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Numerical investigation on vapour-liquid equilibrium and gas solubility in hydrocarbons for binary and ternary systems

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Abstract

Vapour-liquid equilibrium calculation is crucial in oil industry and multi-phase systems such as droplet evaporation. This paper presents a comprehensive numerical analysis of phase equilibrium in multi-component systems at various pressures and temperatures, accounting for high-pressure phenomena including thermodynamic non-ideality and inert gas effects. The phase equilibrium is determined by solving the fugacity equation iteratively to find the equilibrium mole fractions in both liquid and vapour phases. The Peng-Robinson equation of state is used to handle non-idealities and calculate fugacity coefficients. This study details the procedure for computing vapour-liquid equilibrium and evaluates N_2 , O_2 , and CO_2 solubility in liquid alkanes such as heptane, dodecane, and hexadecane. Model performance is validated against experimental data for binary and ternary systems, showing good agreement. Results indicate that density and molecular attractive forces impact gas dissolution. Increased pressure and gas density enhance solubility in the liquid phase, while temperature effects vary between subcritical and supercritical regions. The study also highlights differences in gas solubility between heavy and light fluids.

Keywords: Vapour-liquid equilibrium; Gas solubility; Fugacity; High pressure; Hydrocarbons; Binary and ternary systems

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1. Introduction

Phase equilibrium calculation is important in fuel droplet evaporation, combustion, distillation process design, and nitrogen/carbon dioxide injection in enhanced oil recovery techniques. Therefore, using a simple and practical model to calculate equilibrium mole fractions in numerical models is essential [1,2]. Figure 1 shows a droplet that is evaporating in a gaseous environment. The problem is calculating equilibrium mole fractions of species at the interface, where vapour-liquid equilibrium (VLE) coexists. At low pressures (near or below 1 atm), the dis-

solved gas and real-gas effects are negligible; consequently, Raoult's law can accurately predict the equilibrium mole fractions [3]. At high-pressure conditions, a comprehensive model should consider solubility and real-gas behaviour. In an extensive review, Mühlbauer and Raal [4] have studied two methods to determine the phase equilibrium at high pressures. Two primary approaches, combined and direct methods, have been developed. The combined method utilizes activity and fugacity coefficients to describe the non-idealities of the liquid and vapour phases, respectively. It reliably represents complex systems at low to medium pressures but faces difficulties at high-pressure regions.

Nomenclature

a	– parameter in the Peng-Robinson equation of state representing the intermolecular attractive force, $\text{Nm}^4/\text{kmol}^2$
b	– coefficient in Peng-Robinson equation of state, m^3/kmol
f	– fugacity, N/m^2
g	– Gibbs function, J/kg
k_{ij}	– binary interaction coefficient
n	– mole number
N	– number of species
T	– temperature, K
P	– pressure, N/m^2
R_u	– universal gas constant, $\text{J}/(\text{mol K})$
V	– volume, m^3
x	– mole fraction
Z	– compressibility factor

Greek symbols

μ	– chemical potential, J/kg
γ	– activity coefficient
ϕ	– fugacity coefficient
v	– molar specific volume, m^3/kmol
ω	– acentric factor

Subscripts and Superscripts

c	– critical
l	– liquid phase
v	– vapour phase
i, j	– individual component
r	– reduced

Abbreviations and Acronyms

EOS	– equation of state
VLE	– vapour-liquid equilibrium

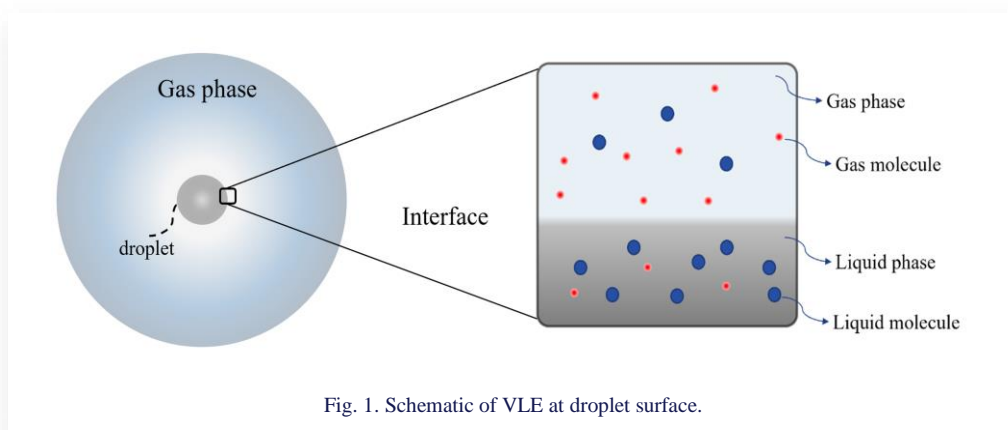


Fig. 1. Schematic of VLE at droplet surface.

