Critical behavior and partial miscibility phenomena in binary mixtures of hydrocarbons by the statistical associating fluid theory

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Predictions of critical lines and partial miscibility of binary mixtures of hydrocarbons have been made by using a modified version of the statistical associating fluid theory (SAFT). The so-called soft-SAFT equation of state uses the Lennard-Jones potential for the reference fluid, instead of the hard-sphere potential of the original SAFT, accounting explicitly for the repulsive and dispersive forces in the reference term. The mixture behavior is predicted once an adequate set of molecular parameters (segment size, dispersive energy, and chain length) of the pure fluid is available. We use two sets of such parameters. The first set is obtained by fitting to the experimental saturated liquid density and by equating the chemical potential in the liquid and vapor phases for a range of temperatures and pressures. The second set is obtained from the previous one, by rescaling the segment size and dispersive energy to the experimental critical temperature and pressure. Results obtained from the theory with these parameters are compared to experimental results of hydrocarbon binary mixtures. The first set gives only qualitative agreement with experimental critical lines, although the general trend is correctly predicted. The agreement is excellent, however, when soft-SAFT is used with the rescaled molecular parameters, showing the ability of SAFT to quantitatively predict the behavior of mixtures. The equation is also able to predict transitions from complete to partial miscibility in binary mixtures containing methane. © *1998 American Institute of Physics.* [S0021-9606(98)51040-9]

I. INTRODUCTION

Knowledge of the thermodynamic properties of pure substances and their mixtures is essential for the design of processes used in the chemical industry, such as distillation, adsorption, and extraction. Unfortunately, such data often are not available, and may be difficult and expensive to obtain experimentally. Reliable equations of state for such compounds may be used to predict, with confidence, the thermodynamic properties, and in particular the phase equilibria behavior at different conditions.

Binary mixtures offer a wider and richer variety of phase behavior than pure fluids. When applying the phase rule to these kinds of systems, one finds not only gas–liquid phase equilibria, but also liquid–liquid and gas–gas coexistence, as well as three-phase regions. Another interesting feature of binary mixtures, not shown by pure fluids, is the fact that the critical points and three-phase coexistence states are not longer fixed thermodynamic points. Due to the presence of the additional component, these points have an extra degree of freedom, making it possible to find them along lines in the three-dimensional thermodynamic space (pressure-temperature-composition). When we increase the number of components to three, the variety of phase behavior is even richer.

The existence of tricritical points in ternary mixtures of hydrocarbons is associated to the presence of a three-phase region, liquid–liquid–gas (LLG), limited by two critical end points, an upper (UCEP) and a lower (LCEP).[1,2] Knowledge of the phase diagrams of binary mixtures of hydrocarbons allows one to select, in a systematic way, which ternary mixtures will exhibit such tricritical behavior.[3–11] In essence, what one looks for is a transition region in the phase diagram of two very similar binary mixtures in which there is a change from complete miscibility to partial miscibility (i.e., presence of a LLG three-phase line close to the critical point of the more volatile component), following the Rowlinson nomenclature.[12–14] There are several hydrocarbon mixtures exhibiting such behavior: methane(1) + *n*-pentane(2) and methane(1)+2,2-dimethylbutane(2) are typical examples of type-II systems in the Scott–Konynenburg classification,[2,15,16] characterized by the absence of the LLG line close to the critical point of methane. On the other hand, methane(1)+*n*-hexane(2) and methane(1)+2,3-dimethylbutane(2) present a type-IV phase behavior, showing partial miscibility close to the critical region of methane. Tricritical points occur at the border between type-II and type-IV behavior. There are cases where experimentally it is hard to distinguish between type-I and type-II, and type-IV and type-V behavior, respectively. The only difference between such types of diagrams is the presence of a three-phase region (LLG) at low temperatures, that ends at an UCEP. Depending on the system, such partially miscible regions can interact with the solid phase of the less volatile component, making it very difficult to confirm the existence of the UCEP at low temperatures.

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From the experimental point of view it is easier to study the three-phase region in binary systems with ethane rather than with methane, since in the first case the three-phase region lies at temperatures close to 40 °C while for methane the temperatures are near −70 °C. This fact is not relevant when one solves the problem theoretically, as long as the equation used does not depend on the thermodynamic conditions of the system. Although some of the traditional equations of state are able to *qualitatively describe* the phase behavior of hydrocarbon mixtures, only a few of them are able to *quantitatively predict* the phase behavior of these mixtures. Only molecular-based equations, with parameters with physical meaning and independent of the thermodynamic conditions, are able to predict with confidence the phase equilibria behavior at different conditions than those used during the fitting procedure. One of the most reliable equations of this type has proved to be the so-called SAFT equation of state (statistical associating fluid theory).[17] This equation is based on Wertheim's first-order thermodynamic perturbation theory for associating fluids,[18–20] using hard spheres as the reference term. The SAFT approach and term was first proposed and defined by Chapman *et al.*:[21,22] it means, in general, to combine a chain reference term with an associating perturbation term for the description of real fluids. SAFT was first widely applied as an equation of state for real fluids by Huang and Radosz.[17] Details of the different extensions of the Wertheim's theory, as well as SAFT, implementation, technical issues, extensions and comparisons with molecular simulations, and experimental results can be found elsewhere.[17,21–45]

In this work we check the ability of a modified version of the SAFT equation (soft-SAFT[42]) to predict the critical behavior of binary mixtures of hydrocarbons. The accuracy of the theory is tested versus experimental results for these systems. The equation is also used to study the existence of partial miscibility of some methane+alkane mixtures, with results compared to experimental results. A previous work[42] has shown the accuracy of this equation for predicting the phase behavior of binary and ternary mixtures of hydrocarbons. The molecular parameters of the pure components (segment size, dispersive energy, and chain length) were obtained by fitting to the experimental liquid density and by equating the chemical potential in both phases. The equation was able to quantitatively predict the vapor pressure of the pure fluids and the phase envelope of binary and ternary mixtures, except near the critical region. As expected from any analytical equation of state, the critical point was always overpredicted with this set of molecular parameters. Since in this work we are interested in checking the ability of soft-SAFT to predict the critical region (and less interested in the whole phase diagram envelope) we have used a second set of molecular parameters, derived from the first one, by rescaling them to the experimental critical temperature and pressure of pure alkanes. This method has been used previously in the literature with other versions of SAFT.[44,45] Both sets of molecular parameters are used to find the phase diagram of several binary mixtures, and to compare the predictions of the soft-SAFT equation with experimental results. In a future work we will use these results to predict the existence of tricritical points in two ternary mixtures of hydrocarbons with methane and ethane.[46]

The rest of this paper is organized as follows. A summary of the soft-SAFT equation of state is described in the following section. In Sec. III we discuss the phase diagram and critical lines calculations with this particular theory. Results of the phase equilibria of methane+alkane binary mixtures are presented and discussed in Sec. IV. Finally, conclusions are given in the last section.

