



Effect of combining rules for cubic equations of state on the prediction of double retrograde vaporization

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In this work, the phenomenon of double retrograde vaporization (DRV) is simulated using the Peng–Robinson equation of state with the classical mixing rules and several combining rules for the cross-energy and cross-co-volume parameters. The binary interaction parameters are set equal to zero in all cases, i.e., the calculations are entirely predictive. An interesting conclusion is that the predictions using the classical combining rules (geometric mean rule for a_{ij})

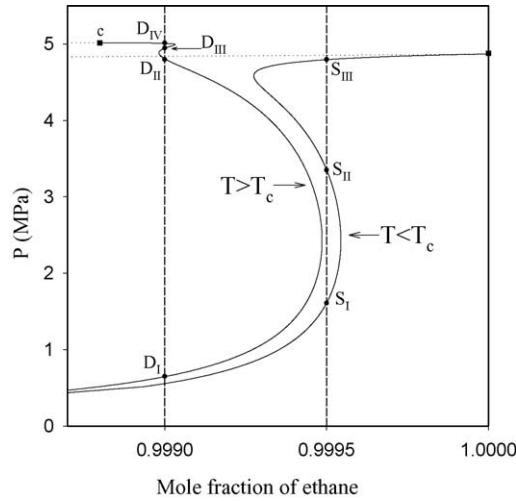


Fig. 1. P - x - y diagram of double retrograde vaporization for the system ethane + limonene at 307.4 and 305.3 K. The solid and dotted curves represent the dew and bubble point curves, respectively.

and that, even though double domes are probably common, triple or more domes are unlikely to ever be identified in nature. Recently, Raeissi and Peters [18] explained DRV based on infinite-dilution critical phenomena. The authors analyzed the volumetric properties of the two phases in equilibrium to establish the criterion for existence of DRV.

Given that the Peng–Robinson EOS with classical mixing and combining rules can predict DRV, it is interesting to evaluate how other rules influence predictions of the phenomenon. In the calculations presented here, we use the classical mixing rules but test different combining rules, motivated by the fact that some combining rules have been shown to improve VLE predictions of cubic EOS in asymmetrical systems. For the cross-energy (a_{ij}) parameter, we test the geometric mean (classical rule) and Berthelot's [19] rules. For the cross-co-volume (b_{ij}) parameter, we use: (a) the arithmetic mean rule (classical rule); (b) the geometric rule proposed by Good and Hope [20], which has been shown to provide good results for second virial coefficients of gas mixtures [21]; (c) the Lorentz rule, which is commonly used in EOS originated from statistical mechanics theory [22]; (d) the Lee et al. [23] rule, used in PVT calculations of the mixture carbon dioxide + *n*-butane with Peng–Robinson EOS; (e) the Sadus [24] combining rule used, which successfully predicts critical diagrams of type III. Sadus [24] reports that this combining rule is more accurate than the Lorentz, arithmetic and geometric combining rules. Cabral et al. [25] recently used a cubic EOS [26] with the classical combining rules and the Sadus [24] combining rule, and compared results from Monte Carlo simulations in the Gibbs ensemble for the phase equilibrium of binary mixtures of Lennard–Jones fluids. It was observed that both combining rules provided similar results for mixtures containing components of similar size. However, the combining rule proposed by Sadus [24] always provided better pre-

dictions when the components had considerable size differences. Since this is the situation in DRV and the phenomenon occurs over narrow ranges of composition and temperature, its prediction constitutes a difficult test for combining rules.

Phase equilibrium conditions were determined by solving the isofugacity equations with either bubble or dew point specifications, in series of isothermal or mole fraction isopleths calculations. Phase stability of the calculated bubble or dew points was tested using the global tangent plane criterion [27] to verify whether a third phase might be present, as discussed in Section 3.

