Modelling the phase behaviour and excess properties of alkane + perfluoroalkane binary mixtures with the SAFT–VR approach

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Abstract

The phase and volumetric behaviour of binary mixtures of n-alkanes and n-perfluoroalkanes at subcritical conditions have been studied using the SAFT–VR equation of state. In previous work [C. McCabe, A. Galindo, A. Gil-Villegas, G. Jackson, Predicting the high-pressure phase equilibria of binary mixtures of perfluoro-n-alkanes plus n-alkanes using the SAFT–VR approach, J. Phys. Chem. B 102 (1998) 8060–8069] the SAFT–VR equation was successfully used to predict the phase behaviour of binary mixtures of low molecular weight n-perfluoroalkanes + n-alkanes. A transferable binary interaction parameter was proposed which enabled the accurate prediction of the critical lines for all the systems studied. In this work we focus on the low pressure liquid–liquid immiscibility displayed by binary mixtures of longer chains (C_5–C_8). New transferable binary interaction parameters for these mixtures are proposed, based on the reproduction of the UCST and excess volumes for the n-hexane + n-perfluorohexane system. With these parameters, predictions are then made for the vapour–liquid equilibria (VLE), liquid–liquid equilibria (LLE) and excess volumes of other binary mixtures without any additional fitting to experimental data. The resulting predictions from the SAFT–VR equation are in good agreement with the available experimental data.
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1. Introduction

Binary mixtures of alkanes and perfluoroalkanes are highly nonideal systems, in spite of the apparent similarity between these substances. They exhibit large regions of liquid–liquid immiscibility, large positive deviations from Raoult's law and large positive excess properties (such as the excess enthalpy and volume), a clear indication of weak unlike interactions. Since the late 40s the potential application of these systems as refrigerant mixtures or as immiscible solvents has motivated their study. However in recent years, perfluoroalkanes have become key fluids in a wide range of fields due to their chemical inertness, biocompatibility and peculiar physical properties [1,2]. For example, from medical applictaions, where they find use as oxygen carriers in blood substitute formulations [3] or as fluids in eye surgery, to technological applications as solvents for biphasic synthesis, fire-extinguishers or lubricants. As a result, considerable work has been done on the theoretical and computational modelling of n-alkane + n-perfluoroalkane mixtures [4–14]. In particular, special attention has been given to understanding the unlike molecular interactions [5,6,14]. These studies concluded that the usual Lorentz–Berthelot combining rules for the crossed intermolecular potential parameters fail to give satisfactory results, because of an unusually weak hydrocarbon–fluorocarbon attractive interaction.

In recent work, McCabe et al. [11] studied the phase behaviour of n-alkane + n-perfluoroalkane binary mixtures. The focus of this work was the high pressure phase behaviour and critical lines for binary mixtures of perfluoromethane + n-alkanes (from methane–heptane) and for symmetric systems

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of the light n-alkanes + n-perfluoroalkanes (from methane to butane). In this study a single binary interaction parameter for all perfluoroalkane + n-alkane systems ($\xi_{12} = 0.9206$) was determined from a fit to the high pressure critical line of the perfluoromethane + n-butane binary mixture. Using this parameter, it was possible to predict the transition from the type II phase behaviour exhibited by the perfluoromethane + ethane and propane binary mixtures, to the type III phase behaviour displayed by the perfluoromethane + n-butane and higher binary mixtures. However, it was observed that as the chain length of the n-alkane component increased, deviations between the theoretical predictions and experimental data occurred. As a result, an additional ξ_{12} was determined ($\xi_{12} = 0.8948$) for the binary mixture involving n-heptane.

In the present work, we concentrate on the phase behaviour of alkane + perfluoroalkane binary mixtures with chain lengths between 5 and 8 carbon atoms for both components. We have therefore determined a set of binary interaction parameters that can be used to accurately predict the phase behaviour of these systems of longer chain molecules. Moreover, we have focused on the liquid–liquid immiscibility found close to ambient temperatures, rather than the high pressure phase behaviour.

