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Simulation of double retrograde vaporization using the Peng–Robinson equation of state

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Abstract

Double retrograde vaporization is a phenomenon characterized by an unexpected retrograde dew point curve at compositions approaching nearly the pure volatile component (component A) and at temperatures very close to the critical temperature of the more volatile component (Tc_A). On the p–x–y diagram, instead of the single-domed dew point curve in the familiar "single" retrograde vaporization, double retrograde vaporization shows two "domes" at temperatures above but close to Tc_A. At temperatures below but close to Tc_A, the dew point curve has an "S"-shape. This results respectively in quadruple- or triple-valued dew points at a specific composition. In this work, the phenomenon of double retrograde vaporization has been simulated using a cubic equation of state. Both the "double-dome" and the "S"-shape curves for the binary systems (ethane + linalool) and (ethane + *d*-limonene) were successfully modelled, even without the use of binary interaction parameters. Results are also obtained by optimizing interaction parameters using experimental bubble point data. Even though double retrograde vaporization has rarely been observed in literature, we believe that it is the normal behaviour that always occurs in binary mixtures in which the two components differ largely enough in molecular symmetry to produce a very steep dew point curve. To further verify this generality, simulations were performed on a number of binary mixtures of different families. Double retrograde vaporization was estimated in every system with a steep dew point curve.
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1. Introduction

Although a great number of studies have been carried out in the field of near-critical phase behaviour, the special phenomenon of "double retrograde vaporization" has rarely been observed. This behaviour was shown experimentally by Chen *et al.* [1] in (methane + butane) where triple-valued dew points were observed in a narrow concentration range for isotherms at and immediately below the critical point of pure methane. The same group [2,3] also noticed double retrograde vaporization in (methane + pentane). In this system, in a narrow concentration range they observed quadruple-valued dew points for isotherms at temperatures immediately above the critical temperature of pure methane. Later, Kahre [4] confirmed the triple-valued dew points previously observed for (methane + butane). In addition, Bischoff and Pitzer [5] found experimentally a similar behaviour in the binary aqueous system with sodium chloride. Using a different experimental approach involving iso-compositional analyses, Raeissi and Peters [6,7] observed quadruple-valued dew points for isopleths within a narrow temperature and pressure range in (ethane + limonene) and (ethane + linalool). In an attempt to simulate double retrograde vaporization, Carnahan *et al.* [8] used the van der Waals equation of state to model (methane + butane) and (methane + pentane). They succeeded in simulating the "S"-shaped dew point curve qualitatively by introducing a "decoupling parameter" in the definition of the mixture parameter "*a*". However, without the use of these decoupling parameters, their results could not reproduce, even qualitatively, the "S"-shaped curve found in (methane + butane). Arai *et al.* [9] used the Benedict-Webb-Rubin equation of state (BWR EOS) to simulate (methane + butane) dew point isotherms. Their calculated results from the original BWR EOS agreed semi-qualitatively with the observed "S"-shaped phenomenon. They then modified the BWR constants C_0, b, and α for methane by matching the methane critical constants, modified the C_0 constant for butane by using vapour pressure data, and introduced a binary interaction parameter. The net effect of these changes produced a near quantitative agreement with the "S"-shaped isotherm. However, it was not possible to calculate the "double-domed" behaviour with quadruple valued dew points. In this study, the complete double-domed retrograde phenomenon at temperatures above Tc_A was also successfully simulated, in addition to the "S"-shaped curve at temperatures below the critical temperature of ethane. This was achieved using the original Peng–Robinson equation of state for (ethane + limonene) and (ethane + linalool). Satisfactory results were obtained, even without the use of binary interaction parameters. To confirm the generality of double retrograde vaporization, this phenomenon was also simulated for a number of different systems for which no experimental evidence of double retrograde vaporization was available.

