

Application of SAFT–VRX to binary phase behaviour: alkanes

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Abstract

In previous work, we developed the crossover SAFT–VR equation of state (SAFT–VRX) for pure fluids by following the crossover approach proposed by Kiselev. The SAFT–VRX equation was shown to be very accurate in the prediction of PVT and phase behaviour for both non-associating and associating fluids. In particular, simple expressions for the potential model parameters for the *n*-alkane homologous series were developed, allowing the prediction of the thermodynamic properties without fitting to experimental data. In this work, we have applied the SAFT–VRX equation to binary mixtures of short-chain *n*-alkanes, using the prescriptions for the model parameters developed previously to determine the pure fluid parameters. The SAFT–VRX equation is found to accurately predict the gas–liquid critical locus and vapor–liquid equilibrium data for the systems studied without fitting to binary experimental mixture data.

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1. Introduction

In the early stages of process design, it is typical for the thermodynamic properties of key pure components and mixtures to be unknown or of limited availability and for these properties to be generated on the basis of engineering correlations. Reliable methods for the theoretical prediction of thermophysical properties and phase equilibria are therefore essential for accurate equipment design, in particular for separation processes, which often represent over 80% of the capital investment and a large fraction of the energy requirements in a typical chemical plant [1]. In this regard, the SAFT equation of state has proven to be a very useful tool in determining fluid phase equilibria.

The SAFT–VR equation in particular, has been successfully applied to describe the phase equilibrium of a wide range of industrially important fluids, such as alkanes [2–5], polymers [6,7], replacement refrigerants [8] and electrolytes

[9]. However, as with essentially all engineering equations of state, the accuracy of the SAFT–VR equation is limited to the region of the phase diagram away from the critical locus of the fluid systems. This is because, asymptotically close to the critical point the SAFT–VR equation, being analytical in the free energy, cannot reproduce the scaling behaviour seen in real fluids and their mixtures [10]. In order to improve the description of the gas–liquid critical locus for pure fluids, the SAFT–VR parameters can be rescaled to the experimental pure fluid critical point, and an accurate representation of the critical locus is obtained. However, despite the success achieved using the rescaled SAFT–VR equation [11–13], poor agreement is obtained at lower pressures, especially at lower temperatures [3,4] and for the coexisting densities.

In order to develop a truly global equation of state, Sengers and co-workers [14–16] and Kiselev et al. [17,18] have introduced crossover theory, which considers the long-range fluctuations observed in the density when approaching the critical point. In particular, Kiselev's approach provides a generalized way to incorporate scaling laws into an analytical equation of state, regardless of its type [17–20]. The resulting crossover equation can be written in closed analytical

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form and reproduces the scaling laws in the asymptotic critical region while being smoothly transformed into the original classical EOS far away from the critical point.

In previous work [21,22], we successfully applied crossover theory to the SAFT–VR equation for pure fluids, deriving the SAFT–VRX equation of state. SAFT–VRX allows the accurate prediction of the thermodynamic properties of fluids both near to, and far from, the critical region for both associating and non-associating systems. In particular, we have applied SAFT–VRX to the accurate modeling of water, alcohols, carbon dioxide and the n -alkane homologous series [21,22]. For the n -alkanes simple relations were developed to determine the SAFT–VRX parameters for linear alkanes from the carbon number and molecular weight, enabling the prediction of the thermodynamic properties and phase behaviour for fluids for which little or no experimental data exists. In all cases, excellent agreement between the theory and experiment is obtained. Furthermore while the crossover terms in the SAFT–VR equation enable the precise description of the whole phase diagram, the need for an accurate classical equation was shown through comparison from the results of the SAFT–VRX equation with a crossover version [23] of the SAFT equation due to Huang and Radosz [24,25].

To continue the development of the SAFT–VRX equation, in this work, we incorporate the crossover theory into the SAFT–VR equation for mixtures. Excellent results have been obtained for the thermodynamic properties of binary mixtures of short-chain n -alkanes, namely ethane, propane, n -butane and n -pentane. We will proceed as follows. In Section 2, we outline the SAFT–VRX equation for mixtures. We then describe the results obtained for the n -alkane binary mixtures studied and comparisons are made with the classical SAFT–VR equation and experimental data in Section 3. Conclusions are drawn in Section 4.