2. Models and theory

Within the SAFT formalism, the free energy of a mixture of associating chain molecules can be written as the sum of four separate contributions:

$$\frac{A}{NkT} = \frac{A^{\text{IDEAL}}}{NkT} + \frac{A^{\text{MONO.}}}{NkT} + \frac{A^{\text{CHAIN}}}{NkT} + \frac{A^{\text{ASSOC.}}}{NkT}, \quad (1)$$

where N is the number of molecules, k Boltzmann's constant, and T the temperature. A^{IDEAL} is the ideal free energy, $A^{\text{MONO.}}$ the contribution to the free energy due to the monomeric segments, A^{CHAIN} the contribution due to the formation of a chain of m monomers, and $A^{\text{ASSOC.}}$ the contribution due to association. We shall not consider the association term since we are dealing with non-associating systems.

The monomer free energy is written as a second-order high temperature perturbation expansion:

$$\frac{A^{\text{MONO.}}}{NkT} = \frac{A^{\text{HS}}}{NkT} + \frac{1}{kT}\frac{A_1}{NkT} + \frac{1}{(kT)^2}\frac{A_2}{NkT}, \quad (2)$$

where A^{HS} is the free energy of the reference hard sphere fluid given by Boublik [15] and Mansoori et al. [16], A_1 is the mean attractive energy, and A_2 describes the energy fluctuations.

The chain term is a function of the number of contacts ($m_i - 1$) and of the contact pair distribution function g_{ii}^{SW}. For a binary mixture,

$$\frac{A^{\text{CHAIN}}}{NkT} = -x_1(m_1 - 1)\ln(g_{11}^{\text{SW}}(\sigma_{11}))$$

$$- x_2(m_2 - 1)\ln(g_{22}^{\text{SW}}(\sigma_{22})) \quad (3)$$

where $g_{ii}^{\text{SW}}(\sigma_{ii})$ is given by the high-temperature expansion

$$g_{ii}^{\text{SW}}(\sigma_{ii}) = g_{ii}^{\text{HS}}(\sigma_{ii}) + \beta\varepsilon_{ii}g_1(\sigma_{ii}). \quad (4)$$

The hard-sphere term $g_{ii}^{\text{HS}}(\sigma_{ii})$ is obtained from the expression of Boublik [15] and a closed form for $g_i(\sigma_{ii})$ can be obtained from the pressure expression (the Clausius virial theorem) and the first derivative of the free energy with respect to the density. For full details of the SAFT–VR expressions the reader is directed to the original paper [17].

3. Results and discussion

In the SAFT–VR approach the molecules are modelled as chains of tangentially bonded spherical segments of hard core diameter σ_{ii}, with the attractive interactions being described by a potential of variable attractive range. In this work, we use a square-well potential of width λ_{ii} and depth ε_{ii}. The potential model parameters σ_{ii}, λ_{ii}, ε_{ii}, for the pure substances are generally obtained by fitting to experimental vapour pressure and saturated liquid density data. For the n-alkanes and the n-perfluoroalkanes, simple empirical relationships proposed in earlier work are used to relate the number of spherical segments m in the model chain, to the number of carbon atoms C in the alkyl chain [9,18]. For the n-alkanes $m = (1/3)(C - 1) + 1$, while for the n-perfluoroalkanes $m = 0.37(C - 1) + 1$. The pure substance parameters for the alkanes, perfluorohexane and perfluoroheptane have already been reported [19–21], while those of perfluoropentane and perfluorooctane were determined in this work. For perfluorooctane, the potential model parameters were determined by fitting to the experimental data of Mustafaev et al. [22,23]; for perfluoropentane, since no experimental results could be found in the literature, we followed a procedure described previously [19] to interpolate between the available parameters for other perfluoroalkanes. Table 1 lists the parameters used in this work to describe the pure components.

The calculation of mixture phase equilibria also requires the determination of a number of cross or unlike parameters.

Table 1
Optimised SAFT–VR parameters for the alkanes and perfluoroalkanes studied

Substance	m	λ	σ (Å)	ε/k (K)	Reference
C_5H_{12}	2.33	1.505	3.931	265.0	[11]
C_6H_{14}	2.67	1.552	3.920	250.4	[11]
C_7H_{16}	3.00	1.563	3.933	251.3	[11]
C_8H_{18}	3.33	1.574	3.945	250.3	[11]
C_5F_{12}	2.48	1.421	4.469	282.0	This work[a]
C_6F_{14}	2.85	1.432	4.456	283.1	[20]
C_7F_{16}	3.22	1.436	4.464	285.3	[21]
C_8F_{18}	3.59	1.462	4.472	274.0	This work[b]

[a] Interpolated according to the procedure described in [19], using the parameters for perfluoroalkanes available in the references cited in the table and in [11].