II. THE SOFT-SAFT EQUATION OF STATE

Since the SAFT equation of state and its technical issues have been discussed in detail previously (see, for example, Blas and Vega[42] and references therein), here we will explain details concerning its implementation to the fluids studied in this work.

Molecules are represented as united atoms or sites: each site is assigned parameter values to represent a specific atom or group of atoms in the molecule of interest. Care must be taken when using the molecular parameters given in this work for other applications: although the molecular parameters have physical meaning (segment diameter, dispersive energy per segment, and chain length), they are *effective* parameters. This is due to the fact that we use a Lennard-Jones potential, instead of an *ab initio* potential.[17,43–45]

The *n*-alkanes are modeled as m Lennard-Jones segments of equal diameter σ, and the same dispersive energy ϵ, bonded tangentially to form the chain. Intermolecular and intramolecular dispersive energies are taken into account through the Lennard-Jones potential,

$$\phi = 4 \sum_i \sum_j \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} \right]. \tag{2.1}$$

This model accounts for three important attributes of chain molecular architecture: the bead connectivity, the excluded volume effects, and the attraction between differents beads. Although the model is simple compared to realistic models, it conserves the relevant features of the real system. Hence we expect to give good results and to accurately predict the thermodynamic properties as well as the phase equilibria.

The equation of state is written in terms of the Helmholtz free energy. The residual Helmholtz free energy ($A^r = A - A^{\text{ideal}}$) of a binary mixture of alkanes can be expressed as a sum of two terms, the reference term, which takes into account repulsions and attractions between different groups in the chains (intermolecular and intramolecular forces) through the Lennard-Jones potential A^{LJ}, and the perturbation term accounting for the chain formation A^{chain},

$$A^r = A^{\text{LJ}} + A^{\text{chain}}. \tag{2.2}$$

The total Helmholtz free energy is then calculated by adding the ideal contribution A^{ideal}.

The ideal term for a mixture of two components with N_m molecules takes the form,

$$A^{\text{ideal}} = N_m k_B T \{ x_1 \ln(\rho_m^{(1)} \Lambda_1^3) + x_2 \ln(\rho_m^{(2)} \Lambda_2^3) - 1 \}, \tag{2.3}$$

where $x_1=N_m^{(1)}/N_m$ and $x_2=N_m^{(2)}/N_m$ are the mole fractions, ρ_m is the molecular density, $N_m^{(1)}$ and $N_m^{(2)}$ are the number of molecules, Λ_i is the thermal de Broglie wavelength, k_B is the Boltzmann's constant, and V is the volume.

A^{LJ} is the Helmholtz free energy of a mixture of spherical Lennard-Jones molecules. We have chosen the Lennard-Jones equation of state by Johnson *et al.*[47]

The contribution to the chain formation is accounted for in the term A^{chain}. This term was independently introduced by Wertheim[20] and Jackson *et al.*[24] and Chapman *et al.*[25] from the first-order perturbation theory for associating spherical molecules. For a binary mixture of alkanes with bond lengths equal to σ_{11} and σ_{22}, the diameter of the Lennard-Jones sites in species 1 and 2, respectively, the final expression takes the form[40,42]

$$A^{\mathrm{chain}}=N_m k_B T\{x_1(1-m_1)\ln y_R^{(11)}(\sigma_{11}) + x_2(1-m_2)\ln y_R^{(22)}(\sigma_{22})\}, \tag{2.4}$$

where m_1 and m_2 are the chain length of species 1 and 2, respectively. $y_R^{(ii)}$ is the contact value of the cavity correlation function for spherical segments of species 1 and 2 in the Lennard-Jones reference fluid. $y_R^{(11)}$ and $y_R^{(22)}$ are easily related to the pair radial distribution functions of the Lennard-Jones fluid, $g_R^{(11)}$ and $g_R^{(22)}$.

Since the Helmholtz free energy is calculated by adding different terms, each of them should be expressed in terms of compositions for mixtures studies. We use the van der Waals one-fluid theory (vdW-1f) to describe the A^{LJ} term of the mixture. In this theory, the residual Helmholtz free energy of the mixture is approximated by the residual Helmholtz free energy of a pure hypothetical fluid,[48] with parameters σ_m and ϵ_m calculated from

$$\sigma_m^3=\frac{\sum_{i=1}^2\sum_{j=1}^2 m_i m_j x_i x_j \sigma_{ij}^3}{\sum_{i=1}^2\sum_{j=1}^2 m_i m_j x_i x_j}, \tag{2.5a}$$

$$\epsilon_m\sigma_m^3=\frac{\sum_{i=1}^2\sum_{j=1}^2 m_i m_j x_i x_j \epsilon_{ij}\sigma_{ij}^3}{\sum_{i=1}^2\sum_{j=1}^2 m_i m_j x_i x_j}, \tag{2.5b}$$

where the mixing rules for a Lennard-Jones mixture have been expressed as a function of the chain molar fractions. The chain term A^{chain} depends explicitly on composition and no changes are needed for mixtures.

To obtain the pair correlation function of a mixture of Lennard-Jones spheres, the same mixing rules (vdW-1f) have been used as in a previous work.[42] For the crossed interactions, the Lorentz–Berthelot combining rules are used.[42] For details, see Eqs. (14), (15), and (16) in Ref. 42. The applicability of the vdW-1f theory, with Lorentz–Berthelot combining rules for binary and ternary mixtures of Lennard-Jones spheres and chains has proved to be excellent in previous studies.[37,49–51]

III. PHASE EQUILIBRIA AND CRITICALITY

In this section we outline the techniques used to obtain the phase equilibria and critical behavior of binary mixtures with the soft-SAFT equation of state. For a more detailed description of the solution of a mixture's equation of state for phase equilibria and critical points, see the work of Scott and Konynenburg.[15,16]

The usual conditions, equality for pressure, temperature, and chemical potential in each phase, for liquid–vapor equilibria in both pure component and binary systems, liquid–liquid equilibria in binary mixtures, and liquid–liquid–gas three-phase coexistence line, as well as for the critical lines, have been found by solving the corresponding equations using the Marquart–Levenberg algorithm.[52]

Binary mixture critical points occur when the second and third derivatives of the Gibbs free energy with respect to composition are equal to zero at constant pressure and temperature, i.e.,

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{P,T}=\left(\frac{\partial^3 G}{\partial x^3}\right)_{P,T}=0. \tag{3.1}$$