2. Theory

In the SAFT approach, the Helmholtz free energy for associating chain molecules is given by:

$$a(T, v, X) = a^{\text{IDEAL}} + a^{\text{MONO}} + a^{\text{CHAIN}} + a^{\text{ASSOC}} \\ = a^{\text{IDEAL}} + a^{\text{RES}} \quad (1)$$

where a^{IDEAL} is the ideal free energy, a^{MONO} is the excess free energy due to the monomers, a^{CHAIN} is the contribution from the formation of chains, and a^{ASSOC} is the contribution due to intermolecular association, which will not be considered in this work. a^{RES} refers to the residual part of Helmholtz free energy and is given by $a^{\text{RES}} = a^{\text{MONO}} + a^{\text{CHAIN}} + a^{\text{ASSOC}}$. In the application of SAFT to real fluids molecules are modeled as chains of hard tangentially bonded, spherical segments that interact through a potential of variable attractive range. In this work, we consider molecules interacting via the

square-well potential:

$$u_{ij}(r_{ij}) = \begin{cases} 0 & r_{ij} \geq \lambda_{ij}\sigma_{ij} \\ -\varepsilon_{ij} & \sigma_{ij} \leq r_{ij} < \lambda_{ij}\sigma_{ij} \\ +\infty & r_{ij} < \sigma_{ij} \end{cases} \quad (2)$$

where r_{ij} is the distance, σ_{ij} is the hard-sphere diameter, and λ_{ij} and ε_{ij} are the range and depth of the attractive potential between two monomer segments i and j .

For mixtures with n components, the ideal Helmholtz free energy is given by:

$$a^{\text{IDEAL}} = \sum_{i=1}^n x_i \ln \rho_i \Lambda_i^3 - 1 \quad (3)$$

where $\rho_i = N_i/V$ is the molecular number density, x_i the mole fraction and Λ_i the thermal de Broglie wavelength of species i .

The monomer free energy for mixtures is given as:

$$a^{\text{MONO}} = \left(\sum_{i=1}^n x_i m_i \right) a^{\text{M}} \quad (4)$$

where m_i is the number of monomer spheres in each chain i , and N_s is the total number of spheres. The monomer energy per sphere, a^{M} , is obtained from the Barker and Henderson high temperature expansion [26–29]

$$a^{\text{M}} = a^{\text{HS}} + \frac{a_1}{kT} + \frac{a_2}{(kT)^2} + \dots \quad (5)$$

where a_1 and a_2 are the first two perturbation terms associated with the attractive energy $-\varepsilon_{ij}$. The free energy of the reference hard-sphere (HS) mixture a^{HS} is obtained from the expression of Boublik [30] and Mansoori et al. [31] as:

$$a^{\text{HS}} = \frac{6}{\pi\rho_s} \left[\left(\frac{\xi_2^3}{\xi_3^2} - \xi_0 \right) \ln(1 - \xi_3) \right. \\ \left. + \frac{3\xi_1\xi_2}{1 - \xi_3} + \frac{\xi_2^3}{\xi_3(1 - \xi_3)^2} \right] \quad (6)$$

where $\rho_s = \frac{N_s}{V} = \rho \left(\sum_{i=1}^n x_i m_i \right)$ is the number density of spherical segments, and the reduced densities ξ_l are defined as:

$$\xi_l = \frac{\pi}{6} \rho_s \left[\sum_{i=1}^n x_{s,i} (\sigma_i)^l \right] \quad (l = 1, 2, 3) \quad (7)$$

where ξ_3 is the overall packing fraction of the mixture. In Eq. (7), σ_i is the hard core diameter of a sphere in chain i and $x_{s,i}$ is the mole fraction of spheres of component i in the mixture,

given by:

$$x_{s,i} = \frac{m_i x_i}{\sum_{k=1}^n m_k x_k} \quad (8)$$

Since the equation of state for mixtures is based on equations for pure fluids, appropriate mixing rules are required to specify the dependence on composition x_i . In the van der Waals (vdW) n -fluid theories [32,33], simple relationships between the pair correlation functions of mixtures and those of the pure components are assumed. The simplest case, the vdW one-fluid mixing rule, gives the definitions of the size, σ_x , energy, ε_x , and potential range parameters, λ_x , as follows:

$$\sigma_x^3 = \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \sigma_{ij}^3 \quad (9)$$

$$\varepsilon_x = \frac{\sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \varepsilon_{ij} \lambda_{ij}^3 \sigma_{ij}^3}{\sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \lambda_{ij}^3 \sigma_{ij}^3} \quad (10)$$

$$\lambda_x^3 = \frac{\sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \varepsilon_{ij} \lambda_{ij}^3 \sigma_{ij}^3}{\sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \varepsilon_{ij} \sigma_{ij}^3} \quad (11)$$

where variables with subscript ij refer to the pair interaction between species i and j . The vdW one-fluid mixing rule can be applied at any level of the equation of state. However, in order to maintain the accuracy of the description of the structure of the HS reference system, we choose to implement the mixing rule only in the perturbation terms for the monomer interactions, which corresponds to the MIX1b mixing rule of Galindo et al. [5]. Hence the mean-attractive energy a_1 for square-well molecules is given as:

$$a_1 = -\frac{2}{3} \rho_s \pi \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \varepsilon_{ij} \sigma_{ij}^3 (\lambda_{ij}^3 - 1) g_0^{\text{HS}} \times [\sigma_x; \xi_x^{\text{eff}}(\lambda_{ij})], \quad (12)$$

and the first fluctuation term in the free energy is given by:

$$a_2 = -\frac{1}{2} \rho_s K^{\text{HS}} \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \varepsilon_{ij} \alpha_{ij}^{\text{VDW}} \times \left\{ g_0^{\text{HS}}[\sigma_x; \xi_x^{\text{eff}}(\lambda_{ij})] + \rho_s \frac{\partial g_0^{\text{HS}}[\sigma_x; \xi_x^{\text{eff}}(\lambda_{ij})]}{\partial \rho_s} \right\} \quad (13)$$

where K^{HS} is the isothermal compressibility for a mixture of hard spheres and is given by the Percus–Yevick expression [34]:

$$K^{\text{HS}} = \frac{\xi_0(1 - \xi_3)^4}{\xi_0(1 - \xi_3)^2 + 6\xi_1\xi_2(1 - \xi_3) + 9\xi_2^3} \quad (14)$$

where the contact value g_0^{HS} and the effective packing fraction ξ_x^{eff} will be specified below.

The contribution to the free energy due to formation of chain molecules from the square-well segments is given by:

$$a^{\text{CHAIN}} = -\sum_{i=1}^n x_i (m_i - 1) \ln[g_0^{\text{HS}}[\sigma_{ii}; \xi_{ii}^{\text{eff}}(\lambda_{ii})] + \beta \varepsilon_{ii} g_1^{ii}(\sigma_{ii})] \quad (15)$$

The term $g_1^{ii}(\sigma_{ii})$ is obtained from a self-consistent calculation of the pressure using the Clausius virial theorem and the first derivative of the free energy with respect to the density [2]. For a mixture of square-well molecules, $g_1^{ij}(\sigma_{ij})$ is given by:

$$g_1^{ij}(\sigma_{ij}) = \frac{1}{2\pi \varepsilon_{ij} \sigma_{ij}^3} \left[3 \left(\frac{\partial a_1^{ij}}{\partial \rho_s} \right) - \frac{\lambda_{ij}}{\rho_s} \frac{\partial a_1^{ij}}{\partial \lambda_{ij}} \right] = \beta \varepsilon_{ij} \left\{ g_0^{\text{HS}}[\sigma_x; \xi_x^{\text{eff}}(\lambda_{ij})] + (\lambda_{ij}^3 - 1) \times \frac{\partial g_0^{\text{HS}}[\sigma_x; \xi_x^{\text{eff}}(\lambda_{ij})]}{\partial \xi_x^{\text{eff}}} \left(\frac{\lambda_{ij}}{3} \frac{\partial \xi_x^{\text{eff}}}{\partial \lambda_{ij}} - \xi_x^{\text{eff}} \frac{\partial \xi_x^{\text{eff}}}{\partial \xi_3} \right) \right\} \quad (16)$$

where the contact value g_0^{HS} of the radial distribution function for a reference mixture of hard spheres at an effective packing fraction ξ_x^{eff} is given by:

$$g_0^{\text{HS}}[\sigma_x; \xi_x^{\text{eff}}] = \frac{1 - \xi_x^{\text{eff}}/2}{(1 - \xi_x^{\text{eff}})^3} \quad (17)$$

The effective packing fraction is given by the Pade expression proposed by Patel et al. [35]:

$$\xi_x^{\text{eff}}(\xi_x, \lambda_{ij}) = \frac{c_1(\lambda_{ij})\xi_x + c_2(\lambda_{ij})\xi_x^2}{[1 + c_3(\lambda_{ij})\xi_x^3]^3} \quad (18)$$

with coefficients given by:

$$\begin{pmatrix} c_1(\lambda_{ij}) \\ c_2(\lambda_{ij}) \\ c_3(\lambda_{ij}) \end{pmatrix} = \begin{pmatrix} -3.16492 & 13.35007 & -14.80567 & 5.07286 \\ 43.00422 & -191.66232 & 273.89683 & -128.93337 \\ 65.04194 & -266.46273 & 361.04309 & -162.69963 \end{pmatrix} \times \begin{pmatrix} \frac{1}{\lambda_{ij}} \\ \frac{1}{\lambda_{ij}^2} \\ \frac{1}{\lambda_{ij}^3} \\ \frac{1}{\lambda_{ij}^4} \end{pmatrix} \quad (19)$$

and the reduced density ξ_x defined as:

$$\xi_x = \frac{\pi}{6} \rho_s \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \sigma_{ij}^3 \quad (20)$$