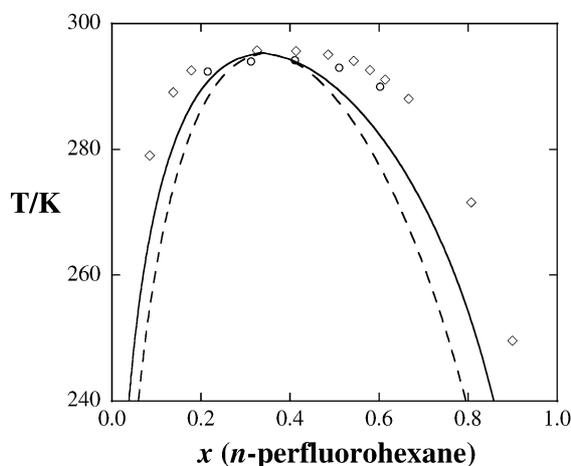[b] Fitted to experimental vapour pressures and saturated liquid densities from [22,23].

Fig. 1. Liquid–liquid coexistence curve for the n-C_6H_{14} + n-C_6F_{14} system. The continuous and dashed lines represent respectively the SAFT–VR curves for $\xi_{12} = 0.840$; $\gamma_{12} = 1.045$ and $\xi_{12} = 0.9374$; $\gamma_{12} = 1$, the diamonds and circles correspond to experimental data from [26] and [12], respectively.

The Lorentz combining rule was used for the unlike hard-core diameter

$$\sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2}, \tag{5}$$

while the unlike dispersive energy was calculated using the modified Berthelot combining rule

$$\varepsilon_{12} = \xi_{12}(\varepsilon_{11}\varepsilon_{22})^{1/2}. \tag{6}$$

A value of $\xi_{12} < 1$ is usually associated with liquid–liquid immiscibility. Additionally, we observed that in order to achieve a better description of the unusual width of the liquid–liquid phase separation envelope for the hexane + perfluorohexane system, a second adjustable parameter γ_{12}, controlling the range of the crossed square-well interactions needs to be introduced. The unlike range parameter was calculated from

$$\lambda_{12} = \gamma_{12} \frac{\lambda_{11}\sigma_{11} + \lambda_{22}\sigma_{22}}{\sigma_{11} + \sigma_{22}}. \tag{7}$$

The unlike interaction parameters ξ_{12} and γ_{12} were determined by fitting to the n-hexane + n-perfluorohexane mixture experimental data, namely the UCST curve and the excess molar volumes at four temperatures. The values obtained were $\xi_{12} = 0.840$ and $\gamma_{12} = 1.045$. In Figs. 1 and 2, respectively we show the experimental and calculated curves for the liquid–liquid equilibrium and the excess molar volumes for this system. It should be noted that the LLE curve predicted with these parameters is considerably broader than that obtained when a single binary interaction parameter is used (the optimised value was determined to be $\xi_{12} = 0.9374$), therefore justifying the use of both ξ_{12} and γ_{12}.

These optimised parameters (ε_{12} and γ_{12}) were then used to predict the vapour–liquid equilibria (VLE), liquid–liquid equilibria (LLE) and excess volumes for a number of alkane + perfluoroalkane binary mixtures with chain lengths between 5 and 8 carbon atoms. The predictions are compared with
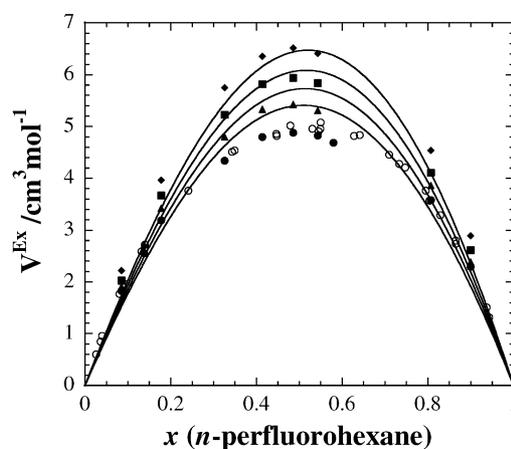
the available experimental data in Figs. 3–6, remembering that ξ_{12} and γ_{12} were determined from a fit to the n-hexane + n-perfluorohexane system and so no additional fitting has been performed to obtain these results. As can be seen from the figure, the shape of the curves and the azeotropic composition are correctly reproduced by the SAFT–VR equation, although the vapour pressure is slightly under-predicted. Figs. 4 and 5 show composition curves for n-hexane + n-perfluoroalkane (perfluoropentane, perfluoroheptane and perfluorooctane) and for n-perfluorohexane + n-alkane (pentane, heptane and octane) binary mixtures respectively. In all cases the SAFT–VR predictions are in excellent agreement with the experimental data. Excess molar volumes as a function of composition were also calculated with SAFT–VR for all the binary mixtures studied and the results are plotted in
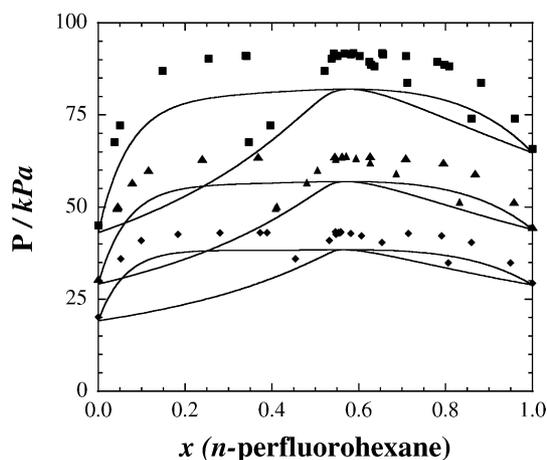