In addition to these equations, classical stability for critical points is required through the extra condition,

$$\left(\frac{\partial^4 G}{\partial x^4}\right)_{P,T}>0. \tag{3.2}$$

The soft-SAFT equation of state is given in terms of the Helmholtz free energy and its natural thermodynamic variables are temperature, volume, and composition. Hence it is more convenient as in other equations of state (van der Waals type) to express the critical conditions in terms of derivatives of the Helmholtz free energy with respect to volume and composition, at constant temperature,

$$A_{2x}A_{2V}-A_{Vx}^2=0, \tag{3.3a}$$

$$A_{3x}-3A_{V2x}\left(\frac{A_{Vx}}{A_{2V}}\right)+3A_{2Vx}\left(\frac{A_{Vx}}{A_{2V}}\right)^2-A_{3V}\left(\frac{A_{Vx}}{A_{2V}}\right)^3=0, \tag{3.3b}$$

where the notation $A_{nVmx}=(\partial^{n+m}A/\partial V^n\partial x^m)_T$ is used for the derivatives of the Helmholtz free energy.[2]

Binary mixtures have been classified in six major groups by van Konynenburg and Scott[2,15,16] depending on their phase behavior. The six principal classes of phase diagrams are easily differentiated by using their projection of the phase diagram over the pressure–temperature plane, as shown in Fig. 1. Type I shows a continuous gas–liquid critical line connecting the critical points of the two pure components. Type II shows a liquid–liquid–gas three-phase line at low temperatures ending at an upper critical end point (UCEP), where a liquid–liquid critical line starts and evolves through high pressures, in addition to the gas–liquid critical line of type I. In type III the gas–liquid critical line is no longer continuous, having two branches, one ending at an UCEP and the other merging into the liquid–liquid critical line. Systems with type IV behavior have two gas–liquid critical lines, one of which ends at an UCEP and the other one at a lower critical end point (LCEP), and a liquid–liquid critical line as in type II. Type V is similar to type IV but with the absence of the liquid–liquid critical line. Finally, type VI is similar to type II with the liquid–liquid inmiscibility disappearing at low temperatures and the corresponding critical line ending at a LCEP.

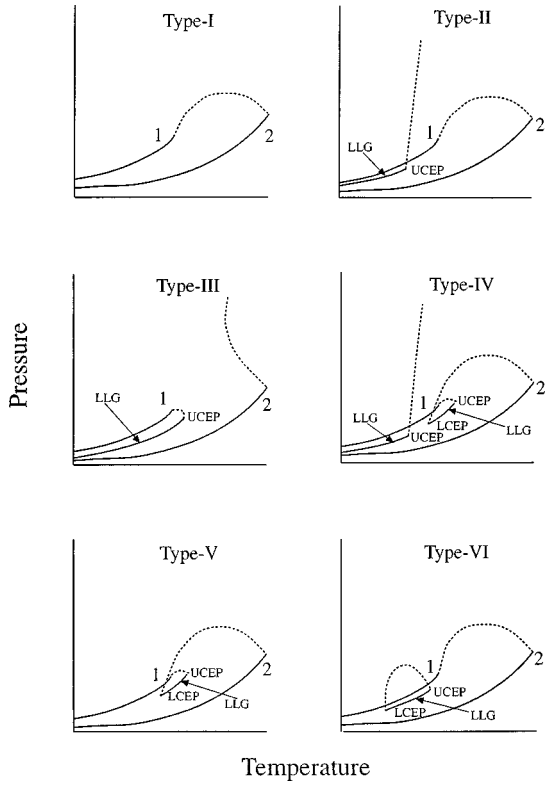

FIG. 1. Pressure-temperature diagrams of the six different classes of phase behavior according to the Scott and Konynenburg classification (Refs. 2, 15, and 16).

IV. RESULTS AND DISCUSSION

Here we check the ability of the soft-SAFT equation of state to predict the critical behavior of some experimental systems. In particular, we have applied the soft-SAFT equation of state to calculate the critical lines of two binary series of hydrocarbons: *n*-butane(1)+alkane(2) and methane(1) +alkane(2). In addition, we have obtained the complete phase diagram of some binary mixtures of the methane series, finding partial miscibility in some of them, as occurs experimentally.[12–16] In all cases we compare theoretical results with experimental data.

In order to study the phase equilibria and the critical lines of binary mixtures with SAFT, molecular parameters for pure compounds, the segment size σ, the dispersive energy ϵ, and the chain length m, are needed. There are two choices of molecular parameters. The first set, found in a previous work,[42] is obtained by fitting to the saturated liquid density and by equating the chemical potential in both phases. These values, shown in Table I, have proved to provide a good representation of the vapor pressure curve, as well as the liquid–vapor coexistence over a wide range of temperatures, except in the region near the critical point. Since in the current study we are interested in *predicting* the critical lines, we have chosen a different approach, which has proven to better predict the critical behavior with other equations of state.[44,45] The second set of molecular parameters has, then, been found from the previous one in the following way. We rescale σ, the segment size and ϵ, the dispersive energy, to the experimental critical pressure and temperature

TABLE I. Nonscaled and scaled molecular parameters to critical properties of pure alkanes. See text for details.

Compound	σ (nm) (nonscaled)	ϵ/k_B (K) (nonscaled)	σ (nm) (scaled)	ϵ/k_B (K) (scaled)	m
Methane	0.3722	147.3020	0.3843	144.9403	1.0000
Ethane	0.3585	190.3750	0.3760	186.6281	1.5936
Propane	0.3657	207.9678	0.3853	203.4697	1.9969
n-butane	0.3801	229.7099	0.4048	224.2150	2.1959
n-pentane	0.3778	232.9734	0.4016	227.4589	2.6991
n-hexane	0.3662	233.6598	0.3908	225.8652	3.3673
n-heptane	0.3697	240.1248	0.3964	231.8685	3.7256
n-octane	0.3787	249.8109	0.4070	239.2301	3.9476
2,3-dimethyl butane	0.3656	229.3312	0.3885	224.1675	3.2991

of pure alkanes; this gives a better representation of the vapor pressure curve near the critical point. It should be noted that although this procedure provides a better description of the phase diagram near the critical region, it does not reproduce the features of the real phenomena. Near the critical point density fluctuations become important and they are not accounted for by this equation of state. To describe such phenomena one should take into account the inhomogeneity of the system near the critical point.

Before presenting results obtained for critical lines we compare the vapor pressure predicted by soft-SAFT with the experimental results to test the accuracy of both sets of molecular parameters. Figure 2 shows the comparison between the predicted vapor pressure curve and the experimental data[53] for the *n*-alkane series, from methane to *n*-octane. Temperature is given in kelvin, pressure in MPa, and molecular density in mol/dm^3. Figure 2(a) presents results obtained with the nonscaled molecular parameters. The agreement between experimental results and predictions is excellent over a wide range of temperatures, except in the region near the critical point. This is due to the fact that we are using an analytical equation of state with classical exponents near the critical region and we are fitting far from this region. As expected, a better representation of the critical region is obtained when using the rescaled molecular parameters, as shown in Fig. 2(b). Notice that this new set of parameters not only gives accurate results near the critical region, but also over the whole range of the experimental temperatures. However, although the description of the pressure–temperature diagram with the rescaled molecular parameters is good, the liquid density is not as accurate as it was with the first set, as expected. This is the price paid by just looking at the critical region. It is not possible to simultaneously predict the critical region *and* the phase envelope over a wide range of temperatures with the *same* set of molecular parameters and an analytical equation such as soft-SAFT.