Following the standard Lorentz–Berthelot combining rules [33], we determine the cross, or unlike parameters in Eqs. (9)–(20) from:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (21)$$

$$\varepsilon_{ij} = (\varepsilon_{ii} \varepsilon_{jj})^{1/2} \quad (22)$$

$$\lambda_{ij} = \frac{\lambda_{ii} \sigma_{ii} + \lambda_{jj} \sigma_{jj}}{\sigma_{ii} + \sigma_{jj}} \quad (23)$$

The expression given above defines the SAFT–VR equation for mixtures. To introduce the crossover terms and obtain the SAFT–VRX equation of state for mixtures, we follow the approach proposed by Kiselev [17,18]. Following this procedure, one needs to first rewrite the classical expression (1) for the Helmholtz free energy in the form:

$$a(T, v) = \Delta a(\Delta T, \Delta v) - \Delta v p_0(T) + a_0^{\text{RES}}(T) + a_0(T) \quad (24)$$

where the critical, or singular part of the Helmholtz free energy, $\Delta a(\Delta T, \Delta v)$, is a function of the dimensionless distance of the temperature from the classical critical temperature $T_{0c}(\Delta T = T/T_{0c} - 1)$ and the molar volume from the classical critical molar volume $v_{0c}(\Delta v = v/v_{0c} - 1)$, the dimensionless pressure $p_0(T) = p(T, v_{0c})v_{0c}/RT$, the dimensionless residual part of the Helmholtz free energy $a_0^{\text{RES}}(T) = a^{\text{RES}}(v_{0c}, T)$ and the dimensionless temperature-dependent ideal gas term $a_0(T)$ along the critical isochore, $v = v_{0c}$. The critical part of the dimensionless Helmholtz free energy can be derived from Eqs. (1) and (24) as:

$$\Delta a(\Delta T, \Delta v) = a^{\text{RES}}(\Delta T, \Delta v) - a_0^{\text{RES}}(\Delta T) - \ln(\Delta v + 1) + \Delta v p_0(\Delta T) \quad (25)$$

which satisfies three critical point conditions:

$$\begin{aligned} \Delta a(\Delta T = 0, \Delta v = 0) &= 0, \quad \left(\frac{\partial \Delta a}{\partial \Delta v} \right)_{\Delta T=0, \Delta v=0} = 0, \\ \left(\frac{\partial^2 \Delta a}{\partial \Delta v^2} \right)_{\Delta T=0, \Delta v=0} &= 0 \end{aligned} \quad (26)$$

Secondly, one needs to replace ΔT and Δv in the critical part of the Helmholtz free energy $\Delta a(\Delta T, \Delta v)$ by renormalized values

$$\begin{aligned} \bar{\tau} &= \tau Y^{-\alpha/2\Delta_1} + (1 + \tau) \Delta \tau_c Y^{2(2-\alpha)/3\Delta_1} \\ \bar{\varphi} &= \varphi Y^{\gamma-2\beta/4\Delta_1} + (1 + \varphi) \Delta v_c Y^{(2-\alpha)/2\Delta_1} \end{aligned} \quad (27)$$

where:

$$\begin{aligned} \alpha &= 0.110, \quad \beta = 0.325, \quad \gamma = 2 - \alpha - 2\beta = 1.24, \\ \Delta_1 &= 0.51 \end{aligned} \quad (28)$$

are the universal critical exponents, $\tau = T/T_c - 1$ is the dimensionless deviation of temperature from real critical temperature T_c , $\varphi = v/v_c - 1$ is the dimensionless deviation of molar volume from real critical molar volume v_c , and $\Delta \tau_c = \Delta T_c/T_{0c} = (T_c - T_{0c})/T_{0c}$ and $\Delta v_c = \Delta v_c/v_{0c} = (v_c - v_{0c})/v_{0c}$ are the dimensionless shifts between the classical critical temperature T_{0c} and critical volume v_{0c} , and the real critical temperature T_c and critical volume v_c . The crossover function Y in Eq. (27) can be written in parametric form [36,37]

$$Y(q) = \left[\frac{q}{1+q} \right]^{2\Delta_1} \quad (29)$$

where the parametric variable q is related to the order parameter φ and dimensionless temperature τ though the crossover SINE model [36,37]

$$\begin{aligned} \left(q^2 - \frac{\tau}{Gi} \right) \left[1 - \frac{1}{4} \left(1 - \frac{\tau}{q^2 Gi} \right) \right] \\ = b^2 \left(\frac{\varphi}{Gi^\beta} [1 + v_1 \varphi^2 \exp(-10\varphi) + d_1 \tau] \right)^2 Y^{(1-2\beta)/\Delta_1} \end{aligned} \quad (30)$$

where Gi is the Ginzburg number for the fluid of interest, $b^2 = 1.359$ is the universal linear-model parameter, and d_1 and v_1 are system-dependent parameters.

