Predicting the High-Pressure Phase Equilibria of Binary Mixtures of Perfluoro-\(n\)-alkanes + \(n\)-Alkanes Using the SAFT-VR Approach

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The phase behavior of perfluoro-(\(n\))-alkane + (\(n\))-alkane binary mixtures is of particular interest given their unexpected large positive deviations from Raoult’s law. Binary mixtures of perfluoromethane + (\(n\))-alkanes from methane to heptane are studied here, illustrating the continuous change in phase behavior from type II to type III that these systems exhibit. Some symmetrical systems that display heteroazeotropy are also examined. Using the statistical associating fluid theory for potentials of variable attractive range (SAFT-VR), we predict the high-pressure phase diagram for each binary mixture studied. The perfluoro-\(n\)-alkane and \(n\)-alkane molecules are treated as attractive spherical segments tangentially bonded together to form chains. We use simple empirical relationships between the number of carbon atoms and the number of segments in each chain. The attractive interactions are included as a square-well potential of depth \(\epsilon\) and range \(\lambda\). The pure component parameters are obtained by fitting to experimental vapor pressure and saturated liquid density data from the triple to the critical point. These optimized parameters are rescaled by the respective experimental critical points and used to determine the critical lines and phase behavior of the mixtures. The critical lines predicted by SAFT-VR for the perfluoro-\(n\)-alkane + \(n\)-alkane mixtures are in excellent agreement with the experimental data and improve significantly the results obtained with the simpler SAFT-HS approach, where the attractive interactions are treated at the mean-field level. This is particularly gratifying as the unlike dispersion interaction between the perfluoroalkane and alkane segments is obtained from a single mixture (perfluorobutane + \(n\)-butane) and then transferred to the other systems.

1. Introduction

One could be forgiven for expecting that perfluoroalkanes would exhibit very similar physical and chemical properties to the alkanes. They are very similar in structure, the fluorine atoms simply replacing the hydrogen atoms in the alkane molecules. However, that is where the similarity ends, as they possess very different physical properties. Binary mixtures of perfluoroalkanes and alkanes are of particular interest as they show substantial deviations from ideality, with large positive excess functions and extensive regions of liquid–liquid immiscibility. As a result of their unusual properties and behavior a large amount of experimental work has been devoted to their study.

By the late 40s the regular solution theory proposed by Hildebrand and Scatchard\(1\) could explain the thermodynamic properties of most solutions of nonpolar mixtures at least qualitatively. It was therefore reasonably proposed by Scott,\(2\) on the basis of the limited data available, that perfluorocarbon solutions would be no exception, and that hydrocarbon fluorocarbon mixtures would be completely miscible in all proportions. In fact subsequent experimental data for symmetrical hydrocarbon + perfluorocarbon mixtures, published in the early 50s (see refs 3–5), showed that these systems display substantial regions of liquid–liquid immiscibility. Various attempts to account for this anomalous behavior followed, with attention being focused on the failure of the geometric-mean assumption that the unlike attractive interactions could be described as the geometric mean of the like interactions: Simons and Dunlap\(3\) proposed the idea of interpenetration between neighboring C–H groups giving an abnormally strong hydrocarbon–hydrocarbon attraction energy leading to the failure of the geometric combining rule; Hildebrand\(4\) suggested that the solubility parameters of the hydrocarbons be empirically increased in order to fit the data, while Simons and Dunlap\(5,6\) suggested further corrections to the regular solution theory to include the effect of volume changes that occur on mixing; Reed\(7\) proposed yet another modification of regular solution theory to take into account size and ionization potential differences between the two components and then in late 50s introduced an additional fitted parameter.\(8\)

Rowlinson\(9\) concluded from a review of the data available that the anomalous behavior displayed by the hydrocarbon and fluorocarbon solutions resulted from an unusually weak hydrocarbon–fluorocarbon attractive interaction. However, this could not be proved as it was impossible to distinguish between a failure in assumptions made in describing the intermolecular forces and a failure in the theory itself. In the early 70s Dantzler and Knobler\(10\) proposed a test of the geometric-mean rule for hydrocarbon–fluorocarbon mixtures, by obtaining data from the interaction virial coefficient \(B_{12}\). The results strongly supported the view that the anomalous behavior of hydrocarbon–fluorocarbon systems was due to the failure of the geometric-mean rule. They discussed possible reasons for such a weak unlike interaction between the two components: noncentral...
forces, large ionization potential differences, and large size differences, concluding that the observed deviation from the geometric-mean prediction was most likely due to the latter. The fact is that despite further experimental and theoretical work on these systems we are still without a convincing explanation, although it is believed to lie in the highly polarizable nature of the fluorine atoms.