A. The *n*-butane series

In this section we present results for the series *n*-butane+*n*-alkane from methane up to *n*-octane. It is generally accepted in the literature that *n*-butane is the first member of the series that behaves regularly with respect to the rest of the members. Methane and ethane, and depending

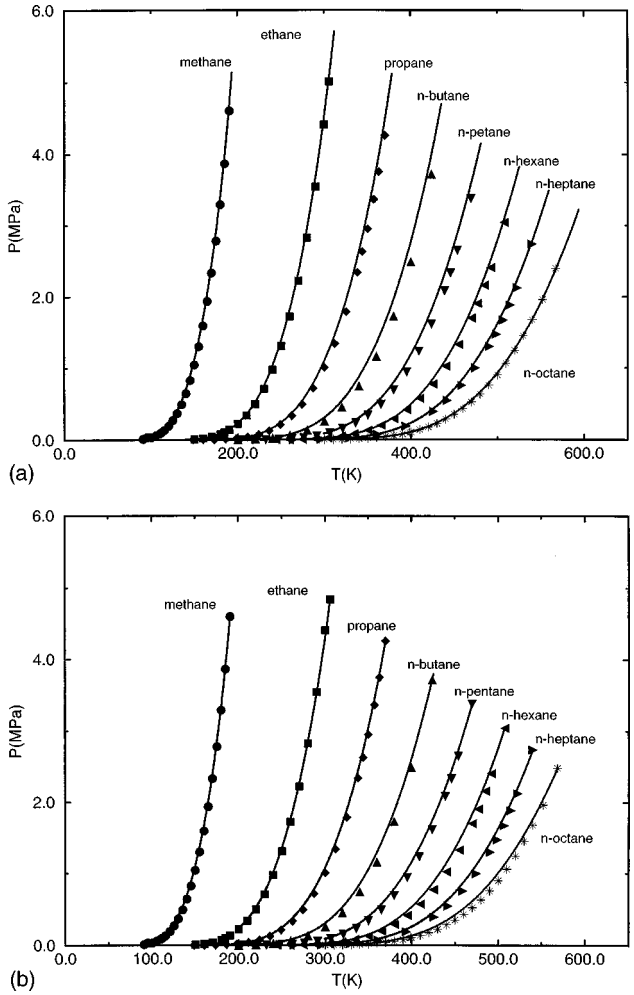

FIG. 2. Vapor pressure curves of the first members of the *n*-alkane series. Solid lines represent predictions from the soft-SAFT equation of state and symbols correspond to the experimental results taken from the literature. (a) Soft-SAFT with nonscaled molecular parameters, (b) soft-SAFT with the scaled parameters. See text for explanation.

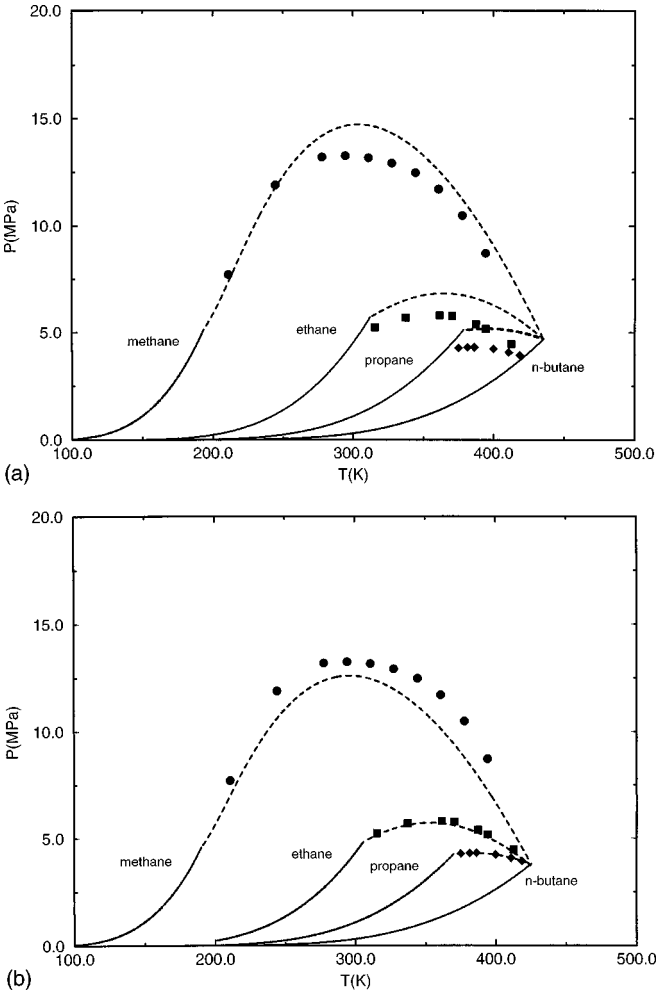

FIG. 3. Pressure-temperature diagram of the first binary mixtures of *n*-butane+*n*-alkane systems predicted by the soft-SAFT equation of state. (a) The predictions by SAFT when the nonscaled molecular parameters are used, (b) the same systems when using scaled parameters. Solid lines are the vapor pressure of pure components, the dotted line is the predicted critical line, and symbols correspond to the experimental critical points of the mixture.

on the thermodynamic property to study, propane as well, show an anomalous behavior with respect to the rest of the series. A typical example of such anomalous phenomena is the well-known effect of dependency of the critical pressure with the number of carbons: critical pressure, when correlated with the number of carbon atoms, is a monotonous decreasing function, except for methane and ethane (the critical pressure of ethane is higher than that of methane). Hence we have chosen to begin this study with binary mixtures of *n*-butane. Note that once the molecular parameters of the pure fluid are obtained, predictions for any binary mixture can be made just by using the Lorentz–Berthelot combining rules, without any further adjustment.