Finally, the crossover expression for the Helmholtz free energy can be rewritten as:

$$a(T, v) = a^{\text{IDEAL}}(T, v) + \bar{a}^{\text{RES}}(T, v) \quad (31)$$

where the renormalized residual part is given by:

$$\begin{aligned} \bar{a}^{\text{RES}}(T, v) \\ = a^{\text{RES}}(\bar{\varphi}, \bar{\tau}) - a_0^{\text{RES}}(\bar{\tau}) + a_0^{\text{RES}}(T) + \bar{\varphi} p_0(\bar{\tau}) \\ - \Delta v p_0(T) - \ln(\bar{\varphi} + 1) + \ln(\Delta v + 1) \end{aligned} \quad (32)$$

Eqs. (27)–(32) completely define the SAFT–VRX equation in the form of the Helmholtz free energy, which is obtained from the classical SAFT–VR equation. We should note that although composition does not explicitly appear in the SAFT–VRX expressions, the crossover parameters Gi , d_1 , and v_1 are implicit functions of x_i . In extending the SAFT–VRX equation to mixtures the following simple linear mixing rules for the crossover parameters are developed from the values for the pure components, i :

$$Gi^{-1}(x) = \sum_{i=1}^n x_i [Gi^{-1}]^{(i)} \quad (33)$$

$$v_1(x) = \sum_{i=1}^n x_i v_1^{(i)} \quad (34)$$

$$d_1(x) = \sum_{i=1}^n x_i d_1^{(i)} \quad (35)$$

In the SAFT–VRX equation for pure fluids [21,22], the renormalization as given by Eq. (32) appears near the real critical point of the fluid as determined by the conditions [38]:

$$P(T_c, v_c) = P_c, \quad \left(\frac{\partial P}{\partial v}\right)_{T_c, v_c} = 0, \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c, v_c} = 0 \quad (36)$$

In binary mixtures, the critical locus can be found from the solution of the following equations

$$P(T_c, v_c, \mu_c) = P_c, \quad \left(\frac{\partial P}{\partial v}\right)_{T_c, v_c, \mu_c} = 0, \\ \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c, v_c, \mu_c} = 0 \quad (37)$$

where the chemical potential of the mixture $\mu = (\partial A/\partial x)_{T,v}$. Eq. (37) implies that near the critical point, the equation of state for a binary mixture should be formulated in terms of the chemical potential, $P = P(T, v, \mu)$, rather than composition $P = P(T, v, x)$. However, this implementation would make the equation of state for mixtures very complex and so in this work, following Kiselev and Friend [18], in Eqs. (27)–(32) we have used pseudo critical parameters defined by the conditions

$$P(T_c, v_c, x_c) = P_c, \quad \left(\frac{\partial P}{\partial v}\right)_{T_c, v_c, x_c} = 0, \\ \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c, v_c, x_c} = 0 \quad (38)$$

The mixture critical shifts, which in the SAFT–VRX equation for mixtures account for the difference between the classical and pseudo critical parameters, can be determined from those for the pure fluids with additional mixing terms [17,18], viz:

$$\Delta\tau_c = \sum_i \Delta\tau_c^{(i)} x_i \quad (39)$$

$$\Delta v_c = \sum_i \Delta v_c^{(i)} x_i \quad (40)$$

where the critical shifts $\Delta\tau_c^{(i)}$ and $\Delta v_c^{(i)}$ for the pure components are determined from Eqs. (48) and (49).

3. Models

For pure non-associating fluids three parameters determine the classical potential, i.e., the hard-core segment diameter, σ , the range of attractive forces λ , and the depth of the attractive interaction ε . The crossover term introduces the Ginzburg number Gi , d_1 and v_1 . Generally these parameters are determined from a direct fit to experimental data. However, for a homologous series like the n -alkanes it is desirable to have predictive models from which the parameters can be determined directly without the need to fit each

component individually. In previous work, from a simultaneous optimization of the SAFT–VRX equation to vapor–liquid equilibrium (VLE) and pvT data for selected n -alkanes, McCabe and Kiselev [22] developed expressions for both the classical and crossover parameters for pure alkanes, viz:

$$m = 1 + a_{m,1}(C_m - 1)^{0.1} + a_{m,2}(C_m - 1) \quad (41)$$

$$\lambda = a_{\lambda,0} + a_{\lambda,1}(C_m - 1)^{0.25} + a_{\lambda,2}(C_m - 1) \quad (42)$$

