Prediction of vapor-liquid equilibrium of ternary system at high pressures

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Abstract   The paper presents a numerical model for analyzing vapor-liquid equilibrium of ternary (three-component) system at high pressures. The gas-phase non-idealities and solubility of gas in liquid are considered in the numerical model. The model is useful for studies involving evaporation of liquid at different pressure and temperature conditions, where the interface liquid and vapor compositions are required. At high ambient pressures, ambient gases dissolve into the liquid. Thus, even a single component liquid fuel evaporating in a high pressure ambient gas, effectively behaves like a two-component liquid system. This study considers a ternary system. The numerical model has been validated against the experimental data available in literature. The validated model is used to study the solubility of ambient gas in a binary liquid mixture at high pressures. The effects of pressure, temperature and liquid phase composition on the solubility of gas in liquid have been studied systematically.

Keywords: Gas solubility; Fugacity; Real gas effects; Multicomponent system; Phase equilibrium

Nomenclature

a –   coefficient in Peng-Robinson equation of state, $\text{Nm}^4/(\text{kmol}^2$
b –   coefficient in Peng-Robinson equation of state, m^3/kmol

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f	–	fugacity
K	–	ratio of vapor-to-liquid-phase mole fraction
k_{ij}	–	binary interaction parameter
P	–	pressure, N/m^2
R	–	universal gas constant, $J/kmol\,K$
T	–	absolute temperature, K
V	–	molar specific volume, $m^3/kmol$
x	–	mole fraction in liquid phase
y	–	mole fraction in gas phase
Z	–	compressibility factor

Greek symbols

| ϕ | – | fugacity coefficient |
| ω | – | Pitzer accentric factor |

Subscripts

c	–	critical
i, j	–	individual component
r	–	reduced

Superscripts

| l | – | liquid phase |
| v | – | vapor phase |

1 Introduction

Liquid fuels are injected as droplets in several applications. Evaporation of these droplets in applications such as internal combustion engines, liquid-propellant rockets and gas turbine engines, highly depends upon the pressure, which typically exceeds the critical pressure of the fuel [1]. Under such high pressure conditions, the gas-phase non-idealities and the liquid-phase solubility of gases become extremely important. In order to analyze liquid droplet evaporation, the composition of gas- and liquid-phases, at the liquid-gas surface is required. At low to moderate pressures, the phase equilibrium at the droplet surface can be established using the Clausius-Clapeyron (or similar) equation. The solubility of ambient gas in the liquid implies that even a single component liquid effectively behaves like a multicomponent system. These high pressure effects are not adequately represented in the low pressure droplet vaporization models, especially when multicomponent liquids are involved. Hence, an accurate representation of high-pressure phase equilibrium is essential for realistic simulation of droplet evaporation under those conditions.

The earliest study of transient droplet burning under supercritical con-

ditions was carried out by Spalding [2]. However, real gas effects and density variations were ignored in that model. Since then several investigators considered the real gas effects in their models, using cubic equations of state such as Redlich-Kwong (RK), Soave (SRK) and Peng-Robinson (PR) equations of state [3–14]. In general, properties were estimated neglecting the effect of pressure in those models. Predominantly, these numerical models considered binary systems [4–14]. In multicomponent droplet evaporation study, the solubility of ambient gas such as nitrogen in the multicomponent liquid phase was neglected [15]. In summary, literature involving numerical simulation of single-phase droplet evaporation under high pressure conditions is commonly available. However, there is a scarcity in evaporation studies involving binary or multicomponent liquid-phase, where the phase equilibrium, considering real gas effects and solubility of ambient gas in the liquid phase, are addressed. This is because of scarcity in literature presenting the vapor-liquid equilibrium (VLE) under high pressure conditions for multicomponent liquid, where real gas effects and solubility of ambient gas are taken into account. Based on this motivation, the main objective of this paper is to predict vapor-liquid equilibrium of a ternary system (two liquids evaporating in to an ambient gas) under high pressure conditions. This model can be eventually used in droplet evaporation or combustion studies at high pressure conditions. As a validation case, vapor-liquid equilibrium of N_2-CO_2-CH_3OH (two gases and one liquid) ternary system at high pressure is compared against experimental data from literature [16]. The effects of pressure, temperature and composition on VLE have been studied in detail.