Fig. 2. Excess volumes for the n-C_6H_{14} + n-C_6F_{14} system. The lines represent the SAFT–VR curves (with $\xi_{12} = 0.840$ and $\gamma_{12} = 1.045$) for the excess volumes at 25 (lower curve), 35, 45 and 55 °C (upper curve); the open circles the experimental data at 25 °C from [27] and the circles, triangles, squares and diamonds the experimental values from [26] at 25, 35, 45 and 55 °C, respectively.

Fig. 3. Vapour–liquid equilibria for the n-C_6H_{14} + n-C_6F_{14} system. The diamonds, triangles and squares represent respectively the experimental data at 25, 35 and 45 °C, from [28]. The lines correspond to the SAFT–VR predictions with $\varepsilon_{12} = 0.840$ and $\gamma_{12} = 1.045$.
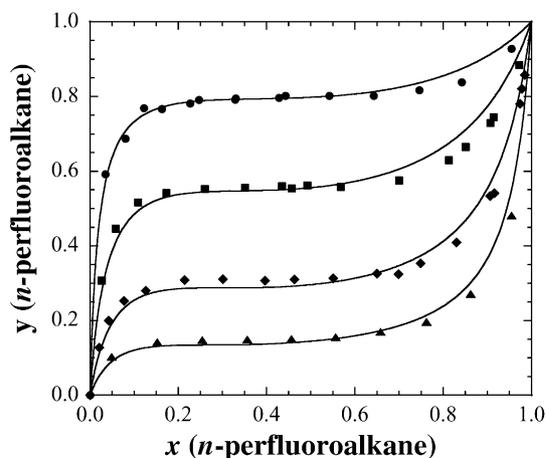
Fig. 4. VLE composition diagram for n-hexane + n-C_nF_{n+2} mixtures: $n = 5$ at 293.15 K (circles), $n = 6$ at 298.15 K (squares), $n = 7$ at 303.15 K (diamonds) and $n = 8$ at 313.15 K (triangles), and experimental data from [12]. The lines represent the SAFT–VR predictions with $\varepsilon_{12} = 0.840$ and $\gamma_{12} = 1.045$.