The pressure–temperature diagrams of the members of the *n*-butane+*n*-alkane series, from *n*-butane(1) +methane(2) to *n*-butane(1)+*n*-propane(2), are shown in Fig. 3. Figure 3(a) represents predictions of the soft-SAFT equation of state with the nonscaled molecular parameters. Solid lines correspond to the vapor pressure curves of pure components. The end lines in all curves represent the predicted critical points of *n*-alkanes. The dashed lines are the critical lines given by soft-SAFT and the symbols represent the experimental critical lines of these mixtures taken from the literature.[54] As can be seen, all are continuous liquid–gas critical lines (type-I behavior according to the Scott and Konynenburg classification[2,15,16]). Although the equation is able to capture the shape of the critical lines, it only agrees qualitatively with experimental data when using this set of parameters. This is an expected result since we are using an analytical equation of state with mean-field mixing rules (van der Waals one-fluid approximation). Figure 3(b) shows the same diagrams as in the previous figure, but using the parameters scaled to critical properties. Note that using the same equation and just rescaling the parameters of the pure components, a quantitative agreement with experimental critical lines of the mixture is obtained. Special attention should be paid to binary mixtures with low molecular weight compounds, such as methane and ethane. These compounds, as previously mentioned, show an anomalous behavior in some thermodynamic properties. The small discrepancies between predictions and experimental results for the critical

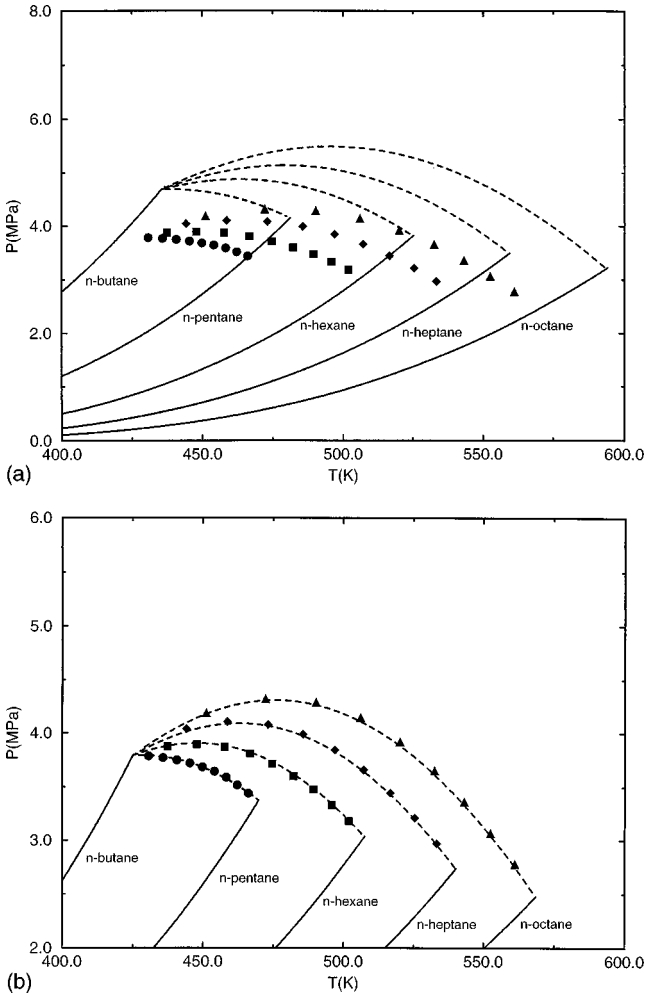

FIG. 4. Detail of the critical region of the pressure-temperature diagram of several binary mixtures of the *n*-butane series. Symbols as in the previous figure. (a) The predictions by SAFT when nonscaled molecular parameters are used, (b) the behavior of the phase diagram when scaled parameters are used.

line of *n*-butane(1)+methane(2) may be due to such effects.

The rest of the *n*-butane series is presented in Fig. 4. It shows the pressure–temperature diagrams for the binary mixtures from *n*-butane(1)+*n*-pentane(2) to *n*-butane(1) +*n*-octane(2). Symbols and lines are used as in Fig. 3. Both the experimental data[54] and the predictions from soft-SAFT show that all these mixtures exhibit continuous gas–liquid critical lines (type-I behavior). Again, the agreement between experimental and theoretical results is excellent when using the second set of molecular parameters. In these figures we show only the vapor pressure curves close to the critical points since we are interested in the critical lines.

B. The methane series

We first show results for the critical lines of three binary mixtures with methane, namely, methane(1)+ethane(2), methane(1)+propane(2), and methane(1)+*n*-butane(2). The pressure-composition diagram of these mixtures is shown in Fig. 5. Symbols and lines are used as in Fig. 3. Here we use the scaled molecular parameters since these have proved to better predict the critical behavior of mixtures. The agreement between the experimental and theoretical results is excellent for methane(1)+ethane(2) and methane(1)+propane(2) mixtures. In the methane(1) +*n*-butane(2) binary mixture, the agreement is poorer, as discussed in the previous section. In all cases the phase behavior corresponds to type-I.[2,15,16] No evidence has been found of partial miscibility at any thermodynamic condition in these mixtures.

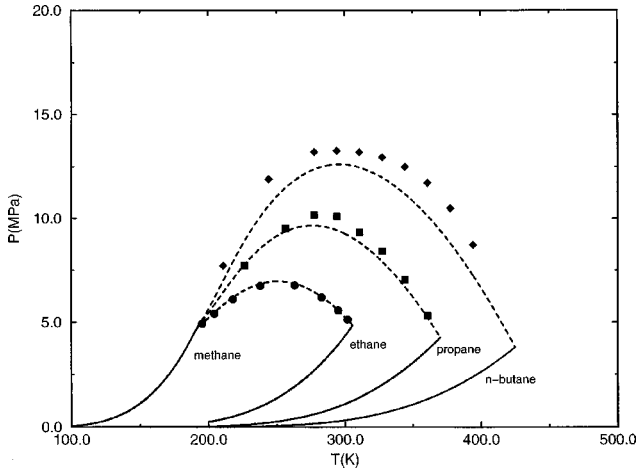

FIG. 5. Pressure-temperature diagram of the first binary mixtures of the methane series. Solid lines represent the predictions of the gas–liquid curve of pure components. Dashed lines are the predictions for the critical lines of the mixtures and symbols are the experimental critical points of the different mixtures. Only scaled molecular parameters are used with SAFT.

Figure 6 shows the pressure-temperature composition diagram of the binary mixture methane(1)+*n*-pentane(2). Only scaled molecular parameters are used for SAFT. Symbols and lines are used as in previous figures. The agreement between predictions from the soft-SAFT equation of state and experimental results is very good. The small differences between both results could be due to the fact that the mixture contains methane, as explained previously.