In this paper we examine the phase behavior of binary mixtures of perfluoromethane + \( n \)-alkanes from methane to heptane. This series is particularly interesting to study as it illustrates the continuity that exists between liquid—liquid and gas—liquid equilibria. Using the classification of Scott and van Konynenburg,\textsuperscript{12,13} systems of perfluoromethane + \( n \)-alkane up to \( n \)-propane show type II phase behavior: a continuous gas—liquid critical line connects the critical points of the pure components, and at lower temperatures a second liquid—liquid critical line extends from the upper critical end point (UCEP) to higher pressures; the three-phase line (liquid—liquid—gas) extends from lower temperatures and pressures to the UCEP where it terminates. As the mutual miscibility of the two components decreases, the region of liquid—liquid immiscibility shifts to higher temperatures, until it eventually interacts with the gas—liquid critical line. At this point, type II phase behavior becomes type III phase behavior, where the liquid—liquid and gas—liquid critical lines are connected. This phase behavior is first observed for the perfluoromethane + \( n \)-butane mixture. In type III mixtures at low temperatures the two liquids are immiscible as indicated by the three-phase line running from low pressure and temperature to the UCEP; a short gas—liquid critical line extends from the UCEP to the gas—liquid critical point of the more volatile component; the second fluid-fluid critical line starts from the gas—liquid critical point of the less volatile component and can extend to higher pressures in a variety of ways (four types of behavior for this critical line are common\textsuperscript{13}). We are only concerned with that shown by perfluoromethane + \( n \)-butane and higher alkanes, where the critical line passes through a temperature minimum before continuing to higher pressures eventually extending beyond the pure component critical point. This behavior is known as gas—gas immiscibility of the second kind.\textsuperscript{13}

High-pressure experimental investigations of the perfluoro-carbon + hydrocarbon systems began around the mid 70s.\textsuperscript{14–16} These provided a more detailed picture of the phase behavior in such systems since earlier work had been limited to normal or low pressures. Jeschke and Schneider\textsuperscript{14} investigated the perfluoromethane + propane and perfluoromethane + \( n \)-butane systems and observed the switch from type II to III phase behavior, but it was De Loos et al.\textsuperscript{17} who investigated the \( n \)-butane system in detail at lower pressures. They compared their results with the calculations of Mendonça\textsuperscript{16} and Deiters,\textsuperscript{18} who predicted the type of phase behavior for a number of perfluoromethane + (\( n \))-alkane mixtures, determining correctly the change from a liquid-liquid critical line for perfluoromethane + propane to gas—gas critical behavior of the second kind for the perfluoromethane + \( n \)-butane system.

We use the SAFT-VR approach\textsuperscript{19,20} for a square-well chain model to predict the fluid phase equilibria of the perfluoro-(\( n \))-alkane + (\( n \))-alkane systems. A comparison with the results obtained from the simpler SAFT-HS approach\textsuperscript{21} where the attractive interactions are treated at the van der Waals level using a one-fluid treatment, will also be discussed.

2. Models and Theory

As in earlier work,\textsuperscript{19,21–25} the alkane and perfluoroalkane molecules are both modeled with a simple united atom approach: \( m \) hard-spherical attractive segments of diameter \( \sigma \) tangentially bonded together to form chains. We use a simple empirical relationship between the number of carbon atoms in the molecule and the number of segments in the model chain obtained by fitting to the critical behavior of the homologous series. For the perfluoroalkanes (component 1), \( m_1 = 0.37(C - 1) + 1 \); hence, a value of \( m_1 = 1 \) corresponds to perfluoromethane, \( m_1 = 1.37 \) to perfluoroethane, \( m_1 = 1.74 \) to perfluoropropane etc. For the alkanes (component 2) \( m_2 = (C - 1)/3 + 1 \). The attractive interactions are described via a square-well potential of width \( \lambda \) and depth \( \epsilon \)

\[
u_{ij}(r) = \begin{cases} 
-\infty & \text{if } r < \sigma_{ij} \\
-\epsilon_{ij} & \text{if } \sigma_{ij} \leq r < \lambda_{ij}\sigma_{ij} \\
0 & \text{if } r \geq \lambda_{ij}\sigma_{ij}
\end{cases} \tag{1}
\]

where \( r \) is the distance between the two segments and \( \sigma_{ij} \) defines the contact distance between spherical cores.

