



Short communication

Examining the effect of binary interaction parameters on VLE modelling using cubic equations of state

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ABSTRACT

Vapor–liquid equilibrium (VLE) data are important in the optimization of thermodynamic cycles. As energy concerns continue to grow, improving the efficiencies of power and refrigeration cycles is increasingly important. Numerical simulations using empirical equations of state provide an excellent alternative to time consuming experimental measurement of VLE data. However, it is important to understand the limitations of using correlative equations for data prediction. In this study, a water–ethanol mixture is simulated with various VLE models. Non-optimal binary interaction parameters are considered and model accuracy is evaluated in terms of average absolute percent deviation (%AAD) between simulated and experimental bubble and dew point pressures. For this system, it is found that as the correlative accuracy of a model increases, the predictive ability decreases. Specifically, the temperature dependence of the binary interaction parameters is shown to be an important consideration for the water–ethanol system when more complex combining rules are implemented.

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1. Introduction

The need for extensive vapor–liquid equilibrium (VLE) data for the optimization of thermodynamic cycles and separation processes has been well-established [1–5]. For example, an understanding of the temperatures, pressures, and compositions at which mixtures are pure liquids or vapors is necessary to properly match operating conditions to working fluids, or alternatively, to correctly select a cycle's working fluid based on operating parameters. Without this knowledge, it is likely that a cycle's efficiency will be greatly diminished, or the cycle may even cease to function altogether. Furthermore, as energy efficiency, and consequently cycle efficiency, becomes increasingly important, the demand for VLE data will only increase [6]. Due to the time-consuming nature of experimental measurement, equations of state (EOSs) have become a significant source of VLE data through various modelling approaches. The most commonly used methods rely on empirical cubic equations of state, implemented in conjunction with mixing and combining rules, to determine mixture properties [7,8]. The combining rules include experimental fitting values, referred to as binary interaction parameters, which lead to largely correlative sets of equations. Consequently, it is important to consider the limits on the predictive calculation of data using these equations.

Recent work has focused on the use of predictive combining rules that account for the temperature within the expression of the binary interaction parameters [9]. Of specific note is the success by Jaubert et al. and Soave et al. in predicting VLE data for hydrocarbons and related mixtures [10–20]. They have used group contribution methods to determine the temperature dependence of the binary interaction parameters implemented in the Peng–Robinson and Soave–Redlich–Kwong equations of state.

In this study, VLE data simulation is based on more traditional VLE models in order to determine the extent of their predictive ability for the highly nonideal water–ethanol system. This allows a better evaluation of the strengths and shortcomings of these simple models for this system. To investigate this concept, an analysis of the dependence of various equation combinations on the accuracy of binary interaction parameters over a range of temperatures is considered.

2. Numerical method

While innumerable equations of state, mixing rules, and combining rules exist, an assortment of some of the most common equations was chosen for this study, with the purpose of including very basic as well as somewhat complex forms. The simplest equation of state capable of simulating both liquid and vapor phases is the van der Waals EOS [21]:

$$Z = \frac{V_m}{V_m - b} + \left(-\frac{a}{RTV_m} \right), \quad (1)$$

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Table 1
Modifications to the van der Waals attractive term for various EOSs [8,22–26].

Equation of state	Attractive term ($-Z^{att}$)
Soave–Redlich–Kwong (SRK)	$\frac{a(T)}{RT(V_m+b)}$
Peng–Robinson (PR)	$\frac{a(T)V_m}{RT[V_m(V_m+b)+b(V_m-b)]}$
Peng–Robinson–Stryjek–Vera (PRSV)	$\frac{a(T)V_m}{RT(V_m^2+2bV_m-b^2)}$

where the first and second terms represent the repulsive and attractive contributions to the compressibility, respectively. The equations of state considered in this study provide improvements to the van der Waals attractive term, various forms of which are listed in Table 1 [8,22–26]. It has been shown that the Peng–Robinson–Stryjek–Vera equation of state is specifically amenable to nonideal systems, such as the water–ethanol mixture studied here [26]. The a and b parameters shown in the EOSs are calculated for a mixture using mixing rules. Standard linear and quadratic mixing rules are used in this study, and their forms for an arbitrary parameter ζ are shown in Eqs. (2) and (3), respectively [8,22,23]:

$$\zeta = \sum_i^N z_i \zeta_{ii}, \quad (2)$$

$$\zeta = \sum_i^N \sum_j^N z_i z_j \zeta_{ij}. \quad (3)$$

In these expressions z_i represents the mole fraction of the i th component, ζ_{ii} is the EOS parameter for a single, pure component and ζ_{ij} depends on mixture behavior and is determined using a combining rule. The combining rules implemented here are shown in Table 2, where k_{ij} and k_{ji} refer to the binary interaction parameters which are of particular interest in this study [8,22–26]. The arithmetic and conventional combining rules are one parameter rules, where $\zeta_{ij} = \zeta_{ji}$. The Margules and van Laar forms are two parameter models with $k_{ij} \neq k_{ji}$.