As mentioned before, we are interested in studying partial miscibility of alkane mixtures by the soft-SAFT equa-

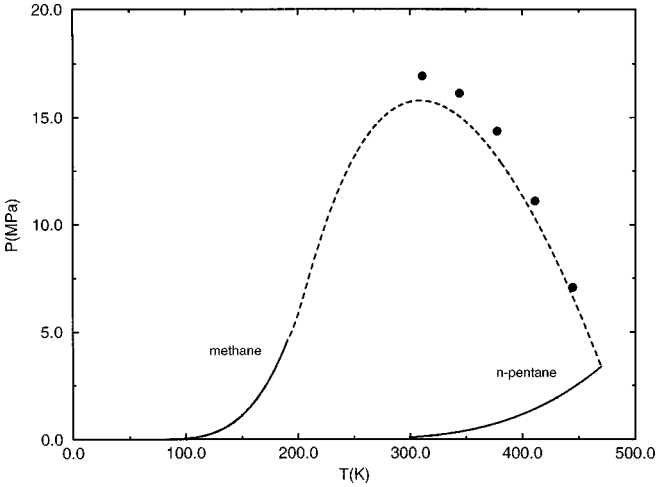

FIG. 6. Pressure-temperature diagram of the mixture methane(1) +*n*-pentane(2). Symbols as in the previous figures. Only scaled molecular parameters are used with SAFT.

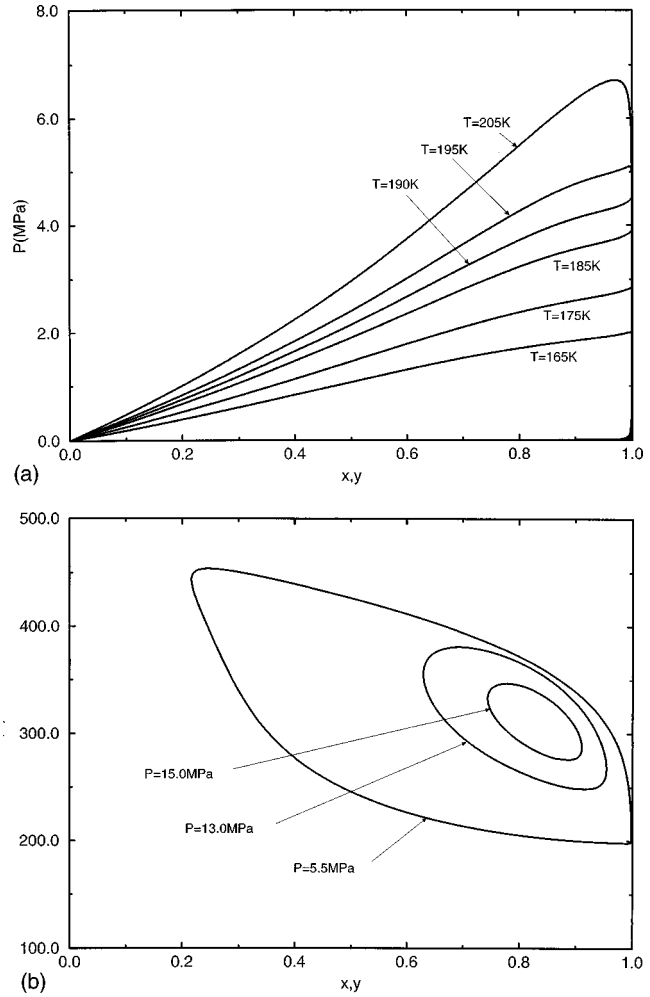

FIG. 7. Projections of the phase diagram of the binary mixture methane(1)+*n*-pentane(2) at different temperatures and pressures. The predictions by SAFT (solid lines) have been calculated using the scaled molecular parameters set. Pressure-composition diagram (a) is shown at several temperatures near the critical temperature of methane. (b) The temperature-composition diagram at different pressures.

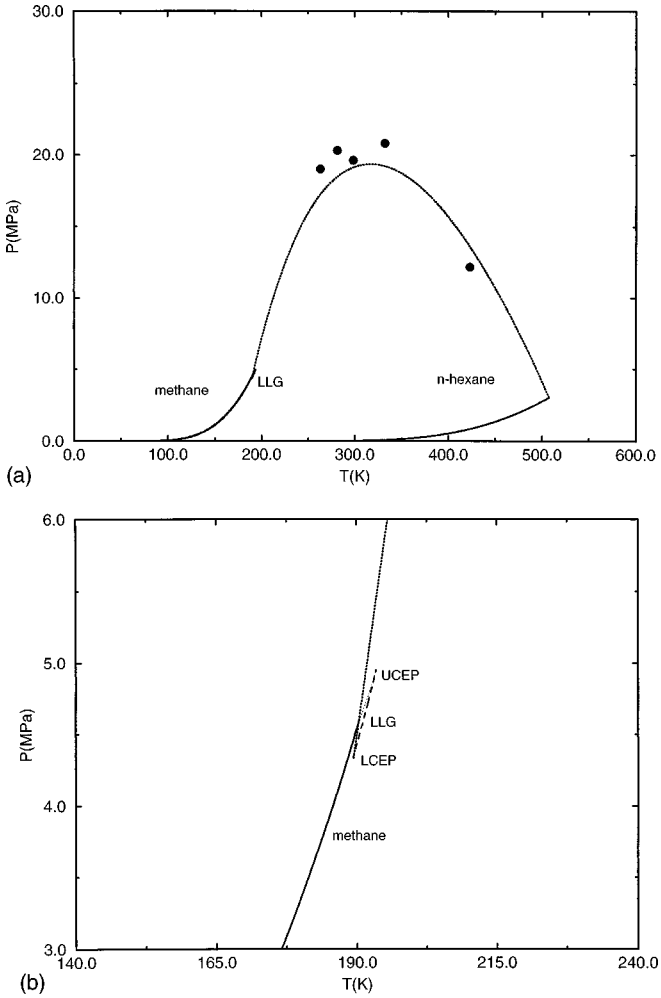

FIG. 8. Pressure-temperature projection of the phase diagram of methane(1)+*n*-hexane(2). (a) The complete phase diagram of the system. (b) The region near the critical point of methane enlarged. Symbols as in the previous figures. Only scaled molecular parameters are used with SAFT.

tion. Our interest is in finding the transition behavior from type-I to type-V. Knowledge of this behavior is very useful in order to select, in a systematic way, ternary mixtures of alkanes (with methane as the first component) that exhibit tricritical behavior. For this purpose we have studied the pressure-composition and temperature-composition diagrams of methane(1)+*n*-pentane(2) at different temperatures and pressures. Results from soft-SAFT are shown in the pressure-composition diagram at temperatures between 165 and 205 K [Fig. 7(a)] and in the temperature-composition diagram at pressures between 5.5 and 15 MPa [Fig. 7(b)]. Predictions show that this mixture has no liquid–liquid immiscibility near the critical region of the methane. Only liquid–vapor equilibria is found over all the temperature ranges studied indicating that this mixture exhibits a type-I phase behavior. These diagrams confirm that the methane(1)+*n*-pentane(2) mixture has no three-phase region near the critical point of methane.