2. Theory

Instead of the usual double-dew points in the familiar single-retrograde condensation, double retrograde vaporization is characterized by an S-shaped or double-domed retrograde dew point curve in the p–x–y diagram. This results in triple- or quadruple-valued dew points for a single composition. Double retrograde vaporization occurs within a very limited composition and temperature range, very close to the critical point of the more volatile component. It is the result of a continuous phase transition from the critical point of the pure volatile component to the critical point of the highly concentrated mixture with the more volatile component. Detailed explanations of this phenomenon and the transitions involved are given elsewhere [6,7]. From an extensive list of experimental phase behaviour studies, only a few have reported double retrograde vaporization. However, we believe that it is not a rare phenomenon at all. On the contrary, and on the basis of the general rule of continuity of phase behaviour, it is the behaviour that we would always expect close to the critical point of the more volatile component in mixtures composed of molecules differing significantly in symmetry. The only reason for the rare observations is that the composition, pressure and temperature range in which double retrograde vaporization occurs may be so small that they are easily missed in actual experiments. If equations of state were capable of predicting the double retrograde vaporization behaviour, they would provide further evidence of the generality of this phenomenon.

As equations of state become more complex and have more parameters, they become more powerful in predicting broader types of unusual and complex phase behaviour. In an attempt to verify the generality of double retrograde vaporization, the simple cubic Peng–Robinson equation of state [10] is used to calculate vapour–liquid equilibria:

$$P = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}(V_\mathrm{m} + b) + b(V_\mathrm{m} - b)}. \tag{1}$$

The constants a and b can be obtained from the pure fluid critical properties using

$$a = 0.457235\frac{R^2T_\mathrm{c}^2}{p_\mathrm{c}}\alpha, \tag{2}$$

$$b = 0.077796\frac{RT_\mathrm{c}}{p_\mathrm{c}}, \tag{3}$$

$$\alpha = \left\{1 + \kappa(1 - \sqrt{T/T_\mathrm{c}})\right\}^2, \tag{4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2, \tag{5}$$

where T_c and p_c are the critical temperature and pressure, respectively, and ω is the acentric factor. When using equation (1) for mixtures, for reasons of simplicity, the classical two-parameter mixing rules are applied:

TABLE 1
Critical temperature T_c, critical pressure p_c and acentric factor ω of the pure components used in the simulation

Substance	T_c/K	p_c/MPa	ω
Ethane	305.4[a]	4.88[a]	0.099[a]
d-Limonene	660.0[b]	2.75[b]	0.313[b]
Linalool	630.5[c]	2.42[c]	0.748[c]

[a] Reference 11.
[b] Reference 12.
[c] Reference 13.

$$a = \sum_i \sum_j x_i x_j a_{ij}, \tag{6}$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \tag{7}$$

where

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}), \quad \text{with } k_{ij} = k_{ji}, \tag{8}$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}), \quad \text{with } l_{ij} = l_{ji}. \tag{9}$$

Using the above equations the calculations were performed using the PE program [11]. The pure component properties are summarised in table 1. In the optimization, the binary interaction parameters k_{ij} and l_{ij} were treated as fitting parameters and optimized at each temperature by minimizing the following objective function:

$$F = \frac{1}{N} \sum_i^N \left| x_i^{\text{expt}} - x_i^{\text{calc}} \right|, \tag{10}$$

where x_i^{expt} and x_i^{calc} denote the experimental and calculated bubble point compositions respectively, and N is the number of data points. The experimental data are taken from Raeissi and Peters [6,7].

3. Results and discussion

The Peng–Robinson equation of state using the one fluid van der Waals mixing rule is capable of qualitatively simulating both the "S"-shaped and double-domed dew point curves of the double retrograde vaporization. This can be seen in figure 1 where the determined phase behaviour of (ethane + *d*-limonene) without the use of interaction parameters is presented at two different temperatures. The solid and dashed lines are the dew point and bubble point curves, respectively and the filled circles indicate the calculated critical points. Below the critical temperature of ethane (305.2 K) the expected "S"-shaped dew point curve is estimated while above this critical point (307.4 K), a distinct double-domed dew point curve is simulated.