2 Thermodynamic model

Liquid surface is assumed to be in thermodynamic equilibrium with the immediate gas (or vapor) phase. Therefore, temperature, pressure and fugacity of each species, in liquid and gas interface, are equal. Also, both liquid- and gas-phases are governed by real gas equation of state (EoS). For a real gas, the P-V-T relationship, represented by cubic equation of state, is commonly used. One such equation is given below [17]

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2} \, .$$

(1)

An equivalent form of the equation is given in terms of compressibility factor 'Z' as,

$$Z^3 - (1 + B^* - uB^*)Z^2 + (A^* + wB^{*2} - uB^* - uB^{*2})Z - A^*B^* - wB^{*2} - wB^{*3} = 0, \tag{2}$$

where $A^* = \frac{aP}{R^2T^2}$ and $B^* = \frac{bP}{RT}$. For Peng-Robinson equation of state, $u = 2$ and $w = $ -1. In Eq. (1), a and b are parametric constants. For Peng-Robinson equation, a and b are expressed as:

$$a = \frac{0.45724R^2T_c^2}{P_c}\left[1 + f\omega\left(1 - T_r^{0.5}\right)\right]^2, \tag{3}$$

$$b = \frac{0.07780RT_c}{P_c}, \tag{4}$$

where $f\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$. Subscripts c and r represent the critical and reduced quantities, respectively. The critical properties and accentric factor (ω) of pure component are taken from literature [18] and are reported in Tab. 1. Peng-Robison equation of state has been employed in this study because of its proven accuracy [6,7,11,18]. The values of a and b are modified for a mixture using the following mixing rules [17]:

$$a_m = \sum_i \sum_j y_i y_j \left(a_i a_j\right)^{1/2}\left(1 - k_{ij}\right), \tag{5}$$

$$b_m = \sum_i y_i b_i, \tag{6}$$

where k_{ij} is binary interaction parameter, its value, as reported in Tab. 2, is obtained from literature [19,20]. A quadratic mixing rule is used in Eq. (5). A cubic gas equation of state, as written in Eq. (2), is solved analytically, separately for vapor- and liquid-phases.

Subsequently, the compressibility factor is used to obtain molar volumes of vapor phase (V^v) and liquid phase (V^l), using the following relations:

$$Z^v = \frac{PV^v}{RT} \quad \text{and} \quad Z^l = \frac{PV^l}{RT}. \tag{7}$$

The largest real root is chosen for the specific volume of the vapor-phase and the smallest real root is taken as a value of the liquid-phase specific volume. The fugacity of liquid-phase must be equal to that of the vapor-phase, as phase equilibrium exists at the interface

$$f_i^v = f_i^l \quad \text{or} \quad y_i\phi^v = x_i\phi^l, \tag{8}$$

Table 1: Critical properties of the components.

Components	Critical temperature [K]	Critical pressure [MPa]	Critical compressibility factor, Z_c	Accentric factor, ω
Nitrogen	126.20	3.390	0.290	0.039
Carbon dioxide	304.10	7.380	0.274	0.239
Methanol	512.58	8.096	0.224	0.557
Heptane	540.30	2.740	0.263	0.349
Dodecane	658.20	1.820	0.240	0.575

Table 2: Binary interaction parameter [19,20]