In this paper we will only summarize the main expressions of the SAFT-VR theory for the square-well potential; the reader should consult refs 19 and 20 for details. The general equation for mixtures of chain molecules formed from hard-core segments with attractive interactions is given followed by the specific expressions for the system of current interest. The Helmholtz free energy \( A \) for an \( n \)-component mixture of chain molecules can be separated into the various contributions as

\[
\frac{A}{NkT} = \frac{A_{\text{IDEAL}}}{NkT} + \frac{A_{\text{MONO.}}}{NkT} + \frac{A_{\text{CHAIN}}}{NkT} \tag{2}
\]

where \( N \) is the total number of molecules, \( T \) is the temperature, and \( k \) is the Boltzmann constant. There is no need to include the association term\textsuperscript{19,20} since we are dealing with a nonassociating system. The ideal contribution to the free energy is given by a sum over all species \( i \) in the mixture\textsuperscript{27}

\[
\frac{A_{\text{IDEAL}}}{NkT} = \sum_{i=1}^{n} \frac{x_i}{\rho_i} \left( A_i^3 - 1 \right) = x_1 \ln \rho_1 A_1^3 + x_2 \ln \rho_2 A_2^3 - 1 \tag{3}
\]

where \( x_i = N_i/N \) is the mole fraction, \( \rho_i = N_i/V \) the molecular number density, \( N_i \) the number of molecules, \( A_i \) the thermal de Broglie wavelength of species \( i \), and \( V \) is the volume of the system. We can express the monomer Helmholtz free energy by

\[
\frac{A_{\text{MONO.}}}{NkT} = \left( \sum_{i=1}^{n} x_i m_i \right) \frac{A^M}{N_i kT} = \sum_{i=1}^{n} x_i m_i a^M = (x_1 m_1 + x_2 m_2) a^M \tag{4}
\]

where \( m_i \) is the number of spherical segments of chain \( i \). Using the Barker and Henderson high-temperature perturbation theory\textsuperscript{28} for mixtures with a hard-sphere reference system, the monomer free energy per segment of the mixture is obtained from the expansion

\[
a^M = a^H + \beta a_1 + \beta^2 a_2 \tag{5}
\]

where \( \beta = 1/kT \) and each term is now for a mixture of spherical segments. The expression of Boublik\textsuperscript{29} and Mansoori et al.\textsuperscript{30} for a multicomponent mixture of hard spheres is used for the reference hard-sphere term.
\[ a^{\text{HS}} = \frac{6}{\pi \rho_0} \left( \frac{\zeta^3}{\zeta_2 - \zeta^3} \right) \ln(1 - \zeta) + \frac{3 \zeta^2}{(1 - \zeta)^2} + \frac{\zeta^3}{\zeta^2(1 - \zeta)^2} \]  

(6)

where \( \rho_0 \) is the total number density of spherical segments and \( \zeta_i \) are the reduced densities defined by

\[ \zeta_i = \frac{\pi \rho_i}{6} \left[ \sum_{j=1}^n x_{ij} \sigma_{ij}^3 \right] \]

\[ = \frac{\pi \rho_i}{6} \left[ x_{i1} \sigma_{i1}^3 + x_{i2} \sigma_{i2}^3 \right] \]  

(7)

Here \( \sigma_i \) is the diameter of the spherical segments of chain \( i \) and \( x_{ij} \) is the mole fraction of segments of type \( i \) in the mixture.