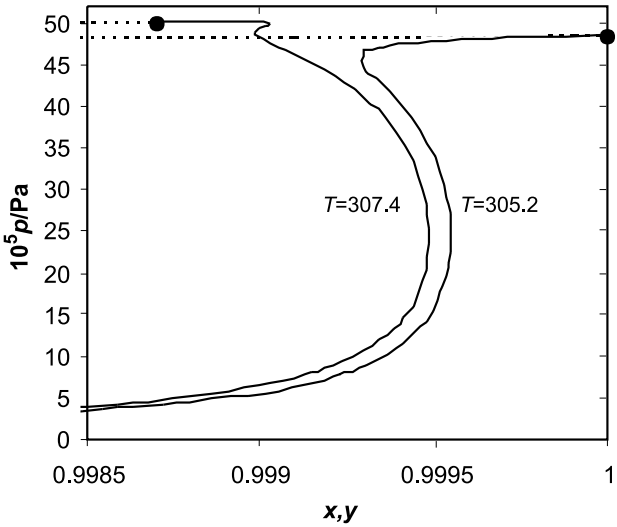

FIGURE 1. Pressure p against the mole fraction of ethane x, y. Double retrograde vaporization predicted for (ethane + d-limonene) using the Peng–Robinson equation of state without binary interaction parameters. The solid and dashed curves represent the dew and bubble point curves respectively and the filled circles represent the simulated mixture critical point.

To see the gradual transitions in the double retrograde vaporization, and also to compare the simulation with experimental data, two sets of results are presented for both binary systems of ethane with limonene and linalool. In one set, no interaction parameters are used while in the other set, the binary interaction parameters are optimised in order to minimise the deviation between experimental and calculated bubble point pressures. Since this work focuses on dew points, it would be logical to optimise using dew points. However, the limited number of available experimental dew points [6,7] has led to optimisation using bubble points instead. The optimised values of the binary interaction parameters k_{ij} and l_{ij}, along with the percentage deviations from experimental data are given in table 2 for both the limonene and linalool binaries.

Figures 2 and 3 present the phase behaviour of (ethane + d-limonene) without binary interaction parameters and with optimised interaction parameters, respectively. The experimental data are given as points while the curves are simulated results. Figure 2 indicates a rather good agreement between experiment and simulation with no interaction parameters. In fact, it is seen that the curves calculated with no interaction parameters simulate the experimental data better than the optimised curves. This is not surprising since optimisation was done using bubble points and not dew points.

Figures 4 and 5 show similar results for (ethane + linalool). In this case the optimized curves represent the experimental data better than the curves calculated with no binary interaction parameters. This may be explained by the fact that both the

TABLE 2
Optimized Peng–Robinson binary interaction parameters and percentage deviation of vapour composition and pressure from experimental values for (ethane + *d*-limonene) and (ethane + linalool) at different temperatures *T*

T/K	No interaction parameters		Optimised interaction parameters			
	10^2 a.a.d. *y*	10^2 a.a.d. *p*	K_{12}	l_{12}	10^2 a.a.d. *y*	10^2 a.a.d. *p*
			{ethane (1) + *d*-limonene (2)}			
305.2	$0.80 \cdot 10^{-3}$	0.19	0.0370	−0.0017	0.026	9.58
305.6	$1.10 \cdot 10^{-3}$	0.53	0.0411	0.0012	0.026	8.53
306.2	$2.70 \cdot 10^{-3}$	1.03	0.0409	0.0010	0.020	8.41
306.8	$6.25 \cdot 10^{-3}$	3.67	0.0407	0.0010	0.036	–
307.4	$7.41 \cdot 10^{-3}$	4.12	0.0407	0.0010	0.035	–
			{ethane (1) + linalool (2)}			
305.2	$3.00 \cdot 10^{-2}$	–	0.0417	−0.0120	0.024	–
305.6	$3.23 \cdot 10^{-2}$	–	0.0415	−0.0122	0.024	–
306.2	$4.19 \cdot 10^{-2}$	–	0.0413	−0.0123	0.027	–
306.8	$3.58 \cdot 10^{-2}$	–	0.0411	−0.0125	0.022	–
307.4	$3.50 \cdot 10^{-2}$	–	0.0408	−0.0127	0.021	3.81

10^2 a.a.d. $y = 100/N|y^{expt} - y^{calc}|/y^{expt}$ and 10^2 a.a.d. $p = 10^2|p^{expt} - p^{calc}|/p^{expt}$.