The Peng–Robinson EOS [28] was used:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \quad (1)$$

where the a and b parameters are given by:

$$a_i = 0.45724 \frac{R^2 T_{c,i}^2}{P_{c,i}} \alpha_i \quad (2)$$

$$\alpha_i = \left\{ 1 + \kappa_i \left[1 - \left(\frac{T}{T_{c,i}} \right)^{1/2} \right] \right\}^2 \quad (3)$$

$$\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (4)$$

$$b_i = 0.07780 \frac{RT_{c,i}}{P_{c,i}} \quad (5)$$

where $T_{c,i}$, $P_{c,i}$ and ω_i are the critical temperature, critical pressure, and acentric factor for each component, respectively.

The classical mixing rules widely used for the a and b parameters in this EOS are:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (7)$$

The combining rules for the cross-energy (a_{ij}) parameters used in this work are:

(A1) The classical rule (geometric mean)

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (8)$$

(A2) The Berthelot's combining rule [19]

$$a_{ij} = b_{ij} \sqrt{\frac{a_i a_j}{b_i b_j}} (1 - k_{ij}) \quad (9)$$

The combining rules used for the cross-co-volume (b_{ij}) parameters are:

Table 1

Values of k_{ij} and ℓ_{ij} in the classical combining rules that correspond to k_{ij} and ℓ_{ij} values equal to zero in the other combining rules (Eqs. (9), (11)–(14))

System	Combining rules	$k_{12} = k_{21}$	$\ell_{12} = \ell_{21}$
Methane + <i>n</i> -butane	A1B2	−0.04186	0.07484
	A1B3	−0.06923	0.05054
	A1B4	−0.08428	0.03717
	A1B5	−0.00012	0.11190
Methane + <i>n</i> -pentane	A1B2	−0.06279	0.10663
	A1B3	−0.10349	0.07242
	A1B4	−0.12684	0.05279
	A1B5	−0.00018	0.15926

(B1) The classical rule (arithmetic mean)

$$b_{ij} = \frac{b_i + b_j}{2}(1 - \ell_{ij}) \quad (10)$$

(B2) The Lorentz rule

$$b_{ij} = \left(\frac{b_i^{1/3} + b_j^{1/3}}{2} \right)^3 (1 - \ell_{ij}) \quad (11)$$

(B3) The Lee et al. [23] rule

$$b_{ij} = \left(\frac{b_i^{2/3} + b_j^{2/3}}{2} \right)^{3/2} (1 - \ell_{ij}) \quad (12)$$

(B4) The rule presented by Sadus [24]

$$b_{ij} = \frac{1}{4 \times 2^{1/3}} (b_i^{1/3} + b_j^{1/3})^2 (b_i + b_j)^{1/3} \quad (13)$$

(B5) The Good and Hope rule [20] (geometric mean)

$$b_{ij} = \sqrt{b_i b_j} (1 - \ell_{ij}) \quad (14)$$

In these combining rules, k_{ij} and ℓ_{ij} are parameters that can be fitted to experimental data. Here, they are set equal to zero in all calculations, since our interest is on comparing the ability of combining rules in DRV predictions without fitted parameters. For isothermal systems, it is interesting to calculate the k_{ij} and ℓ_{ij} values in the classical combining rules that correspond to k_{ij} and ℓ_{ij} values equal to zero in the other combining rules (Eqs. (9), (11)–(14)). Table 1 shows these parameters for the systems methane + *n*-butane and methane + *n*-pentane that are discussed in Section 3.

The fugacity coefficients, and their analytical derivatives, obtained from the EOS and its mixing and combining rules, were automatically obtained and implemented using the Thermath [29] computer algebra program.