The mean-attractive energy represented by the \( a_1 \) term is obtained from the sum of the partial terms corresponding to each type of pair interaction\(^{19,20}\)

\[ a_1 = \sum_{i=1}^n \sum_{j=1}^n x_{ij} \xi_{ij}^2 \]

\[ = x_{i1}^2 a_{11}^i + 2 x_{i1} x_{i2} a_{12}^i + x_{i2}^2 a_{22}^i \]  

(8)

where

\[ a_i^j = -2 \pi \rho \epsilon_i \sum_{j=1}^{\infty} \left( x_{ij} \sigma_{ij}^3 \right)^2 \]

\[ \]  

(9)

\( g_{ij}^{\text{HS}} \) is the radial distribution function for a mixture of hard spheres. Using the mean value theorem\(^{19,20}\), we obtain an expression for \( a_1 \) in terms of the contact value of \( g_{ij}^{\text{HS}} \)

\[ a_1 = -\rho \sum_{j=1}^n \left[ x_{ij} \sigma_{ij}^3 \left( \mathcal{G}_{ij}^{\text{VDW}} \right) \right] \]  

(10)

where

\[ \sigma_{ij}^{\text{VDW}} = 2 \rho \epsilon_{ij} \sigma_{ij}^3 (\lambda_{ij}^2 - 1)/3 \]  

(11)

is the van der Waals attractive constant for the \( i-j \) interaction and \( \zeta_i \) is an effective packing fraction.

In the van der Waals one (VDW-1)-fluid theory \( g_{ij}^{\text{HS}} \) is approximated by the radial distribution function for a single fluid so that eq (10) simplifies to

\[ a_1 = -\rho \sum_{j=1}^n \left[ x_{ij} \sigma_{ij}^3 \left( \mathcal{G}_{ij}^{\text{HS}} \right) \right] \]  

(12)

where \( \sigma_{ij}^{\text{HS}} \) is the contact value of the hard-sphere pair radial distribution obtained from the Carnahan and Starling equation of state\(^{31}\)

\[ \sigma_{ij}^{\text{HS}} \left( \zeta_i, \lambda_{ij} \right) = c_1(\lambda_{ij}) \zeta_i + c_2(\lambda_{ij}) \zeta_i^2 + c_3(\lambda_{ij}) \zeta_i^3 \]  

(13)

The effective packing fraction \( \zeta_i \) in eq (13) is obtained within the VDW-1 fluid approximation from the corresponding packing fraction of the mixture \( \zeta_i \)

\[ \zeta_i = \frac{\pi}{6} \sum_{j=1}^n x_{ij} \sigma_{ij}^3 \]  

(15)

\[ \]  

with

\[ \sigma_i^3 = \sum_{j=1}^n x_{ij} \sigma_{ij}^3 \]  

(16)

The coefficients \( c_1, c_2, \) and \( c_3 \) are approximated by those of the pure fluid\(^{19,20}\)

\[ \left( \begin{array}{c} c_1 \\ c_2 \\ c_3 \end{array} \right) = \left( \begin{array}{ccc} 2.25855 & -1.50349 & 0.249434 \\ -0.669270 & 1.40049 & -0.827739 \\ 10.1576 & -15.0427 & 5.30827 \end{array} \right) \]  

(17)

This corresponds to the MX1b mixing rule of ref 20. The MX1b prescription gives an excellent representation of both vapor—liquid and liquid—liquid critical behavior.\(^{26}\) If the actual packing fraction \( \zeta_i \) of the system is used in order to get \( \zeta_i^{\text{eff}} \) according to the mapping rule for pure components (MX3b mixing rule in ref 20), there are some problems associated with the critical region of the phase diagram. This is a common feature of equations of state for mixtures that use parameters defined for pure fluids beyond the VDW-1 fluid approximation.\(^{19,32}\)

The first fluctuation term \( a_2 \) is given by\(^{19,20}\)

\[ a_2 = \sum_{i=1}^n \left[ x_{ij} \sigma_{ij}^3 \right] \]  

(18)

The terms \( a_i^j \) are obtained from the expressions for \( a_1^i \) with the local compressibility approximation

\[ a_2^i = \frac{1}{2} \mathcal{K}^{\text{HS}} \frac{\partial \sigma_{ij}^3}{\partial \rho} \]  

(19)

where \( \mathcal{K}^{\text{HS}} \) is the hard-sphere isothermal compressibility of Percus-Yevick

\[ \mathcal{K}^{\text{HS}} = -\frac{\zeta_i}{\zeta_0} \frac{1 - \zeta_i^2}{(1 - \zeta_i^2)^2} \]