Binary system	k_{ij}
Nitrogen – carbon dioxide	-0.0170
Nitrogen – methanol	-0.1630
Carbon dioxide – methanol	0.0440
Nitrogen – heptane	-0.1440
Nitrogen – dodecane	-0.2082
Heptane – dodecane	0.0012

where f and ϕ are fugacity and fugacity coefficient, respectively, and y and x are the mole fractions in vapor- and liquid-phases, respectively. Fugacity coefficient of the ith species is calculated using equation [17]

$$\ln \phi_i = \frac{b_i}{bRT}\left(PV - RT\right) - \ln\left[\frac{P}{RT}(V - b)\right] - \frac{a/bRT}{\sqrt{u^2 - Vw}}$$
$$\times \left[\frac{2\sum_j y_j a_{ij}}{a} - \frac{b_i}{b}\right] \ln\left[\frac{2V + (u + \sqrt{u^2 - 4w})b}{2V - (u + \sqrt{u^2 - 4w})b}\right], \tag{9}$$

where $a_{ij} = (1 - k_{ij})\sqrt{a_i b_i}$. Replacing y_i with x_i and using the liquid-phase specific volume, the fugacity coefficient of ith component in the liquid phase is obtained. Equations (2), (7), (8) and (9) are nonlinear equations, therefore, they are solved iteratively. The procedure to evaluate the compositions of liquid- and vapor-phases at the interface, at a given pressure and temperature, is listed below:

1. Ambient temperature, pressure and initial liquid mass and composition are known.

2. The initial composition of vapor-phase at the interface is guessed and initial mole fraction of gas in liquid phase is assumed as zero. Total mass and individual masses of the liquid components are estimated using initial mass and composition.

3. The cubic equation of state, Eq. (2), is solved for both phases separately and the specific volume of both phases are calculated.

4. Fugacity coefficient of each component in liquid- and vapor-phases is calculated using Eq. (9).

5. Inside the liquid, the concentrations of liquid components are known from initial guess or from previous iteration. The corresponding vapor-phase mole fraction is obtained using Eq. (8) for all liquid components. Subsequently, the mole fraction of the last component in vapor-phase is calculated using the identity $\sum_i y_i = 1$.

6. The mole fraction of gas in liquid-phase is found by employing Eq. (8). Mass of the gas in liquid-phase is determined and mole fractions in liquid-phase are updated.

7. The steps 3 to 6 are repeated until the differences between the mole fractions of all the components obtained in previous and current iterations are smaller than 1×10^{-6}.

3   Results and discussion

3.1   Validation

Experimentally determined vapor-liquid equilibrium of a ternary system consisting of N_2-CO_2-CH_3OH is used for validation. Weber *et al.* [16] experimentally evaluated the gas solubility in liquid solvent for binary and ternary (N_2-CO_2-CH_3OH) system at high pressures. They also used a model and validated their predicted results. The mole fraction of CH_3OH in vapor phase was not reported as the concentration of CH_3OH was very low (< 0.003) at $T < 300$ K and any measurement would lead to large error. Validation cases have been chosen at pressures of 5 MPa and 10 MPa at 273.15 K. The ratio of gas-phase mole fraction to liquid-phase mole fraction ($K = y_i/x_i$) is predicted using the high pressure model and is compared against the experimental data of Weber *et al.* [16]. The comparison is

shown in Fig. 1. The comparison is found to be quite satisfactory with a maximum error of around 12% in CO_2 data and around 7% in N_2 data at 5 MPa pressure. The validated model has been subsequently used to study the vapor-liquid equilibrium of N_2-C_7H_{16}-$C_{12}H_{26}$ ternary system at high pressure.
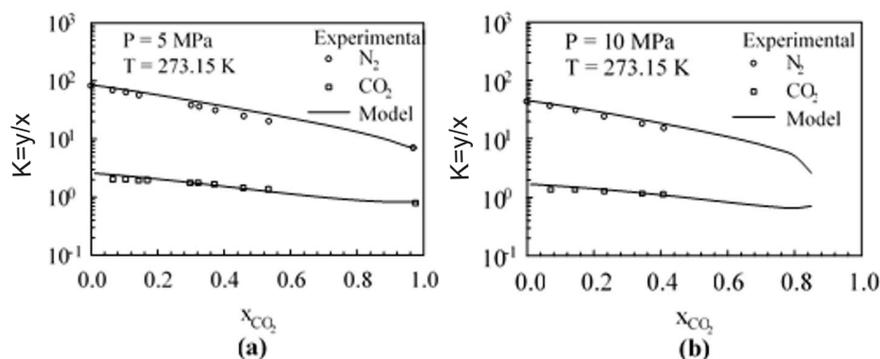

Figure 1: Comparison of K values of N_2-CO_2-CH_3OH ternary system predicted by high pressure model with experimental data of Weber *et al.* [16] at (a) 5 MPa and (b) 10 MPa.

