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Crossover VTSRK equation of state for selected alkane + alkane and CO_2 + alkane binary mixtures

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ABSTRACT

Accurate predictions of the thermodynamic properties of binary mixtures, especially in the critical region, are essential for many chemical process designs. In this study, based on the predictive crossover volume translation SRK equation of state (VTSRK EoS) presented in previous work, the crossover VTSRK EoS for binary mixtures was developed. Composition-dependent mixing rules with one adjustable binary interaction parameter, k_{ij}, were used for the crossover equation to simplify the crossover EoS. The applicability of the crossver EoS was verified against two kinds of binary mixtures, including alkane + alkane and CO_2 + alkane mixtures, because of their wide applications. For the alkane + alkane mixtures with similar intermolecular interactions, the k_{ij} in the vdW-1 mixing rules was set to zero which makes the calculation predictive. For the CO_2 + alkane mixtures which have large difference between intermolecular interactions, the vapor liquid equilibrium (VLE) and single phase $p\rho T$ properties were calculated using k_{ij} obtained from VLE or $p\rho T$ experimental data at one temperature. The crossover VTSRK EoS gives better VLE and $p\rho T$ representations than the VTSRK EoS, especially in the critical region.

1. Introduction

Accurate predictions of the thermodynamic properties of binary mixtures in the near-critical region, including the vapor liquid equilibrium (VLE) and single phase behavior, are very important for chemical process designs and other industries [1,2], such as low grade heat recovery, gas-injected enhanced oil recovery and supercritical fluid extraction. The equation of state (EoS) is an effective tool for representing the thermodynamic properties of fluids. Multiparameter EoSs [3–5] are commonly used to accurately represent the thermodynamic properties, but they are complex. The equations need many adjustable parameters for mixture calculation, which increases the need for precise experimental data. Cubic EoSs, such as the SRK EoS [6] and PR EoS [7], are also widely used because of their simplicity and generality. Since they are based on mean field theory which neglects the density fluctuations in the critical region, the cubic EoSs fail to predict the singular properties near the critical point. Also, the cubic equations cannot accurately predict the saturated liquid densities over wide temperature ranges. Therefore, equations are needed that are accurate both near the critical point and far from the critical point and are relatively simple for mixture calculations.

The volume translation method was proposed to improve the saturated liquid density representation of cubic EoSs [8]. The value of the volume translation term decreases sharply when the temperature decreases from the critical temperature, and becomes constant gradually when the temperature is lower than $0.7T_c$. Therefore, temperature-dependent volume translation terms were proposed [9–11]. Good agreement has been obtained between the prediction results and experimental data. However, as an empirical approach, the volume translation EoS cannot represent the thermodynamic properties near the critical point, because the volume translation EoS is based on mean field theory. Moreover, using temperature-dependent volume translation terms may lead to thermodynamic inconsistencies, such as such as crossed isotherms at high pressures [11,12], $(b-c) < 0$ in the repulsive term [13,14], and isochoric heat capacities less than zero [12]. Since the value of the volume translation term becomes constant when the temperature is lower than $0.7T_c$, using temperature-independent term whose value is equal to the average value for temperatures below $0.7T_c$ can

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greatly improve the representation of the thermodynamic properties far from the critical point. The deviations in the near-critical region of the volume translation EoS are still relatively large although the deviations of the volume translation EoS are smaller than those of the original cubic EoS.

The phase behavior asymptotically close to the critical point can be expressed accurately by the scaling laws with universal critical exponents and scaling functions [15]. Far from the critical point, the thermodynamic properties can be well described by mean field theory with the classical-analytical form. Efforts have been made to incorporate the scaling law near the critical point and mean field theory far from the critical point. White and co-workers [16–18] proposed a recursive procedure based on Wilson's phase-space cell approximation method [19], which introduces only a few microscopic intermolecular potential parameters. However, this approach is complicated and requires additional spline functions for the thermodynamic property representations. Kiselev [20] proposed the crossover theory which has been successfully applied to different EoSs, such as the cubic EoSs [20–27] and the SAFT EoSs [28,29]. However, this method introduces six (or four) crossover parameters to the EoSs. Therefore, more accurate experimental data is needed to obtain the adjustable parameters. Moreover, the crossover parameters are mutually coupled and vary of several orders of magnitude, which complicate the parameter regression process [27].

The thermodynamic properties of binary mixtures in the critical region differ from those of pure fluids. The isomorphism theory of critical phenomena [30–32] indicates that the equation of state for mixtures near the critical point has the same functional form with pure fluids at a fixed field variable (the chemical potential) instead of at a fixed composition. Therefore, the mixing rules should be expressed in terms of the "field" variable (the chemical potential) instead of the "density" variable (the composition x). There are few crossover EoSs for mixtures formulated in terms of the chemical potential [33] because the approach following the isomorphism theory is time-consuming. As shown by Kiselev and Friend [34], mixing rules in terms of the composition can be used as an approximation, if the model does not intend to reproduce all the exact scaling laws for the mixture. The crossover equations developed for pure fluids have been extended to mixture properties [34–37]. However, since the crossover equation based on the Kiselev method introduces six (or four) crossover parameters, the crossover parameters for the pure fluids have to be correlated by experimental data prior to the mixture calculations, which complicates the procedure.