To study tricritical phenomena another binary mixture with methane showing type-V phase behavior is needed. We have studied in detail the phase diagram of two candidates: methane(1)+*n*-hexane(2) and methane(1)+2,3-dimethylbutane(2). Although the structure of the second component in these mixtures is different both of them are seen as identical in the SAFT approach since this is a first-order perturbation theory and it does not distinguish between different locations of atoms in the same molecule. However, when fitting to experimental data, different values obtained for σ and ϵ for *n*-hexane and 2,3-dimethylbutane can be used. This is due to the fact that these molecular parameters are *effective* and somehow include the real structure of the group atoms.[42]

Figure 8 shows the pressure-temperature diagram of the mixture methane(1)+*n*-hexane(2). Lines are predictions from soft-SAFT (with scaled molecular parameters) and symbols are experimental data for the liquid–gas part of the critical line.[54] The complete diagram can be seen in Fig. 8(a). The critical region of methane is enlarged in Fig. 8(b), where both critical end points (UCEP and LCEP) bounding the three-phase line can be seen. The positions of the UCEP and LCEP predicted by the soft-SAFT equation are given by $T_{\mathrm{UCEP}}=193.45$ K, $P_{\mathrm{UCEP}}=4.952$ MPa, $x_{\mathrm{UCEP}}=0.998$, $T_{\mathrm{LCEP}}=189.35$ K, $P_{\mathrm{LCEP}}=4.335$ MPa, and $X_{\mathrm{LCEP}}=0.948$, and those obtained experimentally[2,55,56] are $T_{\mathrm{UCEP}}=195.91$ K,

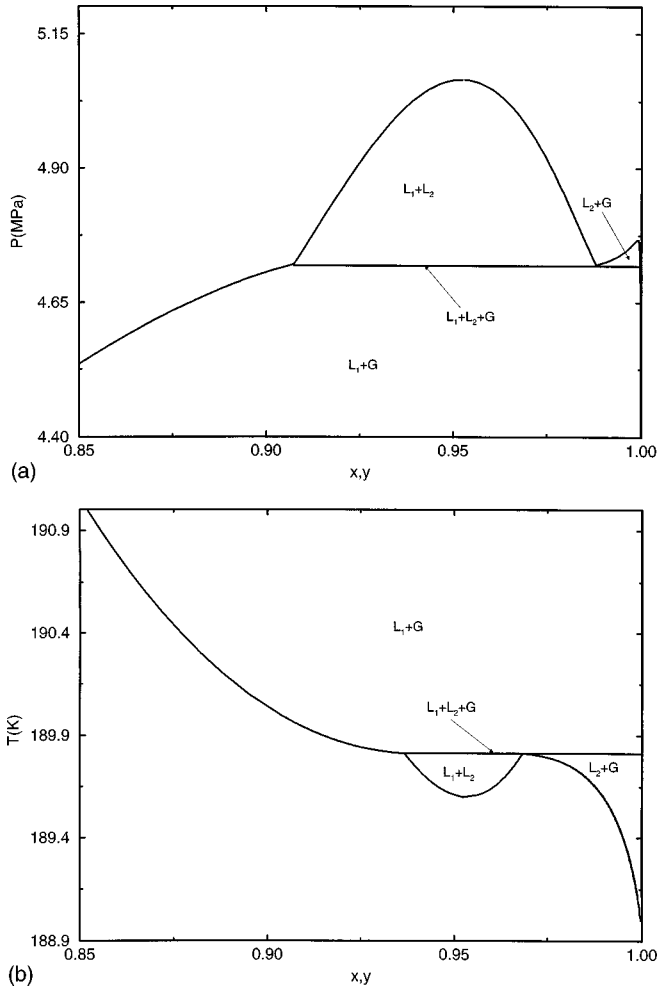

FIG. 9. Projections of the phase diagram of methane(1)+n-hexane(2) at different temperatures and pressures. All predictions by SAFT have been calculated using the scaled molecular parameters set. (a) The pressure-composition diagrams at 192 K. Three phase liquid–liquid–gas line, as well as liquid–liquid inmiscibility regions can be seen. (b) The temperature-composition diagrams of the system at 4.4 MPa.

$P_{\mathrm{UCEP}}=5.206$ MPa, $x_{\mathrm{UCEP}}=0.9976$, $T_{\mathrm{LCEP}}=182.46$ K, $P_{\mathrm{LCEP}}=3.415$ MPa, and $X_{\mathrm{LCEP}}=0.9286$. The difference between theory and experiments is less than 6% in all cases, except for the pressure of the LCEP, where deviations from experiments go up to 25%.

We have also studied the pressure-composition and temperature-composition diagrams for this mixture. Figure 9(a) shows the pressure-composition diagram at 192 K. Only an enlarged region near the three-phase line is shown. Two liquid–gas regions can be seen below and above the three-phase line. Also, a liquid–liquid inmiscibility region with an upper critical solution temperature (UCST) can be observed at pressures above the liquid–liquid–gas line, as expected from Fig. 8. Both L_2+G and L_1+L_2 regions are very small compared to the L_1+G region showing that liquid–liquid–gas and liquid–liquid inmiscibility phenomena in this mixture is small compared to the liquid–gas coexistence.

The temperature-composition plane of the methane(1)+n-hexane(2) mixture at 4.4 MPa is shown in Fig. 9(b). At these conditions the system exhibits the liquid–liquid–gas as well as liquid–liquid inmiscibility below the three-phase line, as expected from Fig. 8.

We have also studied the binary mixture methane(1)+2,3-dimethylbutane(2). Soft-SAFT predicts similar diagrams than those obtained for methane(1)+n-hexane(2) and results are not shown here.

V. CONCLUSIONS

The soft-SAFT equation of state is able to predict the critical lines of several mixtures of alkanes as well as partial miscibility. Results obtained from this equation with two different sets of molecular parameters have been compared to experimental results. The agreement between theoretical and experimental results is remarkably good when the molecular parameters of the pure components are rescaled to the critical properties. However, with these sets of parameters the overall agreement between the phase envelope obtained by the equation and the experimental one is poorer than when fitting over a wide range of temperatures and pressures. Hence it has been shown that soft-SAFT is able to quantitatively predict both phase envelopes and critical behavior. Care must be taken during the fitting procedure depending on the properties to be studied.

In particular, soft-SAFT is able to capture the shape of critical lines of binary mixtures of hydrocarbons with both sets of parameters. A quantitative agreement with experimental data is obtained when the molecular parameters are rescaled.