3.2 Parametric studies

For the parametric study, a ternary system consisting of N_2-C_7H_{16}-$C_{12}H_{26}$ has been considered. The pressure is varied from 0.5 MPa to 10 MPa, which is higher than the critical pressure of individual components (Tab. 1), and the temperature is varied in the range from 300 K to 600 K. Initial liquid-phase mole fractions are taken as 0.3 and 0.7, for heptane and dodecane, respectively. The same initial liquid mass has been considered for all the cases, expect for those where the effect of composition is studied. The effects of pressure, temperature and composition on the solubility of N_2 in liquids, C_7H_{16} and $C_{12}H_{26}$, are presented subsequently.

3.2.1 Effect of pressure

To study the effect of the pressure on the solubility of N_2 gas in liquids, C_7H_{16} and $C_{12}H_{26}$, the pressure is varied from 0.5 MPa to 10 MPa. Two ambient temperatures, 360 K and 500 K, have been considered. Figures

2 and 3 show the variation of liquid- and vapor-phase mole fractions as a function of pressure. From Fig. 2a, it is seen that the mole fraction of nitrogen in liquid-phase increases almost linearly with a rise in pressure, while those of heptane and dodecane decrease almost linearly with an increase in pressure. Figure 2b shows that nitrogen is predominantly present in gas-phase, whereas heptane and dodecane are present in very small quantities, irrespective of the pressure.

This is because the temperature is quite low (360 K) and the liquids have not vaporized enough. There is a small variation in the gas-phase mole fractions of nitrogen and heptane at low pressure due to low saturation temperature. Nitrogen mole fraction in liquid-phase varies from 0.016 at 0.5 MPa to 0.303 at 10 MPa, whereas in vapor phase, it changes from 0.9530 to 0.9934 for the same rise in pressure. The solubility of gas in a binary liquid mixture is quite apparent from this result.
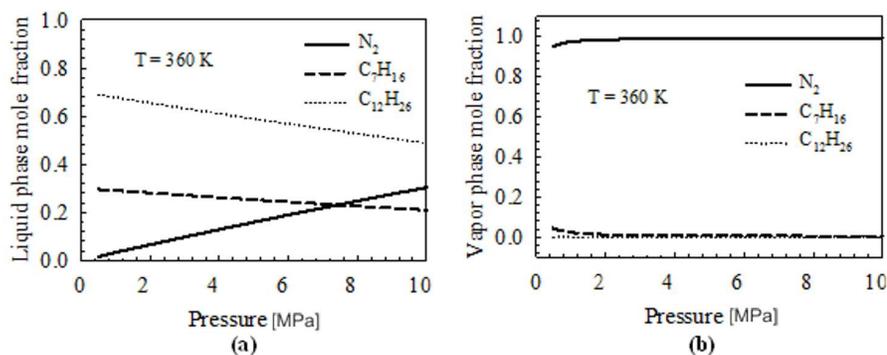

Figure 2: Variation of mole fractions of (a) liquid- and (b) vapor-phases with pressure at 360 K.

Figure 3 shows VLE of ternary mixture at a high temperature of 500 K as a function of pressure. At high temperature and low pressure, the evaporation rates of heptane and dodecane are higher and thus vapor phase mole fractions of heptane and dodecane are higher than those at 360 K. Additionally at moderate to high pressures, the evaporation is sluggish and this causes vapor-phase mole fractions of heptane and dodecane to decrease.