In contrast, the direct method overcomes these challenges and requires fewer binary interaction coefficients. However, there are difficulties in using this model for complex polar systems. Rojas et al. [5] studied the effect of the equation of state (EOS) on the solubility of hydrogen gas in pyrolysis gasoline. Considering the cubic EOS of Redlich-Kwong, the classical quadratic mixing rules, and the correlation function S93 for hydrocarbons and S72 for hydrogen gas, the average absolute relative deviation on the prediction of solubility of hydrogen in pyrolysis gasoline was reported as 3.1%. Ghosh [6] showed that Peng-Robinson and Redlich-Kwong have acceptable accuracy in computing phase equilibrium among the cubic equation of states. Lyu et al. [7] studied the solubility of carbon dioxide in methanol in the temperature range of 213 K to 273 K and up to 3 MPa pressure based on the γ - ϕ method. This study calculated the activity coefficient from Wilson and non-random two-liquid models. They showed that the Wilson model has better accuracy in determining the mole fraction. Chaparro et al. [8] measured and modelled VLE and surface tension for the hexane + ethanol + cyclopentyl methyl ether. The theoretical predictions of vapour-liquid equilibrium using Peng-Robinson Stryjek-Vera equation of state and non-random two-liquid model (NRTL) are in good agreement with the reported experimental data of the ternary mixture. Laursen et al. [9] proposed a straightforward VLE device with

vapour phase recirculation to test the gas solubility using liquid phase sampling. Höhler [10] introduced a novel apparatus for investigating gas solubility in solvents, such as alcohols and ketones, across a temperature range of 253 K to 453 K. They showed that adding acetone can increase gas solubility. Yang et al. [11] studied the impact of non-ideal VLE on multi-component droplet evaporation. The results suggest that an ideal VLE model may result in incorrect evaporation process predictions when the component structures, like those of ethanol and isooctane, exhibit considerable differences. Ray et al. [12] studied the effect of pressure, temperature, and liquid phase composition on the solubility of gas in a ternary system. It was observed that gas solubility in the liquid phase increases significantly at high pressures. In the numerical studies carried out in this field, the procedure of computing the mole fraction of components in ternary systems and more has not been outlined in detail. Nor have the effect of pressure and temperature on the gas solubility at different compositions in the liquid phase been investigated.

This paper aims to provide a more fundamental understanding of VLE and gas dissolution in the liquid phase by considering non-ideal behaviour across a wide range of pressures and temperatures. Additionally, a detailed procedure for determining equilibrium mole fractions in ternary systems, which is not adequately covered in existing literature, is described. This model

could eventually be applied to studies of droplet evaporation or combustion under high-pressure conditions. As validation, the vapour-liquid equilibrium of six systems is compared against existing experimental data. Extensive research has investigated the impact of pressure, temperature, and composition on VLE.

2. Numerical model

2.1 Phase equilibrium at high pressures

Three criteria must be met at the liquid- and vapour-phase interface to establish phase equilibrium in a multi-component mixture. First, thermal equilibrium must be achieved in both phases. Additionally, mechanical forces at the interface should be balanced. These two criteria indicate that temperature and pressure at the liquid- and vapour-phase interface must be equal [13]. In summary, the criteria for temperature and pressure equilibrium can be expressed as follows:

$$T^v = T^l, \quad (1)$$

$$P^v = P^l, \quad (2)$$

where P and T represent pressure and temperature, and superscripts v and l refer to the vapour and liquid phases, respectively. It is also necessary for the chemical potential to be equal at the interface of both phases. If this criterion is not met, mass transfer will occur from one phase to another [13]. Since the partial molar Gibbs function is equivalent to the chemical potential, it can be written for each species as follows:

$$\mu_i^v = \mu_i^l \rightarrow g_i^v = g_i^l, \quad i = 1, 2, \dots, N, \quad (3)$$

where μ is the chemical potential, g refers to the Gibbs function, and N represents the number of species in the system. Gibbs function of i th species in the mixture is defined as follows:

$$dg_i = R_u T d(\ln f_i)_T, \quad (4)$$

where R_u is the universal gas constant, and f refers to fugacity. According to Eq. (4), Eq. (3) is rewritten in terms of fugacity as follows:

$$\ln f_i^v = \ln f_i^l \rightarrow f_i^v = f_i^l, \quad i = 1, 2, \dots, N. \quad (5)$$