The analysis of the effect of combining rules on the prediction of S-shaped dew point curves and of DRV is based on comparisons with the experimental data available for

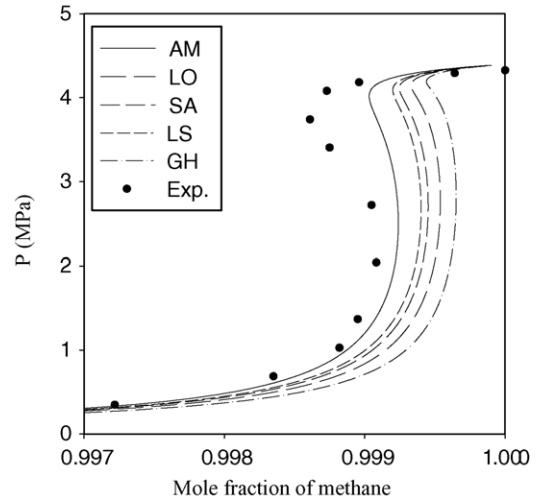


Fig. 2. Isothermal dew points for the system methane + *n*-butane at 189.06 K using the GM combining rule for a_{ij} and several combining rules for b_{ij} . Experimental data points Chen et al. [1].

these types of behavior in non-electrolyte binary mixtures. Figs. 2 and 3 present results of dew points calculations for the methane + *n*-butane system at 189.06 K using the geometric mean (GM) and the Berthelot (BE) combining rule for a_{ij} , respectively. The critical properties used in the simulation are taken from Poling et al. [30]. Each of these combining rules for a_{ij} is used with the arithmetic mean (AM), Lorentz (LO), Sadus (SA), Lee et al. (LS) and Good and Hope (GH) combining rules for the b_{ij} parameter. These calculations are compared to experimental results [1], also included in the figures. The use of the GM rule for a_{ij} and the AM rule for b_{ij} (Fig. 2) provides the best agreement with experimental data. Furthermore, by comparing the corresponding curves

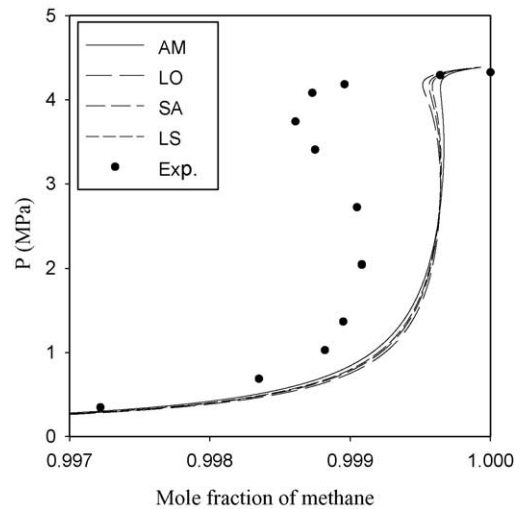


Fig. 3. Isothermal dew points for the system methane + *n*-butane at 189.06 K using the BE combining rule for a_{ij} and several combining rules for b_{ij} . Experimental data points: Chen et al. [1].