Variation trend of nitrogen mole fraction in vapor phase is opposite to that of heptane and dodecane. The liquid-phase mole fractions of species have almost similar trends at 500 K, as observed for the temperature of 360 K (Fig. 2a), but for the values, which are dependent on temperature.
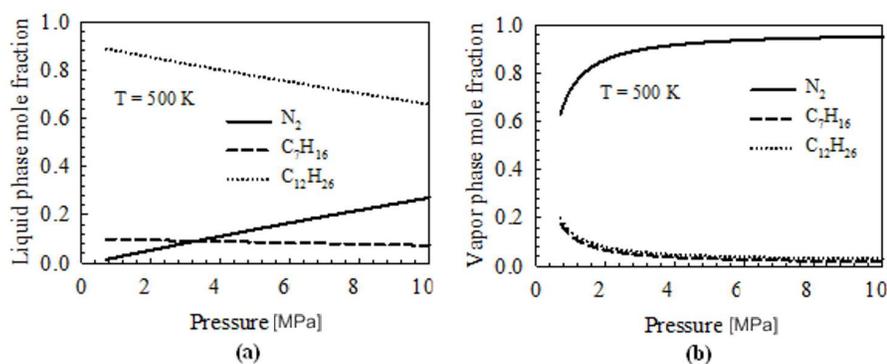
Figure 3: Variation of mole fractions of (a) liquid- and (b) vapor-phases with pressure at 500 K.

3.2.2 Effect of temperature

To study the effect of temperature on the solubility of N_2 gas in liquids, C_7H_{16} and $C_{12}H_{26}$, the temperature has been varied in the range from 300 K to 600 K, while the pressure was kept constant at 5 MPa. Figure 4 shows the variation of liquid- and gas-phase mass fractions as a function of temperature at 5 MPa. From Fig. 4a, it is observed that the mass fraction of nitrogen in liquid-phase gradually decreases with increase in temperature, reaches a local minimum and then increases. The liquid-phase mass fractions of heptane and dodecane gradually increase, reach local maximum values and decrease slightly. However, all these changes are notably small.
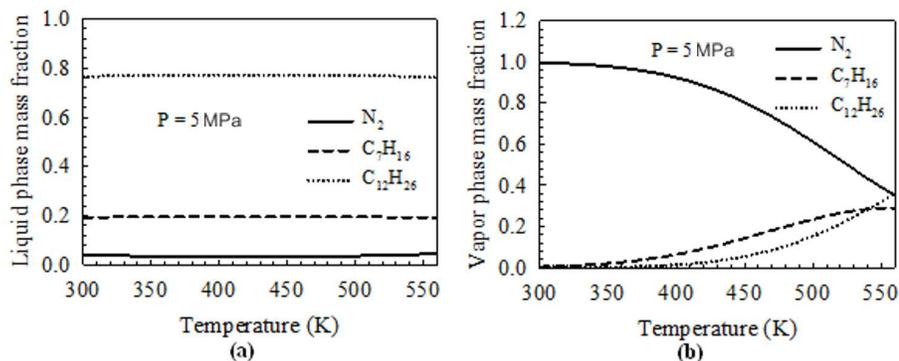

Figure 4: Variation of mass fractions of (a) liquid- and (b) vapor-phases with temperature at 5 MPa.

On the other hand, in the vapor-phase, as shown in Fig. 4(b), the mass fractions of heptane and dodecane are quite small at low temperatures. They increase with temperature gradually. It is observed that the mass fraction of heptane is notably higher than that of dodecane in the temperature range from 370 K to 530 K due to its higher volatility. For the initial liquid-phase mole fractions of 0.3 and 0.7, considered for heptane and dodecane, respectively, as the temperature approaches the saturation temperature of heptane at 5 MPa, its vapor-phase mass fraction plateaus. The vapor-phase mass fraction of dodecane monotonically increases as the temperature increases. As a result of these, the nitrogen mass fraction in the gas-phase decreases as shown in Fig. 4b.

3.2.3   Effect of composition

In order to study the effects of liquid-phase composition on the solubility of N_2 gas, the temperature and pressure are maintained at 560 K and 5 MPa, respectively. At the initial state, it is assumed that liquid consists of heptane and dodecane, of varying composition, and there is no dissolved nitrogen in each of these cases. The liquid mixture is exposed to a nitrogen environment at high pressure. Based on pressure, temperature and composition, the nitrogen dissolves in to the liquid. Similarly, heptane and dodecane, which are absent in the vapor-phase initially, evaporate and form their vapors. The initial liquid-phase mole fraction of heptane has been varied from 0.1 to 0.7. Figure 5 shows the variations of liquid- and vapor-phase mole fractions of species as a function of initial liquid-phase mole fraction of heptane.

