = surface area of molecule of species i
x = mole fraction in liquid phase
y = mole fraction in vapor phase
z = compressibility factor
Z_m = maximum coordination number

Greek letters

ϵ_{ij} = characteristic energy per unit surface area for segmental interactions of type $i - j$
ρ = density
σ_{ij} = hard-core diameter for $i - j$ segmental repulsion
τ = constant equal to 0.7405

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