In Eq. (5), f_i is defined as [2]

$$f_i = x_i \varphi_i P \quad (6)$$

or

$$f_i = x_i \gamma_i f_i^0 \quad (7)$$

where x , φ , γ , and f^0 denote mole fraction, fugacity coefficient, activity coefficient, and standard-state fugacity. Although Eqs. (6) and (7) can be defined for any phase, Eq. (6) is usually used for the vapour phase (known as φ method), and Eq. (7) is employed for the liquid phase (known as γ method). Although the γ method is simpler to use at low pressures, when the system's temperature is above one of the species' critical temperatures, it can be challenging to use γ methods. In this condition, it is preferred to use the φ method for both phases [13].

In this study, Eq. (6) is employed to calculate the mole fraction in both phases, known as φ - φ method. In reference [14], the following equation is proposed to calculate the fugacity coefficient, which can be used for any substance and in any phase:

$$R_u T \ln(\varphi_i) = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{R_u T}{V} \right] dV - R_u T \ln Z. \quad (8)$$

In Eq. (8), Z is the compressibility factor, V is the volume, and n_j is the mole number of the j th species. According to this equation, the fugacity coefficient is a function of temperature, pressure, and mole fraction. The right-hand side of Eq. (8) is calculated using the equation of state. Due to simplicity and acceptable accuracy, cubic equations of states are utilized. Among these equations, the Peng-Robinson equation of state considers the real-gas behaviour of the gas phase at high pressures and provides better accuracy in predicting the mole fraction of components.

The Peng-Robinson equation of state can be written as follows [14]:

$$P = \frac{R_u T}{v-b} - \frac{a}{v(v+b)+b(v-b)}, \quad (9)$$

where v is the molar volume, a and b are functions of critical temperature and pressure for pure substances. In a multi-component mixture, these coefficients are functions of critical temperature, critical pressure, and mixture composition, which are calculated using mixing rules [14]. Parameter a accounts for attractive forces between molecules while parameter b represents the volume occupied by a molecule. Equation (9) can be written as a cubic polynomial in terms of v as follows:

$$v^3 + \left(b - \frac{R_u T}{P} \right) v^2 + \left(\frac{a}{P} - 3b^2 - 2 \frac{b R_u T}{P} \right) v + \left(b^3 + \frac{R_u T b^2}{P} - \frac{ab}{P} \right) = 0. \quad (10)$$

Equation (10) has either one or three roots depending on the number of phases in the system. In a two-phase system where both liquid- and vapour phases coexist, the largest root represents the molar volume of the vapour, and the smallest root is the molar volume of the liquid. In other cases, if only one phase exists in the system, the equation has one positive root. If there are two positive roots as a solution, one is physically meaningless.

By combining the compressibility factor definition ($Z = Pv/(R_u T)$) and Eq. (10), the Peng-Robinson equation of state can be written as follows:

$$Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0. \quad (11)$$

The values of A and B are defined as follows:

$$A = \frac{aP}{R_u^2 T^2}, \quad (12)$$

$$B = \frac{bP}{R_u T}, \quad (13)$$

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij}, \quad (14)$$

$$b = \sum_{i=1}^N x_i b_i, \quad (15)$$

$$b_i = \frac{0.0778 R_u T_{ci}}{P_{ci}}, \quad (16)$$

$$a_{ii} = \frac{0.457254 R_u^2 T_{ci}^2}{P_{ci}} [1 + f(\omega_i)(1 - \sqrt{T_{ri}})]^2, \quad (17)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_{ii} a_{jj}}, \quad (18)$$

$$T_{ri} = \frac{T}{T_{ci}}, \quad (19)$$

$$f(\omega) = 0.3746 + 1.5423\omega - 0.2699\omega^2. \quad (20)$$

In these equations, subscript c refers to critical parameters, T_{ri} stands for the reduced temperature, ω represents the acentric factor, and k_{ij} is the binary interaction coefficient, which is independent of temperature, pressure, and mole fraction and is usually assumed to be zero in density calculation [3]. However, considering this parameter as zero in the phase equilibrium calculation can lead to significant errors. The value of k_{ij} is taken from [3]. By solving Eq. (11), the compressibility factor of the mixture for the liquid phase (Z^l) and the vapour phase (Z^v) can be determined. Additionally, combining Eqs. (8) and (9) define the fugacity coefficient as follows:

$$\ln \phi_i = \frac{b_i}{b R_u T} (Pv - RT) - \ln \left[\frac{P}{R_u T} (v - b) \right] + \frac{a/b R_u T}{\sqrt{4+b}} \left[\frac{2 \sum_j x_j a_{ij}}{a} - \frac{b_i}{b} \right] \ln \left[\frac{2v + (2 + \sqrt{8})b}{2v - (2 + \sqrt{8})b} \right]. \quad (21)$$