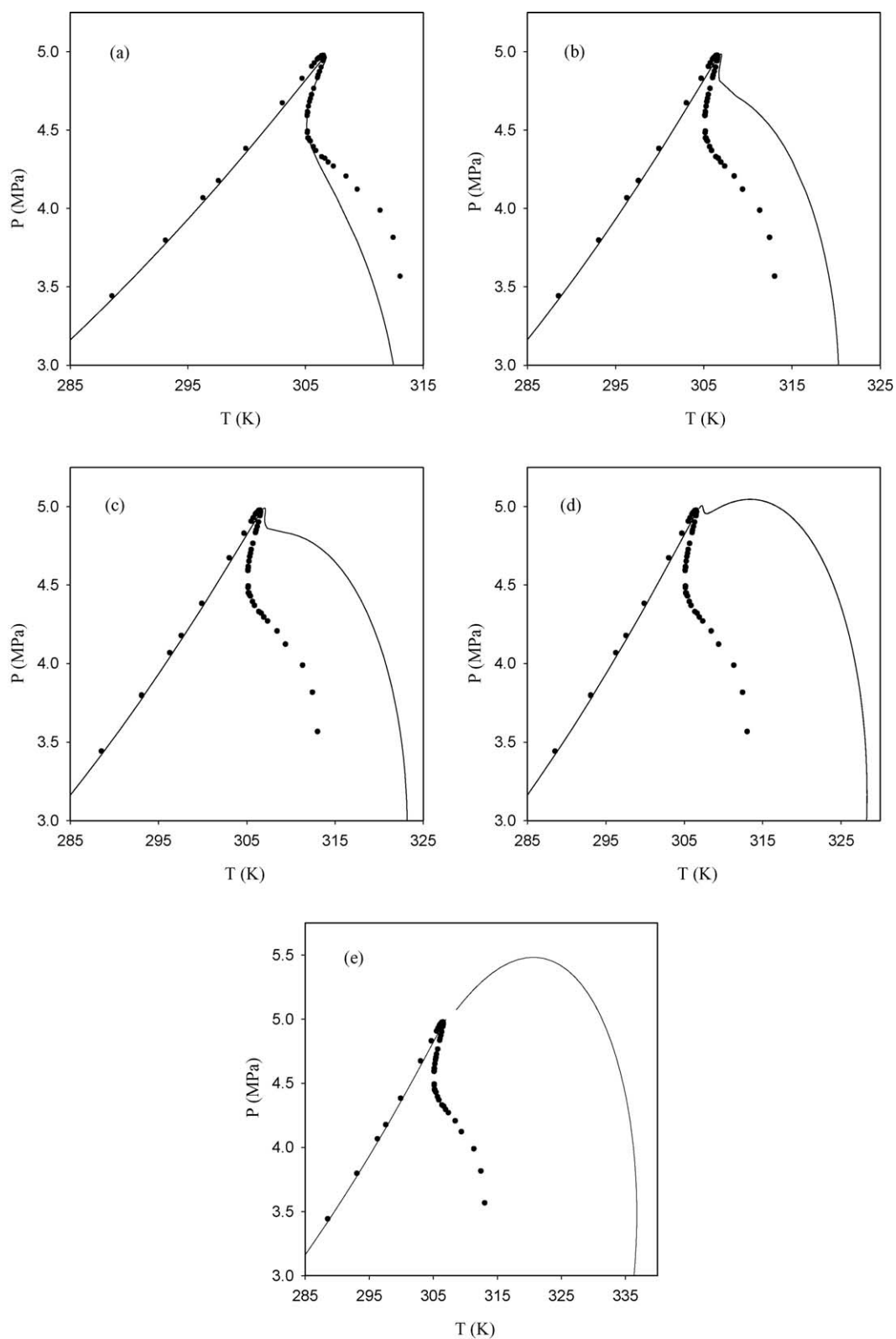


Fig. 4. Mole fraction isopleths for the system ethane + limonene at 99.93% in ethane using the GM combining rule for a_{ij} and several combining rules for b_{ij} : (a) AM, (b) LS, (c) SA, (d) LO, and (e) GH. Experimental data (points): Raeissi and Peters [7].