The main purpose of this study is to develop an EoS for binary mixtures with lower number of adjustable parameters that accurately predicts the thermodynamic properties in the critical region and the liquid density at wide temperature range. In previous study [25], the crossover volume translation SRK (VTSRK) EoS was presented. All the parameters in the equation were constant or expressed as functions of the critical parameters and the acentric factor which makes the equation predictive. In this work, combined with the mixing rules in terms of the composition, the crossover VTSRK EoS for binary mixtures was developed to represent the VLE and single phase properties. The applicability of the EoS is evaluated for two kinds of binary mixtures, including alkane + alkane (methane + ethane, methane + propane, propane + butane, propane + pentane, propane + *i*-butane, butane + *i*-butane, pentane + hexane, pentane + heptane, hexane + heptane) and CO_2 + alkane (CO_2 + ethane/propane/butane/*i*-butane/pentane/hexane/cyclopentane) mixtures. Alkane + alkane and CO_2 + alkane mixtures are two very different kinds of fluid mixtures with sufficient experimental data and have many applications in engineering fields, such as in organic Rankine cycles and oil recovery enhancement. The intermolecular interactions between different alkane molecules are of similar nature, and the interactions between CO_2 and alkane molecules are of different natures. Comparisons were made between the prediction results of the crossover VTSRK EoS and experimental data.

2. Thermodynamic model

Combining SRK EoS with the volume translation approach, the VTSRK is obtained as [11]

$$p = \frac{RT}{v + c - b} - \frac{a(T)}{(v + c)(v + c + b)} \tag{1}$$

$$a(T) = 0.42748\left(\frac{R^2 T_c^2}{p_c}\right)\alpha(T) \tag{2}$$

$$b = 0.086646\left(\frac{RT_c}{p_c}\right) \tag{3}$$

$$\alpha(T) = \left[1 + m\left(1 - T_r^{0.5}\right)\right]^2 \tag{4}$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{5}$$

$$c = \frac{RT_c}{p_c}\left(\frac{1}{3} - Z_c\right)c_1 \tag{6}$$

$$c_1 = -2.184\exp\left(-45.7247\left(\frac{1}{3} - Z_c\right)\right) + 0.2658 \tag{7}$$

where p is the pressure, T is the temperature, v is the molar volume, R is the ideal gas constant, a and b are the parameters of the SRK EoS, c is the volume translation term, T_c and p_c are the critical temperature and the critical pressure, T_r is the reduced temperature (T/T_c), ω is the acentric factor, and Z_c is the critical compressibility factor.

Applying the crossover method [20] to the VTSRK EoS, the dimensionless Helmholtz free energy of the crossover VTSRK EoS for a pure fluid is:

$$A^*(T, v) = A^*_{cr}(\Delta T, \Delta v) + A^*_{bg}(T, v) \tag{8}$$

$$\begin{aligned} A^*_{cr}(\Delta T, \Delta v) = {} & A^*_{res}(\Delta T, \Delta v) - A^*_{res}(\Delta T, 0) - \ln(\Delta v + 1) \\ & + \Delta v p^*_0(\Delta T) \end{aligned} \tag{9}$$

$$A^*_{bg}(T, v) = -\Delta v p^*_0(T) + A^*_{res}(T, v_{0c}) + A^*_{id}(T) \tag{10}$$

where $\Delta T = T/T_{0c} - 1$ is the dimensionless distance from the classical critical temperature, T_{0c}, and $\Delta v = v/v_{0c} - 1$ is the dimensionless distance from the classical critical volume, v_{0c}. $p^*_0(T) = p(T, v_{0c})v_{0c}/RT$ is the dimensionless pressure, $A^*_{res}(T, v_{0c})$ is the dimensionless residual of the Helmholtz energy along the critical isochore and $A^*_{id}(T)$ is the dimensionless temperature-dependent ideal-gas Helmholtz free energy.

The classical dimensionless temperature, ΔT, and the order parameter, Δv, in the critical part are replaced by renormalized values as:

$$\begin{aligned} \overline{\tau} &= \tau \Upsilon^{-\alpha/2\Delta_1} + (1 + \tau)\Delta\tau_c \Upsilon^{2(2-\alpha)/3\Delta_1} \\ \overline{\varphi} &= \varphi \Upsilon^{(\gamma - 2\beta)/4\Delta_1} + (1 + \varphi)\Delta\varphi_c \Upsilon^{(2-\alpha)/2\Delta_1} \end{aligned} \tag{11}$$