Fig. 5. VLE composition diagram for n-C_nH_{n+2} + n-perfluorohexane mixtures: $n = 5$ at 293.65 K (circles), $n = 6$ at 298.15 K (squares), $n = 7$ at 298.15 K (diamonds) and $n = 8$ at 313.15 K (triangles), and experimental data from [12]. The lines represent the SAFT–VR predictions with $\varepsilon_{12} = 0.840$ and $\gamma_{12} = 1.045$.
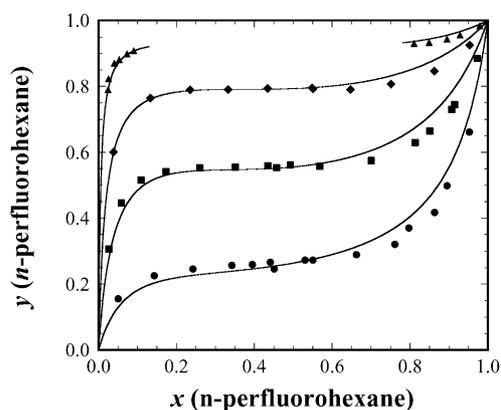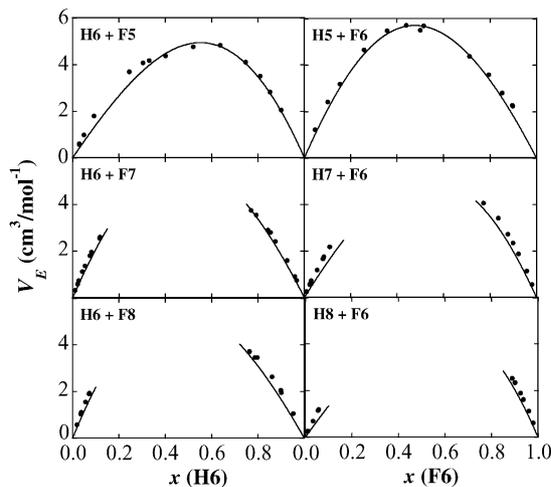

Fig. 6. Excess volumes for n-alkane + n-perfluoroalkane systems. The circles represent experimental data from [27] and the lines the SAFT–VR predictions with $\varepsilon_{12} = 0.840$ and $\gamma_{12} = 1.045$.

Table 2
The UCST's of n-alkane + n-perfluoroalkane binary mixtures predicted from the SAFT–VR equation compared with experimental data. H_n and F_n, respectively represent an alkane or perfluoroalkane with n carbon atoms

	H₅	H₆	H₇	H₈
F₅	267[a]	288[a]	310[a]	328[a]
	266[b]	288[b]		
F₆	273[a]	295[a]	317[a]	335[a]
	273[b]	294[c]/296[b]	315[c]/316[b]	335[b]
F₇	280[a]	304[a]	325[a]	343[a]
	282[b]	303[b]	323[b]	343[b]
F₈	286[a]	312[a]	335[a]	355[a]
	288[d]	299[d]	320[d]	349[b]

[a] Theoretical values.
[b] Experimental values from [25].
[c] Experimental values from [12].
[d] Experimental values from [24].

Fig. 6. As can be seen the agreement with the experimental values is excellent, remembering that these results are true predictions as the binary interaction parameters used are taken from the perfluorohexane + hexane system and no additional fitting to experimental data is performed when a new binary mixture is studied.

Finally, UCST's were calculated for all the systems. The results are presented in Table 2, alongside the available experimental data. The predictions are, for most cases, within experimental error or the differences between authors; larger discrepancies are seen only for the systems studied by Edmonds [24].

4. Conclusions

We have used the SAFT–VR equation of state to describe the phase and volumetric behaviour of n-alkane + n-perfluoroalkane binary mixtures at subcritical conditions for chain lengths between 5 and 8 carbon atoms, this being the limit of available experimental data. A new set of unlike binary interaction parameters, ξ_{ij} and γ_{ij}, were proposed, which were determined from a simultaneous fit to the UCST and excess molar volumes of the n-hexane + n-perfluorohexane system. These parameters were then used in a transferable fashion to predict the properties of the other binary mixtures studied. We find that the SAFT–VR predictions for the VLE, LLE and excess molar volumes of these systems are in close agreement with experimental data, without the need for additional fitting.

List of symbols

A	Helmholtz free energy
A_1	mean attractive Helmholtz free energy
A_2	Helmholtz free energy fluctuations
C	number of carbon atoms in chain
g_{ii}	contact pair distribution function of component i
k	Boltzmann's constant

m	number of monomeric segments in chain
N	number of molecules
P	pressure
T	temperature
V^{Ex}	excess volume
x	mole fraction in liquid
x_i	mole fraction of component i
y	mole fraction in vapour

Greek letters

ε_{ij}	square well depth between components i and j
γ_{ij}	binary interaction parameter
λ_{ij}	square well width between components i and j
σ_{ij}	hard-core collision distance between components i and j
ξ_{ij}	binary interaction parameter

Superscripts

ASSOC.	association contribution
CHAIN	chain formation contribution
HS	hard sphere fluid contribution
IDEAL	ideal contribution
MONO.	monomer contribution
SW	square-well fluid contribution

Acknowledgments

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