At the given pressure and temperature, from Fig. 5a, it is observed that equilibrium mole fraction of heptane in liquid-phase increases with an increase in the initial mole fraction of heptane. However, when the initial mole fraction of heptane is higher than around 0.55, the equilibrium mole fraction of heptane in liquid phase becomes almost a constant. There is monotonous decrease in mole fraction of dodecane in liquid phase with an increase in initial mole fraction of heptane. Also, the mole fraction of nitrogen in the liquid phase increases gradually with an increase in initial mole fraction of heptane till around 0.55. Beyond this value, the rate of increase in nitrogen mole fraction increases, clearly showing the dependence of its solubility on liquid phase mole fractions.

As the initial mole fraction of heptane in liquid increases, its vapor-phase mole fraction also increases continuously (Fig. 5b). Due to its low
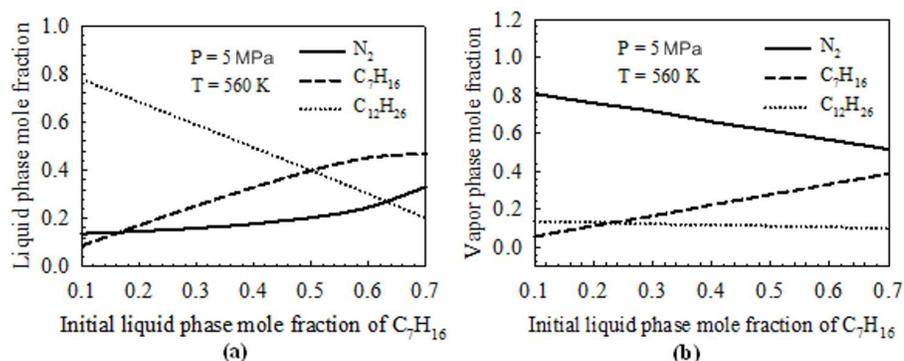
Figure 5: Variation of mole fractions of (a) liquid- and (b) vapor-phases as a function of the initial liquid phase mole fraction of heptane at 5 MPa and 560 K.

volatility, the vapor-phase mole fraction of dodecane remains almost a constant – in fact, there is a slight decrease in its value as the initial mole fraction of heptane in liquid increases. Vapor-phase nitrogen mole fraction gradually decreases as fuel vapors replace it.

4 Conclusions

A numerical model, which includes the gas-phase non-idealities and the liquid-phase solubility of gases, is used for estimating VLE of multicomponent liquid at high pressure with dissolved gas. For studies involving droplet evaporation, VLE at the droplet surface is quite important. This model can predict the liquid- and vapor-phase composition of a multicomponent droplets at high pressure, including non-ideal behavior and ambient gas solubility. The model has been used to predict a ternary system. The results from the present model have been compared against the experimental data available in literature. A good agreement is observed between predicted and measured data. The validated model has been used to study the effects of pressure, temperature and initial liquid-phase composition on the solubility of nitrogen gas in liquid heptane and dodecane. It has been observed that the solubility of gas in liquid phase is significantly high at high pressures.

There is significant change in the liquid phase mole fraction of nitrogen when pressure changes from low pressure to high pressure. At high pressures, the mole fraction of nitrogen in liquid phase slowly decreases

with increase in temperature, reaches a local minimum and then gradually increases as it approach boiling point of most volatile component in the droplet. The solubility of nitrogen gas in liquid phase is almost constant for low and moderate initial concentration of heptane in the droplet at high pressure, whereas it increases at high initial heptane concentration. As the initial mole fraction of heptane in liquid increases, its vapor-phase mole fraction also increases continuously, the mole fraction of dodecane remains almost a constant and nitrogen mole fraction in vapor-phase gradually decreases as fuel vapors replace it.

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