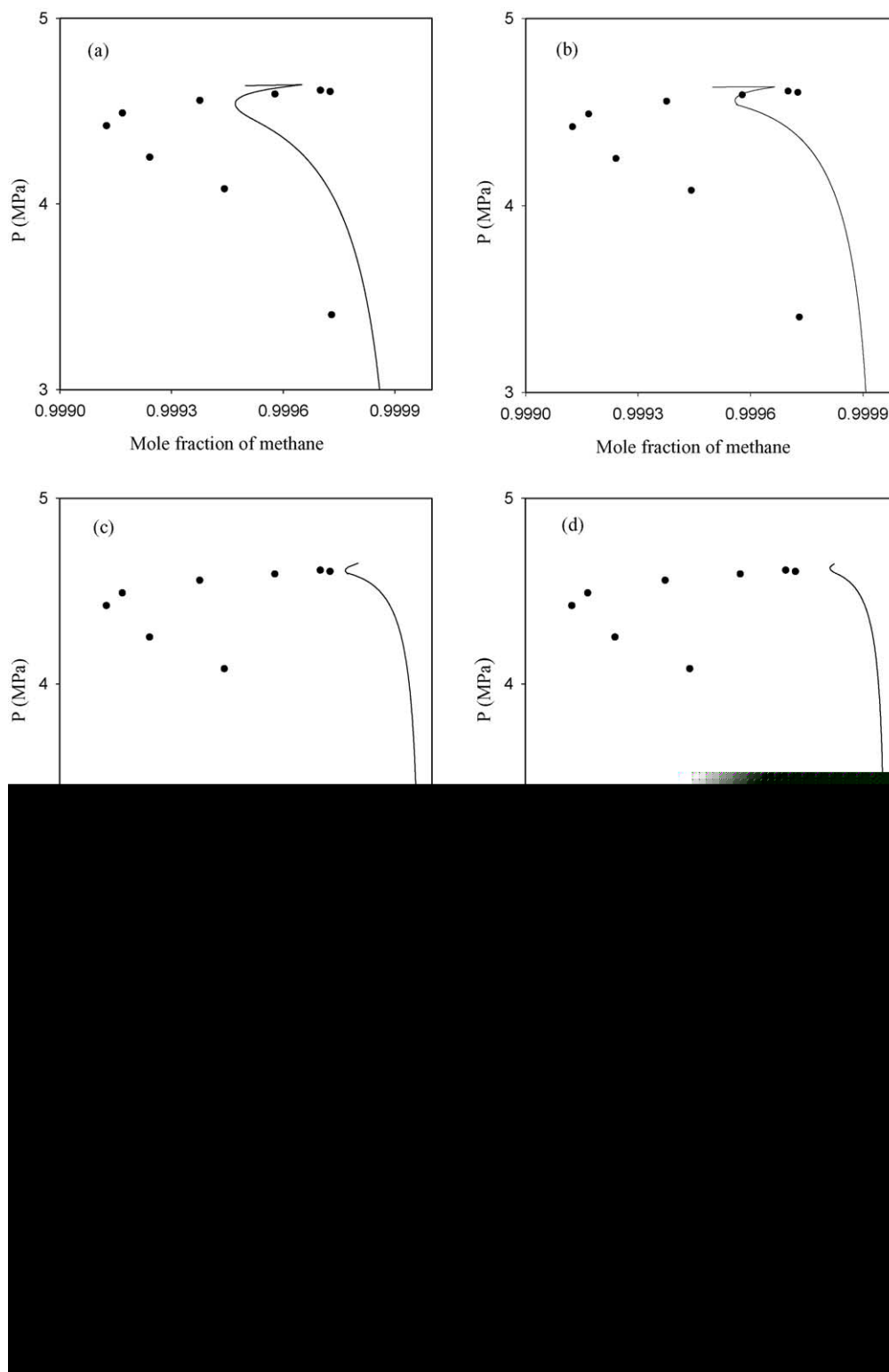


Fig. 5. Isothermal dew points for the system methane + *n*-pentane at 191.08 K. (a) GM with AM, (b) GM with LS, (c) BE with SA, (d) BE with AM and (e) BE with LS. Experimental data (points): Chen et al. [1].

in Figs. 2 and 3, it is observed that when the same combining rule is used for b_{ij} , the GM rule for a_{ij} always produced better results. Note that with the choice of the GH combining rule for b_{ij} , the Berthelot (BE) rule for a_{ij} reduces to the GM rule for a_{ij} , and for this reason, this curve does not appear in Fig. 3.

Fig. 4 shows the mole fraction isopleths for the ethane + limonene system at 99.93% in ethane. The critical properties used in the simulation are taken from Raeissi and Peters [12] and the experimental data, from Raeissi and Peters [7]. Use of the GM rule for a_{ij} and the AM rule for b_{ij} (Fig. 4a) again provides the best result when compared to experimental data. Predictions of DRV worsen as we change the combining rule for b_{ij} in Fig. 4b–d, until DRV is no longer predicted (Fig. 4e). Using the BE combining rule for a_{ij} , all the combining rules used for b_{ij} fail to predict DRV and plots similar to Fig. 4e are obtained.