We have found a transition from type-I (methane+n-pentane) to type-V behavior (methane-n-hexane, methane+2,3-dimethylbutane). This transition is necessary to observe tricritical phenomena in ternary mixtures containing methane. In a later work, tricritical points of ternary mixtures with methane will be located using the SAFT approach.[46]

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[1] B. Widom and G. Sundar, Fluid Phase Equilibria **30**, 1 (1986).
[2] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed. (Butterworth Scientific, London, 1982).
[3] B. Widom, J. Phys. Chem. **77**, 2196 (1973).
[4] R. B. Griffiths, J. Chem. Phys. **60**, 195 (1974).
[5] J. L. Creek, C. M. Knobler, and R. L. Scott, J. Chem. Phys. **67**, 366 (1977).
[6] J. L. Creek, C. M. Knobler, and R. L. Scott, J. Chem. Phys. **74**, 3489 (1981).
[7] R. L. Scott, J. Chem. Phys. **86**, 4106 (1987).
[8] M. C. Goh, J. Specovius, R. L. Scott, and C. M. Knobler, J. Chem. Phys. **86**, 4120 (1987).
[9] E. Fernandez-Fassnacht, A. G. Williamson, A. Sivaraman, R. L. Scott, and C. M. Knobler, J. Chem. Phys. **86**, 4133 (1987).
[10] M. C. Goh, R. L. Scott, and C. M. Knobler, J. Chem. Phys. **89**, 2281 (1988).

[11] E. de Miguel and M. Telo da Gama, J. Chem. Phys. **107**, 6366 (1997).
[12] J. S. Rowlinson and P. I. Freeman, Pure Appl. Chem. **2**, 329 (1961).
[13] A. J. Davenport and J. S. Rowlinson, Trans. Faraday Soc. **59**, 78 (1963).
[14] A. J. Davenport, J. S. Rowlinson, and G. Saville, Trans. Faraday Soc. **62**, 322 (1966).
[15] R. L. Scott and P. H. van Konynenburg, Discuss. Faraday Soc. **49**, 87 (1970).
[16] P. H. van Konynenburg and R. L. Scott, Philos. Trans. R. Soc. London, Ser. A **298**, 495 (1980).
[17] S. H. Huang and M. Radosz, Ind. Eng. Chem. Res. **29**, 2284 (1990); **30**, 1994 (1991).
[18] M. S. Wertheim, J. Stat. Phys. **35**, 19 (1984); **35**, 35 (1984); **42**, 459 (1986); **42**, 477 (1986).
[19] M. S. Wertheim, J. Chem. Phys. **85**, 2929 (1986).
[20] M. S. Wertheim, J. Chem. Phys. **87**, 7223 (1987).
[21] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, Fluid Phase Equilibria **52**, 31 (1989).
[22] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, Ind. Eng. Chem. Res. **29**, 1709 (1990).
[23] C. G. Joslin, C. G. Gray, W. G. Chapman, and K. E. Gubbins, Mol. Phys. **62**, 8431 (1987).
[24] G. Jackson, W. G. Chapman, and K. E. Gubbins, Mol. Phys. **65**, 1 (1988).
[25] W. G. Chapman, G. Jackson, and K. E. Gubbins, Mol. Phys. **65**, 1057 (1988).
[26] W. G. Chapman, ''Theory and simulation of associating liquid mixtures,'' Ph.D. dissertation, Cornell University, Ithaca, 1990.
[27] W. G. Chapman, J. Chem. Phys. **93**, 4299 (1990).
[28] M. Banaszak, R. O'Lenick, Y. C. Chiew, and M. Radosz, J. Chem. Phys. **100**, 3803 (1994).
[29] M. Banaszak, Y. C. Chiew, and M. Radosz, Phys. Rev. E **48**, 3760 (1993).
[30] J. K. Johnson, E. A. Müller, and K. E. Gubbins, J. Phys. Chem. **98**, 6413 (1994).
[31] D. Ghonasgi and W. G. Chapman, J. Chem. Phys. **100**, 6633 (1994).
[32] E. A. Müller, L. F. Vega, and K. E. Gubbins, Mol. Phys. **83**, 1209 (1994).
[33] E. A. Müller, L. F. Vega, and K. E. Gubbins, Int. J. Thermophys. **16**, 705 (1995).
[34] J. Chang and S. I. Sandler, Chem. Eng. Sci. **49**, 2777 (1994).
[35] F. V. Tavares, J. Chang, and S. I. Sandler, Mol. Phys. **86**, 1451 (1995).
[36] A. Gil-Villegas, A. Galindo, P. J. Whitehead, J. J. Mills, and G. Jackson, J. Chem. Phys. **106**, 4168 (1997).
[37] F. J. Blas and L. F. Vega, Mol. Phys. **92**, 135 (1997).
[38] J. K. Johnson and K. E. Gubbins, Mol. Phys. **77**, 1033 (1992).
[39] D. Ghonasgi and W. G. Chapman, Mol. Phys. **79**, 291 (1993); **80**, 161 (1993); **83**, 145 (1994).
[40] D. Ghonasgi and W. G. Chapman, AIChE. J. **40**, 878 (1994).
[41] J. M. Walsh and K. E. Gubbins, Mol. Phys. **80**, 65 (1993).
[42] F. J. Blas and L. F. Vega, Ind. Eng. Chem. Res. **37**, 660 (1998).
[43] Y.-H. Fu and S. I. Sandler, Ind. Eng. Chem. Res. **34**, 1897 (1995).
[44] A. Galindo, P. J. Whitehead, G. Jackson, and A. N. Burgess, J. Phys. Chem. **100**, 6781 (1996).
[45] A. Galindo, P. J. Whitehead, G. Jackson, and A. N. Burgess, J. Phys. Chem. B **101**, 2082 (1997).
[46] F. J. Blas, A. D. Mackie, and L. F. Vega (unpublished).
[47] J. K. Johnson, J. Z. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).
[48] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1990).
[49] V. I. Harismiadis, N. K. Koutras, D. P. Tassios, and A. Z. Panagiotopoulos, Fluid Phase Equilibria **65**, 1 (1991).
[50] A. M. Georgoulaki, I. V. Ntouros, A. Z. Panagiotopoulos, and D. P. Tassios, Fluid Phase Equilibria **100**, 153 (1994).
[51] P. C. Tsang, O. N. White, B. Y. Perigard, L. F. Vega, and A. Z. Panagiotopoulos, Fluid Phase Equilibria **107**, 31 (1995).
[52] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran* (Cambridge University Press, Cambridge, England, 1986).
[53] B. D. Smith and R. Srivastava, *Physical Science Data: Thermodynamic Data for Pure Compounds, Part A: Hydrocarbons and Ketones* (Elsevier, New York, 1986), Vol. 25.
[54] C. P. Hicks and C. L. Young, Chem. Rev. **75**, 119 (1975).
[55] R. J. J. Cheng, P. S. Chappelear, and R. Kobayashi, J. Chem. Eng. Data **21**, 213 (1976).
[56] Y.-N. Lin, R. J. J. Cheng, P. S. Chappelear, and R. Kobayashi, J. Chem. Eng. Data **22**, 402 (1977).