As is common, only the linear mixing rule was considered for the co-volume parameter in the equations of state [27]. This simplification removes the dependence of the repulsive term on cross-interaction effects and therefore removes the need for a combining rule for its calculation. Conversely, the use of both of the mixing rules and all of the combining rules listed was permitted for the calculation of the attractive parameter. Fugacity coefficients were calculated for the various combinations of the equations, and equilibrium was determined via the iterative $\phi - \phi$ approach [22,28]. Laguerre's method was implemented for the numerical solution of the compressibility equation in order to guarantee the convergence of the calculation [29].

3. Results and discussion

In this study, a mixture of water and ethanol was considered with the temperature fixed at different values between 298.15 K

Table 2
Combining rules considered in this study [8,22–26].

Combining rule	ζ_{ij}
Arithmetic (A)	$\frac{1}{2}(1 - k_{ij})(\zeta_{ii} + \zeta_{jj})$
Conventional (C)	$(1 - k) \sqrt{\zeta_{ii} \zeta_{jj}}$
Margules form (M)	$(1 - z_i k_{ij} - z_j k_{ji}) \sqrt{\zeta_{ii} \zeta_{jj}}$
van Laar form (vL)	$\left(1 - \frac{k_{ij} k_{ji}}{z_i k_{ij} + z_j k_{ji}}\right) \sqrt{\zeta_{ii} \zeta_{jj}}$

Table 3

Optimal binary interaction parameters determined for a water–ethanol mixture at 323.15 K, modelled with the PRSV equation of state, the linear mixing rule for the b parameter, the quadratic mixing rule for the a parameter, and the specified combining rule for cross-interaction terms.

Combining rule	$k_{12,optimal}$	$k_{21,optimal}$
Arithmetic	−0.015	N/A
Conventional	−0.105	N/A
Margules form	−0.08	−0.12
van Laar form	−0.12	−0.09

and 343.15 K. Optimal binary interaction parameters for each temperature and each equation set were determined by varying the parameter values until the average absolute percent deviation between experimental and simulated bubble and dew point pressures was minimized. This process was carried out using experimental data at five different temperatures, as tabulated in the *Vapor Liquid Equilibrium Data Collection* [30,31]. One set of optimized binary interaction parameter values is given in Table 3, for the Peng–Robinson–Stryjek–Vera equation of state at a temperature of 323.15 K.

3.1. Perturbation of optimal binary interaction parameters

The optimal binary interaction parameters were subsequently perturbed by $\pm 15\%$ to determine the effect of erroneous parameters on the simulated results. The perturbed values were calculated from the optimal values, such as those shown in Table 3, using Eq. (4):

$$k_{ij,perturbed} = (1 \pm 0.15) \times k_{ij,optimal}. \quad (4)$$

Fig. 1a illustrates the bubble and dew point curves for a mixture at 323.15 K. These particular results were modelled using the Peng–Robinson–Stryjek–Vera (PRSV) equation of state, the quadratic mixing rule for a , and the arithmetic combining rule. Data calculated using both the optimal (solid lines) and perturbed (dotted lines) binary interaction parameter are shown. Fig. 1 displays the same curves modelled with the same equation of state and mixing rule, but using the van Laar combining rule with both binary interaction parameters, k_{12} and k_{21} , perturbed equally.

A comparison of these two figures shows qualitatively that the van Laar combining rule is more accurate than the arithmetic combining rule when provided optimal binary interaction parameters. However, the difference between the results using optimal parameters and those using perturbed parameters is also larger for the van Laar combining rule. This illustrates that the van Laar form is also more strongly dependent on the accuracy of the parameters. The average absolute percent deviations between experimental and simulated data (%AAD) for these results are shown in Table 4. The %AAD is determined by taking an average of the %AADs from the dew and bubble point data:

$$\%AAD = \frac{1}{2} (\%AAD_{bubble} + \%AAD_{dew}), \quad (5)$$

Table 4

Average absolute percent deviations (%AAD) using optimal and perturbed binary interaction parameters modelled with the PRSV equation of state, the linear mixing rule for the b parameter, the quadratic mixing rule for the a parameter, and the combining rule specified below, at 223.15 K.

Combining rule	Optimal	Perturbed
Arithmetic	3.265	3.336
Conventional	3.265	6.549
Margules	1.721	6.440
van Laar	1.718	6.474

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