$$m\sigma = a_{\sigma,0} + a_{\sigma,1}(m \cdot M_w)^{0.5} + a_{\sigma,2} \left(\frac{m \cdot M_w}{1 + a_{\sigma,4} C_m}\right) \\ + a_{\sigma,3} \left(\frac{m \cdot M_w}{1 + a_{\sigma,4} C_m}\right)^{0.75} \quad (43)$$

$$m\varepsilon = a_{\varepsilon,0} + a_{\varepsilon,1}(m \cdot M_w)^{0.5} + a_{\varepsilon,2}(m \cdot M_w)^{0.75} \\ + a_{\varepsilon,3}(m \cdot M_w) \quad (44)$$

$$Gi^{-1} = a_{g,0} + a_{g,1}(C_m) + a_{g,2}(C_m)^{1.5} \quad (45)$$

$$v_1 = \frac{a_{v,0} + a_{v,1} C_m}{1 + a_{v,2} C_m} \quad (46)$$

$$d_1 = a_{d,0} + a_{d,1} C_m \quad (47)$$

where C_m is the number of carbon atoms in the n -alkane chain, M_w the molecular weight, and $a_{x,i}$ where $x = m, \sigma, \varepsilon$ or λ are fitted coefficients. The critical shifts for the pure components are expressed as functions of the Ginzburg number

$$\Delta\tau_c = -\frac{\delta_\tau Gi}{1 + Gi} \quad (48)$$

$$\Delta v_c = -\frac{\delta_\eta Gi}{1 + Gi} \quad (49)$$

and the coefficients $\delta_\tau = 0$ and $\delta_\eta = 2.086$ were proposed for n -alkanes [22]. With the parameters given by Eqs. (41)–(49), excellent agreement between the SAFT–VRX predictions and experimental data was obtained for pure n -alkanes that were not included in the optimization procedure [22], validating the use of these equations.

4. Results and discussion

We have applied the SAFT–VRX equation to study the phase equilibrium of binary mixtures of short-chain n -alkanes, namely ethane, propane, n -butane and n -pentane. For the calculation of the mixture critical locus, we adopted the algorithm proposed by Heidemann and Khalil [39]. Phase diagrams are predicted for each system and compared directly to experimental data as well as the classical SAFT–VR results with both optimized and rescaled parameters. The values of the SAFT–VRX parameters used for the n -alkanes, as determined from Eqs. (41)–(47) with coefficients given in reference [22], are listed in Table 1.

Table 1
SAFT–VRX parameters for ethane, propane, *n*-butane and *n*-pentane

	Ethane	Propane	<i>n</i> -Butane	<i>n</i> -Pentane
m	1.996	2.377	2.740	3.094
σ (Å)	3.475	3.649	3.776	3.875
λ	1.627	1.640	1.647	1.651
(ε/k_B) (K)	139.202	153.235	163.707	171.886
G_i^{-1}	7.214	6.923	6.651	6.394
d_1	0.458	0.469	0.480	0.492
v_1	0.00861	0.00666	0.00568	0.00509

The p – T projection of the phase diagram for the ethane (1) + *n*-butane (2) binary mixture is presented in Fig. 1. Excellent agreement between the SAFT–VRX description and experimental data for both the pure fluids and the gas–liquid critical line is observed. We note that no binary mixture data is used in the calculations and so the results are pure predictions. For comparison we also present the SAFT–VR prediction using optimized parameters. As expected, in this case the pure component critical points, and therefore the gas–liquid critical line is over-predicted. As discussed in the introduction, these optimized pure component parameters can be rescaled with respect to the experimental critical points and similar agreement between the experimental data and the SAFT–VRX equation is then obtained for the critical temperatures and pressures. In Figs. 2 and 3 we show the critical locus and p – T slices of the phase diagram for the ethane + *n*-butane binary mixture, respectively. In both figures, the SAFT–VR prediction with optimized parameters overestimates the critical temperatures and pressures, while we note that the SAFT–VRX and SAFT–VR equation with rescaled parameters give nearly identical predictions for the gas–liquid critical locus. The slight shift observed in the p – T slices of the phase diagram for the SAFT–VRX equation is

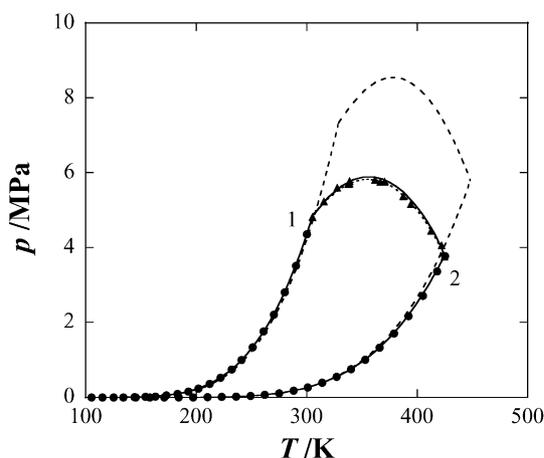


Fig. 1. p – T projection of the phase diagram for the binary mixture of ethane(1) + *n*-butane(2). The solid lines correspond to the predictions of the SAFT–VRX equation; the critical line obtained from the SAFT–VR equation with optimized (dashed) and rescaled (dotted) parameters is also shown. The filled circles represent the vapor-pressure data for pure ethane and *n*-butane [45] and the triangles represent the gas–liquid critical locus data of [46].