(20)

Finally, the contribution to the free energy due to chain formation is expressed in terms of the contact value of the background correlation function\(^{19,20}\)

\[ A^{\text{CHAIN}} = \sum_{i=1}^n x_i (m_i - 1) \ln y_{ij}^{\text{SW}}(\sigma_{ij}) \]

\[ = -x_i (m_i - 1) \ln y_{ij}^{\text{SW}}(\sigma_{ij}) - x_j (m_j - 1) \ln y_{ij}^{\text{SW}}(\sigma_{ij}) \]  

(21)

where \( y_{ij}^{\text{SW}}(\sigma_{ij}) = g_{ij}^{\text{SW}}(\sigma_{ij}) \exp(-\beta \epsilon_{ij}) \). We obtain \( y_{ij}^{\text{SW}}(\sigma_{ij}) \) from the high-temperature expansion of \( g_{ij}^{\text{SW}}(\sigma_{ij}) \)

\[ g_{ij}^{\text{SW}}(\sigma_{ij}) = g_{ij}^{\text{HS}}(\sigma_{ij}) + \beta \epsilon_{ij} g_{ij}^{\text{SW}}(\sigma_{ij}) \]  

(22)

The hard-sphere term \( g_{ij}^{\text{HS}} \) is given by the expression of Boublík\(^{29}\)
Density, from the critical to the triple point. These optimized experimental data for the vapor pressure and saturated liquid density, and compared with the available experimental data. The theory using a square-well model of variable attractive range 

\[ g_i(a_i; \xi) = \frac{1}{1 - \xi} + \frac{D_i}{(1 - \xi)^3} + 2 \left( \frac{D_i}{(1 - \xi)^3} \right)^2 \]  

with the parameter \( D_i \) defined by 

\[ D_i = \frac{a_i a_i}{\sum_{i=1}^{n} x_i a_i^3} \]  

The term \( g_i(a_i; \xi) \) is obtained from a self-consistent representation of the pressure \( p \) from the Clausius virial theorem and from the density derivative of the Helmholtz free energy  

\[ g_i(a_i; \xi) = g_i^{HS}(a_i; \xi) + (\lambda - 1) \frac{\partial g_i^{HS}(a_i; \xi)}{\partial \xi} + \left( \lambda - 3 \right) \frac{\partial g_i^{eff}(a_i; \xi)}{\partial \xi} \]  

We should note that in the SAFT-HS approach the attractive forces are described at the van der Waals level, and the hard-sphere contact value is used in the expression for the chain contribution.

Using standard thermodynamic relationships, other thermodynamic properties can be obtained from the Helmholtz free energy such as the chemical potential 

\[ \mu_i = \left( \frac{\partial A}{\partial N} \right)_{T,V,N_{\text{m}}} \]  

and the compressibility factor 

\[ Z = \frac{pV}{nkT} = \frac{\sum_{i=1}^{n} \left( \frac{\mu_i}{kT} \right)}{nkT} \]  

These are the functions required for the determination of the critical and phase behavior of the mixture. The gas–liquid–liquid critical lines can be determined by equating the second and third derivatives of the Gibbs free energy with respect to the mole fraction to zero. Phase equilibrium between phases I and II in mixtures requires that the temperature, pressure, and chemical potential of each component in each phase be equal  

\[ T^I = T^II, \quad p^I = p^II, \quad \mu^I = \mu^II \]  

These conditions are solved numerically using a simplex method.

3. Results and Discussion

Theoretical phase diagrams for each perfluoro-(n)-alkane + (n)-alkane binary mixture are obtained within the SAFT-VR theory using a square-well model of variable attractive range and compared with the available experimental data. The parameters for each pure component are obtained by fitting to experimental data for the vapor pressure and saturated liquid density, from the critical to the triple point. These optimized pure component parameters are then rescaled to the respective critical points since our main interest is in the critical lines. The values of the parameters used in our study for the perfluoro-(n)-alkanes and (n)-alkanes are given in Tables 1 and 2, respectively. In Figure 1a we show the vapor pressures obtained with the SAFT-VR approach for methane through n-octane, and in Figure 1b the vapor pressures for perfluoromethane through perfluoro-n-butane, together with the corresponding experimental data.