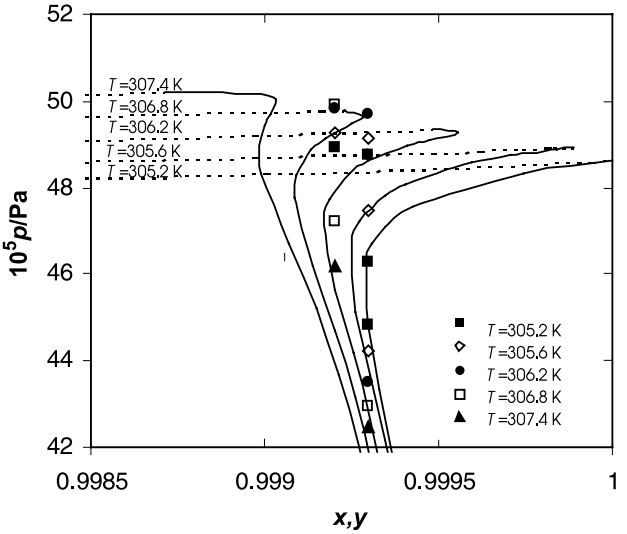

FIGURE 2. Pressure *p* against the mole fraction of ethane *x*, *y*. Experimental and simulated phase behaviour for (ethane + *d*-limonene) at five different temperatures. The solid and dashed curves represent respectively the dew and bubble point curves simulated with the Peng–Robinson equation of state without the use of binary interaction parameters. The points are experimental data taken from reference 6.

molecular size difference and structural difference between ethane and linalool are greater than those between ethane and limonene, leading to a stronger dependence on interaction parameters for (ethane + linalool).

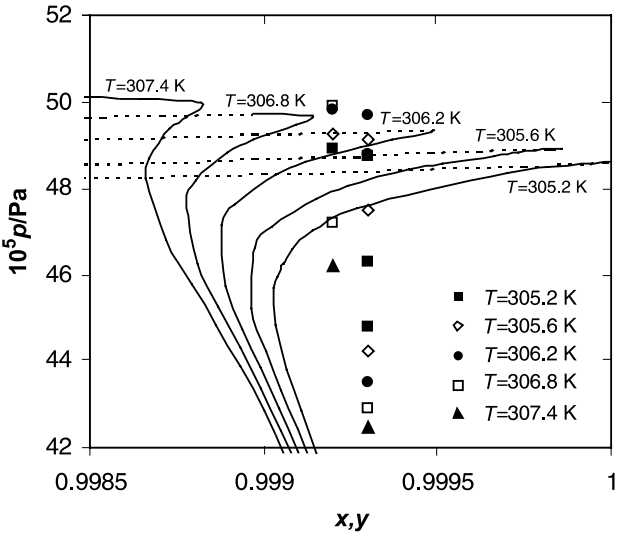

FIGURE 3. Pressure p against the mole fraction of ethane x, y. Experimental and simulated phase behaviour for (ethane + d-limonene) at five different temperatures. The solid and dashed curves represent respectively the dew and bubble point curves simulated with the Peng–Robinson equation of state with optimized binary interaction parameters. The points are experimental data taken from reference 6.

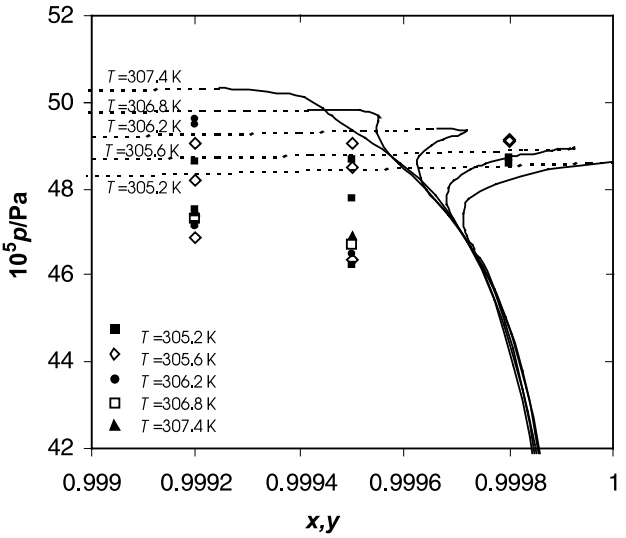

FIGURE 4. Pressure p against the mole fraction of ethane x, y. Experimental and simulated phase behaviour for (ethane + linalool) at five different temperatures. The solid and dashed curves represent respectively the dew and bubble point curves simulated with the Peng–Robinson equation of state without the use of binary interaction parameters. The points are experimental data taken from reference 7.