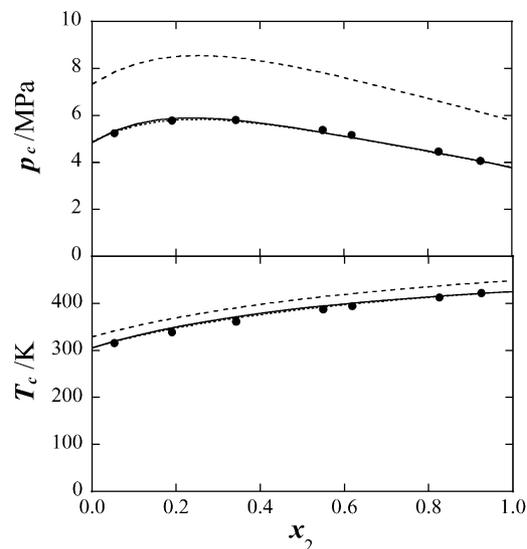


Fig. 2. (a) P_c – x_2 and (b) T_c – x_2 projections of the gas–liquid critical line for the ethane(1) + *n*-butane(2) phase diagram. The solid line corresponds to the SAFT–VRX prediction, the dashed line to the SAFT–VR obtained with optimized parameters, the dotted line to the SAFT–VR with rescaled parameters and the symbols experimental data [47].

to be expected since we used the vdW one-fluid mixing rule formulated in terms of composition. This is because close to the critical point the mixtures will possess a pure-fluid-like behaviour at fixed chemical potential $\tilde{\mu} = (\partial a/\partial x)_{T,v}$, rather than composition x [40–43]. In general, the conditions $x = \text{Const}$ and fixed $\tilde{\mu} = \text{Const}$ do not coincide, and in order to improve the representation of the VLE surface for binary mixtures in the critical region the crossover equation of state needs to be formulated in terms of the “field” variable $\tilde{x} = \exp(\tilde{\mu})/(1 + \exp(\tilde{\mu}))$ [38].

The benefit of using the SAFT–VRX equation of state over the SAFT–VR equation with rescaled parameters in the critical region is clearly demonstrated in Fig. 4 where we present T – ρ slices of the phase diagram for the ethane + *n*-butane

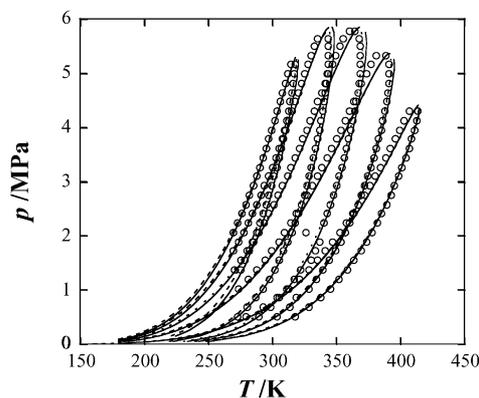


Fig. 3. Constant x p – T slices of the ethane(1) + *n*-butane(2) phase diagram at $x_2 = 0.8251, 0.549, 0.3423, 0.1782$ and 0.0529 (from right to left). The solid lines correspond to the SAFT–VRX predictions, the dashed lines to the SAFT–VR prediction with rescaled parameters and the symbols correspond to the experimental data [47].

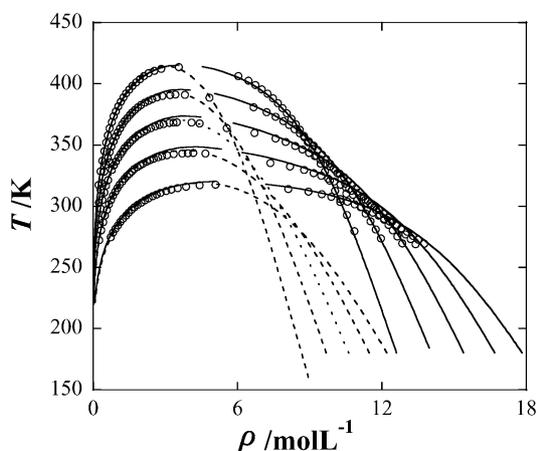


Fig. 4. Constant xT - ρ slices of the ethane(1) + n -butane(2) phase diagram at $x_2 = 0.8251, 0.549, 0.3423, 0.1782$ and 0.0529 (from right to left). The solid lines correspond to the SAFT-VRX predictions, the dashed lines to the SAFT-VR prediction with rescaled parameters and the symbols represent the experimental data [47].