<table>
<thead>
<tr>
<th>Table 1: Optimized Square-Well Intermolecular Potential Parameters for (n)-Alkanes</th>
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<tbody>
<tr>
<td>Substance</td>
</tr>
<tr>
<td>CH(_4)</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
</tr>
<tr>
<td>C(_4)H(_8)</td>
</tr>
<tr>
<td>C(_5)H(_12)</td>
</tr>
<tr>
<td>C(_6)H(_14)</td>
</tr>
<tr>
<td>C(_7)H(_16)</td>
</tr>
<tr>
<td>C(_8)H(_18)</td>
</tr>
</tbody>
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* \( m \) is the number of spherical segments in the model, \( \lambda \) the range parameter, \( \sigma \) the diameter of each segment, and \( \epsilon \) the well depth. \( T^c_\text{m} = kT/b_\text{m} \) and \( p^c_\text{m} = p_b/\alpha_\text{m} \) are the reduced critical temperature and pressure, where \( \alpha = 4be/(\lambda^3 - 1) \) and \( b = \pi\sigma^6/6 \).
The study of phase equilibria in mixtures also requires the determination of a number of cross, or unlike, parameters. The following combining rules\textsuperscript{13} were used to obtain the unlike size and energy parameters

\begin{equation}
\sigma_{ij} = \frac{\sigma_1 + \sigma_2}{2} \tag{29}
\end{equation}

\begin{equation}
\epsilon_{ij} = \xi (\epsilon_1 \epsilon_2)^{1/2} \tag{30}
\end{equation}

where eq 29 corresponds to the Lorentz rule and \( \xi \) in eq 30 describes the departure of the system from the Berthelot rule and the extensive regions of liquid–liquid immiscibility displayed by these mixtures. The unlike mean field energy \( \epsilon_{ij} \) is treated as an adjustable parameter that we optimize by changing \( \xi \) to give the best representation of the continuous liquid–liquid gas–liquid critical line in the perfluoromethane + \( n \)-butane system. The perfluoromethane + \( n \)-butane system was chosen to fit the correction parameter \( \xi \) since this system exhibits the change in phase behavior from type II to type III, displaying maxima and minima in the high-pressure critical line. This correction parameter is used in a transferable fashion for the other perfluoromethane + (\( n \))-alkane systems, so eliminating the need for refitting. A value of \( \xi = 0.9206 \) is obtained by optimization. The unlike range parameter is obtained from the arithmetic mean of the pure component values as in previous papers\textsuperscript{25,26}

\begin{equation}
\lambda_{ij} = \frac{\lambda_i \sigma_i + \lambda_j \sigma_j}{\sigma_i + \sigma_j} \tag{31}
\end{equation}

The \( pT \) projection of the \( pTx \) surface for the perfluoromethane + methane system is presented in Figure 2. As discussed in the Introduction this system shows type II phase behavior with two distinct critical lines. As observed experimentally the gas–liquid critical line is a short almost straight line between the critical points of the two pure components,\textsuperscript{36} and at lower temperatures we have the locus of UCSTs, which gradually increase with pressure. The literature value for the UCEP, most clearly seen in the inset of Figure 2, is 94.5 K,\textsuperscript{37} with a predicted value of 91.3 K. However, given that we are fitting the unlike interaction parameter to the perfluoromethane + \( n \)-butane system we are achieving very good agreement between our theoretical predictions and the experimental data. In Figure 3 we present three constant temperature \( px \) slices as predicted with the SAFT-VR approach with the corresponding experimental data for the perfluoromethane + methane system. We reproduce the experimental data reasonably well, and it should be noted that at these temperatures we are just above the locus of UCST’s and hence the dew point curve is quite flat. Since we are mainly interested in the behavior of the critical lines of the perfluoroalkane + \( n \)-alkane systems, we rescale the optimized parameters to the experimental critical points of the respective pure components; this gives a better representation curve near the critical point with a detriment to the saturated liquid densities, and hence in Figure 3 we overpredict the pure component pressure in the \( px \) slices compared to the experimental values.