For the methane + *n*-pentane system, Fig. 5 presents dew points calculations at 191.08 K. The critical properties used in the simulation are taken from Poling et al. [30]. At this temperature, only the coupling of the GM rule for a_{ij} with

the AM rule for b_{ij} and of the BE rule for a_{ij} with the AM rule for b_{ij} predict two phases in equilibrium at all compositions (Fig. 5a and d). The following coupling of combining rules: GM rule for a_{ij} and the LS rule for b_{ij} ; BE rule for a_{ij} and the SA rule for b_{ij} ; BE rule for a_{ij} and the LS rule for b_{ij} predict DRV (Fig. 5b, c and e) but also the existence of three phases at equilibrium (Fig. 6a–c) over a narrow mole fraction range close to the critical point of methane. The other coupling of combining rules considered here do not predict DRV and, for conciseness, their results are not shown. We could find no experimental data indicating the existence of three phases in equilibrium for this system in the literature. The experimental evidence available [31] indicates that *n*-hexane is the first *n*-alkane that when mixed with methane presents partial liquid phase immiscibility and has a critical diagram of type V [32], according to the van Konynenburg and Scott [33] classification.

Fig. 7 shows the mole fraction isopleths for the ethane + linalool system at 99.98% in ethane. The critical properties used in the simulation are taken from Raeissi and Peters [12] and the experimental data, from Raeissi and Pe-