binary mixture. We can see that the agreement between the SAFT-VRX predictions, and experimental data is excellent for both the liquid and gas phase densities. A slight over-prediction of the critical temperature is observed close to the critical density for each mixture studied, however, we note that in this region of the phase diagram the experimental results carry greater uncertainty. As expected the SAFT-VR description significantly underestimates the liquid densities as a result of the rescaling of the parameters to the experimental critical points.

Finally in Fig. 5, we present the gas-liquid critical line for four binary n -alkane mixtures: ethane + propane, ethane + n -butane, propane + n -butane, and n -butane + n -pentane. These systems all display type I phase behaviour, in the scheme of van Konynenburg and Scott [44] with continuous critical

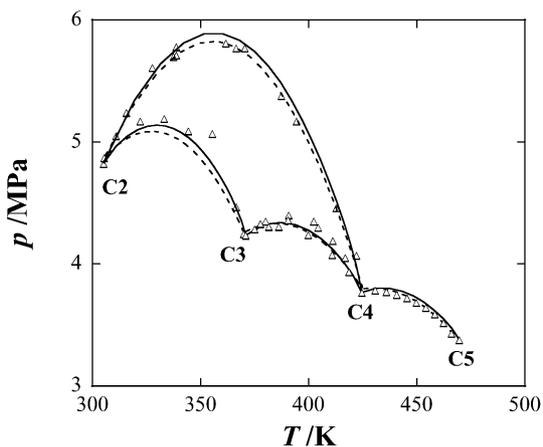


Fig. 5. p - T projection of the gas-liquid critical lines for the binary mixtures of ethane + propane, ethane + n -butane, propane + n -butane and n -butane + n -pentane. The triangles represent the experimental data [46], the solid lines the SAFT-VRX prediction and the dotted lines SAFT-VR with rescaled parameters.

lines between the critical point of the two pure components. For each binary mixture, we observe excellent agreement between the SAFT-VRX predictions and the experimental data. Again we note that no adjustable parameters were used in these calculations and therefore they represent true predictions.

5. Conclusions

We have developed the crossover SAFT-VR equation (SAFT-VRX) for mixtures by incorporating the crossover formulation proposed by Kiselev [17] into the original classical equation of state. We have successfully applied the new equation of state to binary mixtures of short-chain n -alkanes. Good agreement is achieved for phase equilibrium properties when compared to experimental data without the need for adjustable binary interaction parameters. While the SAFT-VR approach with rescaled parameters can achieve excellent agreement with experimental data in the p - T projection of the phase diagram poor agreement is seen for the liquid densities. The SAFT-VRX equation is able to accurately describe the whole fluid phase diagram and therefore accurately represents not only the gas-liquid critical locus but also the vapor-liquid equilibrium boundary. Currently we are applying the SAFT-VRX equation to long-chain n -alkane and other binary mixtures to further test the theory.

List of symbols

a	Helmholtz free energy; coefficients
b	universal linear-model parameter
c	coefficients for effective packing fraction expression
C	carbon number
d_1	rectilinear diameter amplitude
g	contact value; radial distribution function
G_i	Ginzburg number
k	Boltzmann constant
K	isothermal compressibility
m	number of segments in model chain
N	number of molecules
p	pressure
q	parametric variable in crossover function
r	distance between molecules
T	temperature
u	square-well potential
v	molar volume
v_1	crossover parameter in Y
x	mole fraction of molecule; field variable
X	composition vector
Y	crossover function

Greek letters

α	universal critical exponent for specific heat
β	universal critical exponent for the coexistence curve
δ	coefficients for critical shifts

ε	depth of square-well potential
γ	universal critical exponent for susceptibility
Δ	difference
Δ_1	universal critical exponent
$\Delta\varphi$	order parameter
$\Delta\bar{\varphi}$	renormalized order parameter
λ	width of square-well potential
ρ	density
σ	hard core diameter
μ	chemical potential
τ	reduced temperature difference
$\bar{\tau}$	renormalized temperature difference
ξ	reduced density, packing factor
Λ	thermal de Broglie wavelength

Subscripts

0	classical; along the critical isochore
c	critical
ij	pair interaction between species i and j
s	segment
x	pseudo one-fluid

Superscripts

ideal	ideal-gas contribution
mono	monomeric contribution
assoc	association contribution
chain	chain contribution
eff	effective
hs	hard sphere
I	components

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