When we look at the next member of the alkane homologous series with perfluoromethane, we achieve excellent agreement between SAFT-VR predictions and experimental results as seen in Figure 4. The line of UCSTs for perfluoromethane + ethane has shifted to higher temperatures and also extends to higher pressures with a positive slope. The predicted value for the UCEP is 153.8 K, compared with 150.1 K observed experimentally.\textsuperscript{38} Figure 5 shows a constant pressure \( Tx \) slice for the perfluoromethane + ethane system compared with experimental points.\textsuperscript{38} The solid curve represents the SAFT-VR prediction using MX1b mixing rule described earlier, and the dashed that of MX3b where the actual packing fraction of the system \( \zeta_3 \) is used to obtain \( \zeta_{3f} \) according to the mapping rule for pure components.\textsuperscript{19,20} The MX3b mixing rule was used in a previous paper,\textsuperscript{25} however, as can be seen from Figure 5 when studying systems that exhibit large regions of liquid–liquid immiscibility, we find inconsistencies in the description of the UCST when it is used. The MX1b mixing rule gives an excellent representation of both the vapor–liquid and liquid–liquid critical behavior.

**Figure 2.** \( pT \) projection for perfluoromethane (1) + methane (2) compared with the SAFT-VR prediction. The circles represent the experimental values for the vapor pressures of the pure components,\textsuperscript{34} the diamonds the liquid–liquid critical points,\textsuperscript{16} and the triangle the UCEP.\textsuperscript{37} The continuous curves represent the SAFT-VR vapor pressures for the pure components and the dashed curves the gas–liquid and liquid–liquid critical lines.

**Figure 3.** \( px \) slices at 110.5, 108.5, and 105.5 K for perfluoromethane (1) + methane (2) compared with SAFT-VR predictions. The diamonds correspond to the experimental data\textsuperscript{40} and the continuous curves the theoretical predictions.
in binary mixtures of perfluoromethane + n-alkanes, as can be seen from the comparison in Figure 5. The theory, although slightly overpredicting the UCST,\textsuperscript{17} describes the liquid–liquid coexistence curve very well.

For the perfluoromethane + propane binary mixture (Figure 6), we again accurately represent the fluid phase equilibria of this system albeit for the limited experimental data available. The line of UCSTs has shifted to higher temperature, indicating that the two components are becoming less miscible as the chain length of the n-alkane is increased. \( T_x \) slices for this system over a wide pressure range, from 10 to 200 MPa, are shown in Figure 7. The SAFT-VR approach predicts the liquid–liquid coexistence envelopes very well given the range of the experimental data and the flatness of the curves close to the liquid–liquid critical point.

The systems studied so far all display type II phase equilibria, but when the perfluoromethane + n-butane binary mixture is examined we observe type III phase behavior. This system is especially interesting to study as it is clearly intermediate between types II and III, still retaining the features of the liquid–liquid and gas–liquid critical lines. As discussed earlier we fit the unlike interaction parameter to this system in order to describe the pressure maximum and minimum of the continuous gas–liquid/liquid–liquid critical line. The dotted line in Figure 8 is the SAFT–HS prediction for the high-pressure critical line; a notable improvement is found with the SAFT-VR approach. The SAFT-VR prediction is remarkably accurate passing through a temperature minima at 231 K, compared with the experimental value of 236 K,\textsuperscript{39} and extends to higher pressures with a positive slope resulting in gas–gas immiscibility of the second kind. Focusing on the inset of Figure 8, we can see the region close to the critical point of perfluoromethane more clearly. The solid curve is the predicted three-phase line, running from low temperatures and pressures to the UCEP, where it meets a short gas–liquid critical line. Given the
extremely small temperature range, the SAFT-VR approach describes this critical region reasonably accurately, only very slightly overestimating the UCEP; the experimental values are 242.89 K and 4.697 MPa, and the predicted values 248.85 K and 4.869 MPa.