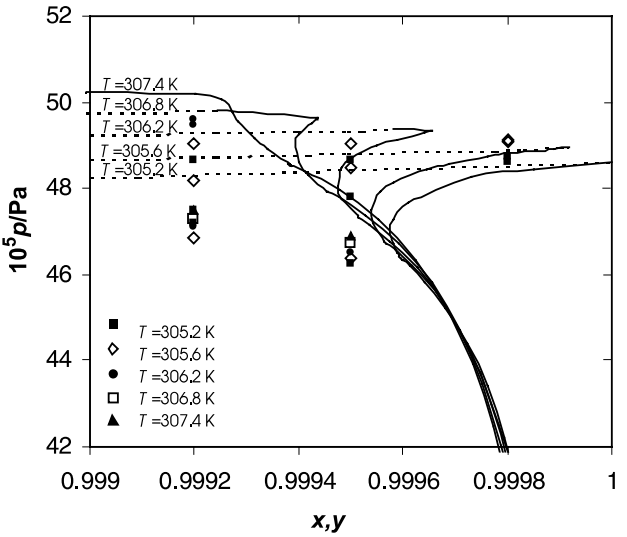

FIGURE 5. Pressure p against the mole fraction of ethane x, y. Experimental and simulated phase behaviour for (ethane + linalool) at five different temperatures. The solid and dashed curves represent respectively the dew and bubble point curves simulated with the Peng–Robinson equation of state with optimized binary interaction parameters. The points are experimental data taken from reference 7.

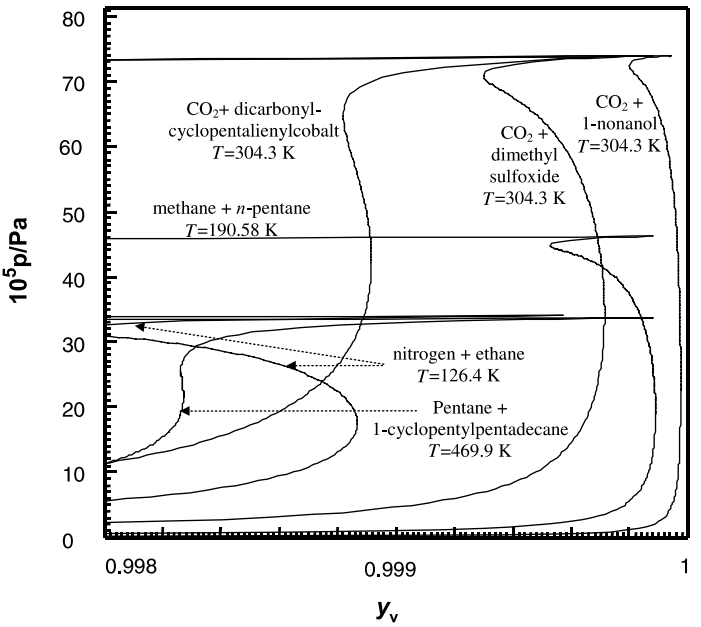

FIGURE 6. Pressure p against the mole fraction of the more volatile component y_v. Phase behaviour for some binary systems close to the critical point of the more volatile component obtained by the Peng–Robinson equation of state without binary interaction parameters.

By considering the percentage deviation from experimental data and also by considering that all cubic equations of state lack accuracy near the critical region, it may be concluded that the simple Peng–Robinson equation of state is fairly capable of predicting the double retrograde dew point behaviour. One must also note that the optimization was performed using bubble points and not dew points. Better results would be expected if dew points were used.

To investigate the generality of double retrograde vaporization as suggested by Raeissi *et al.* [6,7], a number of binary systems from completely different structural families were also simulated with the PR-EOS without the use of binary interaction parameters. The results are shown for six systems in figure 6. It was observed that every investigated system with differences in molecular structures large enough to result in steep dew point curves, displayed a double retrograde vaporization behaviour.

4. Conclusion

The phenomenon of double retrograde vaporization has been successfully simulated with a simple cubic equation of state. Both the "S"-shaped curve and the "double-domed" curve are obtained for the binary (ethane + limonene) and (ethane + linalool). The deviations from experimental data are satisfactory, however, the predictions are better for the limonene binary system, which has less structural difference between its constituents. The calculations for a number of other binary systems from different structural families also exhibit the double retrograde vaporization phenomenon. This is another evidence of the generality of this phenomenon.

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