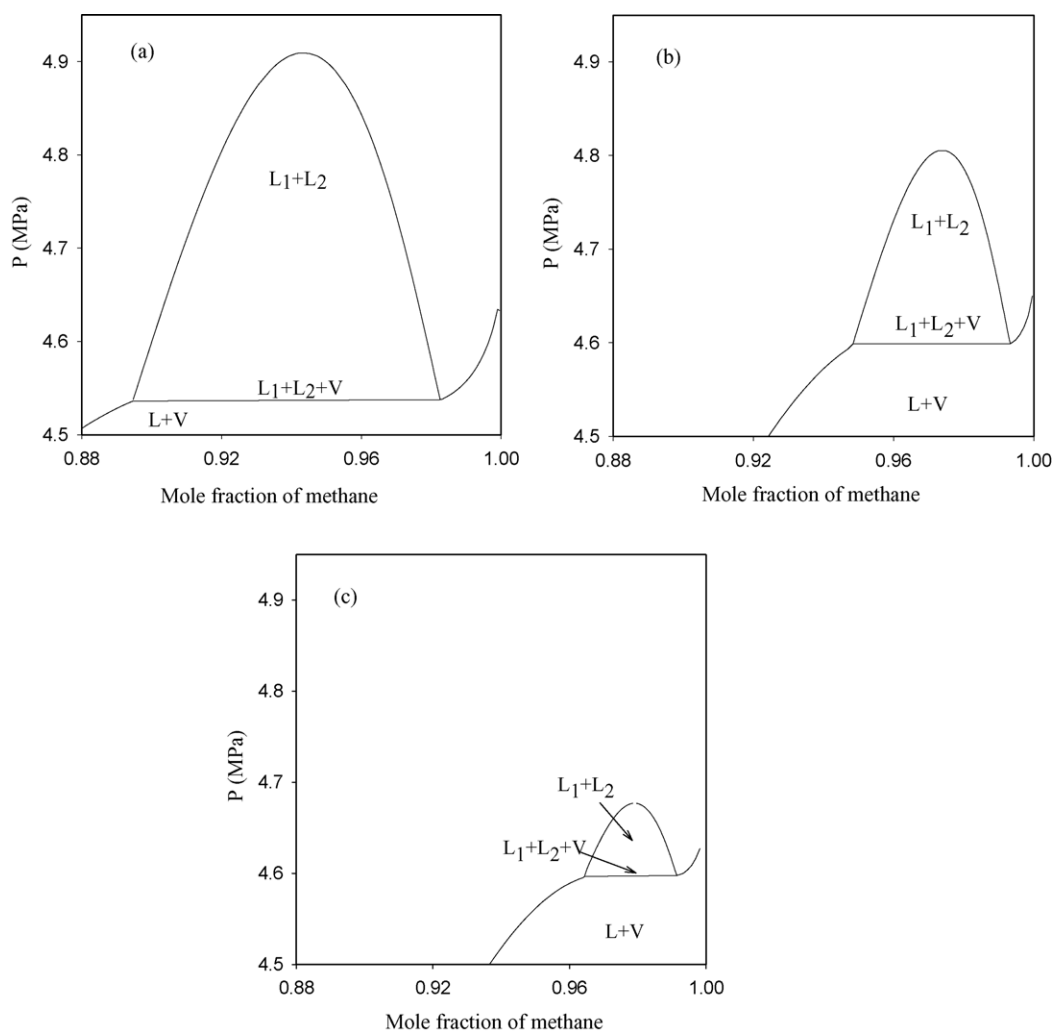


Fig. 6. Liquid-liquid immiscibility for the system methane + *n*-pentane at 191.08 K. (a) GM with LS, (b) BE with SA, and (c) BE with LS.

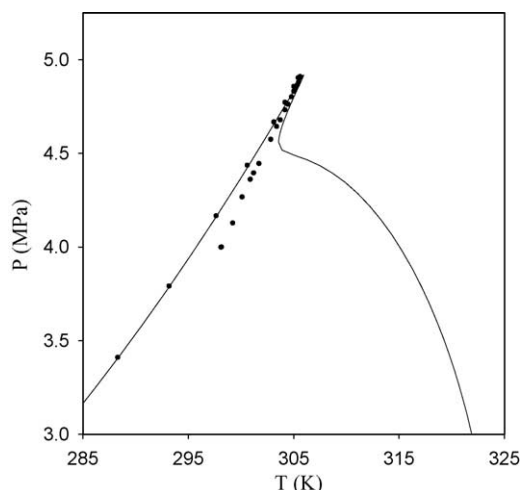


Fig. 7. Mole fraction isopleths for the system ethane + linalool at 99.98% in ethane using the GM combining rule for a_{ij} and AM combining rule for b_{ij} . Experimental data (points): Raeissi and Peters [8].

ters [8]. As in the previous cases, the coupling of the GM rule for a_{ij} with the AM rule for b_{ij} (Fig. 7) provides the best agreement with experimental data, even though there are large deviations in the dew point curve. However, predictive calculations for this system are difficult. For example, Raeissi and Peters [12] compared the use of the Peng–Robinson EOS with the binary interaction parameters k_{ij} and ℓ_{ij} set equal to 0, as in this work, and with values fitted using experimental data. In the latter case, they obtained significantly agreement with experimental data, what was attributed to the large differences in both molecular size and structure. Espinosa et al. [16] used a group-contribution EOS, the GCEOS, but had to define specific binary interaction parameters for ethane with the alcohol group in linalool for a satisfactory representation of mole fraction isopleths for this system.

In this work, we predicted double retrograde vaporization using the Peng–Robinson equation of state with the classical mixing rules and several combining rules, some of which have been recently identified as good modeling choices for mixtures containing components with large size difference. In spite of this fact, an interesting conclusion is that the predictions using the classical combining rules (geometric mean rule for a_{ij} and arithmetic mean rule for b_{ij}) provide the best agreement with the experimental data for all the systems tested. Another interesting observation is that several combining rules for b_{ij} , other than the arithmetic mean rule for b_{ij} , predict the existence of three phases in equilibrium in a very narrow temperature range close to the critical temperature of methane in the methane + n -pentane system. However, experimental evidence suggests that n -hexane is the first n -alkane to present partial liquid phase immiscibility with methane.

List of symbols

a	equation of state parameter
a_{ij}	cross-energy parameter
b	equation of state parameter
b_{ij}	cross-co-volume parameter
k_{ij}	binary interaction parameter for a_{ij}
ℓ_{ij}	binary interaction parameter for b_{ij}
P	pressure
R	universal gas constant
T	temperature
v	molar volume

Greek letters

α	equation of state temperature dependence function
κ	intermediate function in equation of state
ω	acentric factor

Subscripts

c	critical state
i, j	component indexes

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