In Figure 9 we show the pT projection for the perfluoromethane + n-pentane system. Here, we clearly have a type III phase diagram with gas–gas immiscibility of the second kind at higher pressures than those shown, which is well-represented by the theoretical prediction. The quoted minimum in this high-pressure critical line is 271 K, and the continuous curves represent the experimental vapor pressures for the pure components, and the dashed curves correspond to the critical lines.

mental values and SAFT-VR predictions. The perfluoromethane + n-hexane predictions show a slight deviation from the experimental data, as seen in Figure 10, however the n-heptane mixture shows a more significant deviation of about 70 K. In order to study binary mixtures of longer chain length, we refitted the cross-interaction parameter to the high-pressure critical line, obtaining a $\xi$ value of 0.8948, and the dotted curve that with $\xi = 0.9206$. When looking at the $p_x$ slices for this system shown in Figure 12 at high temperatures we have two two-phase regions as a consequence of the temperature minimum. The high-pressure
region can be assigned to a liquid–liquid and the low-pressure to a gas–liquid coexistence. As the temperature decreases, the two phase regions move toward each other until they merge at the point of double contact, below which there is only a single two-phase region. This can be seen very clearly in Figure 12 where we compare SAFT-VR predictions with experimental data at three constant temperatures. The SAFT-VR approach reproduces the experimental data well, the theoretical slices being slightly narrower than those observed experimentally.

The critical lines for perfluoromethane + methane through perfluoromethane + n-hexane are summarized in Figure 13. We can clearly see type II phase behavior for the systems up to and including propane, where the liquid–liquid critical line is very close to the critical point of perfluoromethane. For the n-butane system, the liquid–liquid critical line has passed the critical point of perfluoromethane and merged with the gas–liquid critical line to give us type III phase behavior. It is important to note that we adjust the cross-interaction parameter $\xi$ to describe accurately the maximum and minimum in the critical pressure for the perfluoromethane + n-butane system, and then transfer the $\xi$ parameter to the other binary systems up to n-hexane. The systems studied beyond n-butane describe more typical type III phase behavior, with the high-pressure critical line passing through a temperature minimum before extending to higher pressures with a positive slope corresponding to gas–gas immiscibility of the second kind. This minimum shifts to higher temperatures with increasing chain length of the n-alkane, indicating a decrease in the mutual solubility of the two components. Using this transferable parameter approach we reproduce the experimental data extremely well, seeing only a slight deviation between theory and experiment as chain length increases.

We have also studied a number of symmetrical perfluoroalkane + (n)-alkane binary systems. The phase diagrams of such mixtures are characterized by type II behavior with the addition of heteroeazeotropy, which arises because the three-phase line lies above the vapor pressure curves of both pure components. The $pT$ projection of the $pTx$ surface for the perfluorobutane + n-butane system is shown in Figure 14; the azeotropic line can be seen more clearly at low temperatures and pressures where there are a few experimental data points, shown in the inset of the figure. The triangle represents the UCST (232 K) to which we fitted the unlike interaction parameter obtaining a value of $\xi = 0.9234$, which is very similar to $\xi = 0.9206$, which we obtained for the unsymmetrical systems. The SAFT-VR approach provides a good representation of the phase diagram for this system; unfortunately, there is limited experimental data available, although there is good agreement with the azeotropic
Figure 15. $pT$ slices at 259.95 K, 253.62 K, 246.35 K, and 238.45 K for butane (1) + perfluorobutane (2) compared with SAFT-VR predictions. The diamonds describe the experimental data and the solid curves the predictions.

Figure 16. $pT$ projection for propane (1) + perfluoropropane (2) compared with the SAFT-VR predictions. The circles correspond to the experimental vapor pressure data, the triangle corresponds to the theoretical prediction of the vapor pressure phase behavior of propane and propane system compared with SAFT-VR predictions. Again the slice at 203.5 K is just above the UCST and is therefore very narrow and flat, this effect decreasing as temperature increases.

4. Conclusion

We have used SAFT-VR, a version of the SAFT approach for potentials of variable attractive range, to describe the phase behavior of perfluoro-(n)-alkane + (n)-alkane systems. The parameters for the pure components are rescaled to the experimental critical points as we are concentrating on high-pressure phase behavior. Although we lose some accuracy on the vapor pressure curves, fitting to the critical point gives a better representation of the critical lines. The $\xi$ parameter is obtained from a fit to a single binary mixture and used in the calculation of the unlike interaction for the other systems of interest. Using our parameters in this transferable fashion we avoid the need for refitting when studying a new system and still obtain a good description of the phase equilibrium for all systems studied, seeing only a slight deviation between theory and experiment for longer chain lengths. Since we are interested in the high-pressure behavior of the systems studied, MX3b would provide an accurate description of vapor-liquid equilibria but is not appropriate for critical behavior.

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References and Notes

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