By using the definition of the compressibility factor, Eq. (21) can be reformulated as follows:

$$\ln \phi_i = \frac{b_i}{B} (Z - 1) - \ln(Z - B) + \frac{A}{B\sqrt{8}} \left[\frac{b_i}{b} - \frac{2\sqrt{a_i}}{a} \sum_j x_j \sqrt{a_j} (1 - k_{ij}) \right] \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]. \quad (22)$$

In summary, to establish phase equilibrium between a multi-component liquid and vapour mixture, Eqs. (1), (2), and (5) must be satisfied. The equilibrium mole fraction of i th species in the mixture can be calculated using Eq. (5), which can be written as follows:

$$f_i^v = f_i^l \rightarrow x_i^v \phi_i^v = x_i^l \phi_i^l. \quad (23)$$

For a system comprising N species (where $N > 1$), $2N$ mole fractions are determined: N mole fractions in the liquid phase and N mole fractions in the vapour phase. Therefore, there must be a total of $2N$ equations to close the system of equations. N equations can be obtained from Eq. (23). Additionally, since the sum of mole fractions in the liquid- and vapour-phase is equal to unity, two more equations are added to the system of equations as follows:

$$\sum_{i=1}^N x_i^v = 1, \quad \sum_{i=1}^N x_i^l = 1. \quad (24)$$

Hence, for a binary system ($N = 2$), Eqs. (23) and (24) yield a system of 4 equations. However, if there are more than two

components in the system, additional equations are required. In such cases, by specifying the mole fraction ratios of components, the number of equations becomes equal to the number of unknowns, resulting in a system of $2N$ equations and $2N$ unknowns. For example, in a ternary system such as heptane-hexadecane-nitrogen, the system of equations is:

$$x_1^v \phi_1^v = x_1^l \phi_1^l, \quad (25)$$

$$x_2^v \phi_2^v = x_2^l \phi_2^l, \quad (26)$$

$$x_3^v \phi_3^v = x_3^l \phi_3^l, \quad (27)$$

$$\sum_{i=1}^3 x_i^v = 1, \quad (28)$$

$$\sum_{i=1}^3 x_i^l = 1, \quad (29)$$

$$\frac{x_1^l}{x_2^l} = \text{constant}. \quad (30)$$

Subscripts 1, 2, and 3 refer to heptane, hexadecane, and nitrogen, respectively. In a ternary system, Ray et al. [12] considered the mole fraction ratio (Eq. (30)) as the initial value in the liquids, while Juanos et al. [15] considered it as the stoichiometric mole ratio in a quaternary system. This assumption is acceptable since the amount of dissolved gas in the liquid phase is small compared to the other components.

Following the methodology outlined by Ray et al. [12], the procedure for determining the mole fractions of the liquid- and vapour-phase under thermodynamically equilibrium conditions at a certain pressure and temperature can be summarized as follows:

- 1) The temperature, pressure, and initial mole fractions of species in the liquid phase ($x_i^{l,old}$) are known.
- 2) The initial mole fractions of species in the vapour phase ($x_i^{v,old}$) are computed using Raoult's law.
- 3) By solving the Peng-Robinson equation of state using $x_i^{l,old}$ and $x_i^{v,old}$, the compressibility factors for both phases are determined (Eq. (11)).
- 4) The fugacity coefficients for each species in the liquid and vapour phases are calculated using Eq. (22).
- 5) Employing the mole fraction of the liquid phase ($x_i^{l,old}$), the mole fractions of the vapour phase components are determined by Eq. (23). The mole fraction of the last component is calculated using Eq. (24).
- 6) The mole fraction of dissolved gas in the liquid phase is calculated using Eq. (23), while the mole fractions of other components in the liquid phase are determined using Eq. (24) along with the known component ratio specified in Eq. (30).
- 7) Steps 3 to 6 are repeated until the convergence condition is met ($|x_i^{new} - x_i^{old}| < 10^{-6}$).

3. Results and discussion

3.1. Validation

Four binary systems and two ternary systems, for which experimental data are available in the literature, were selected to validate the model. This collection encompasses a wide range of

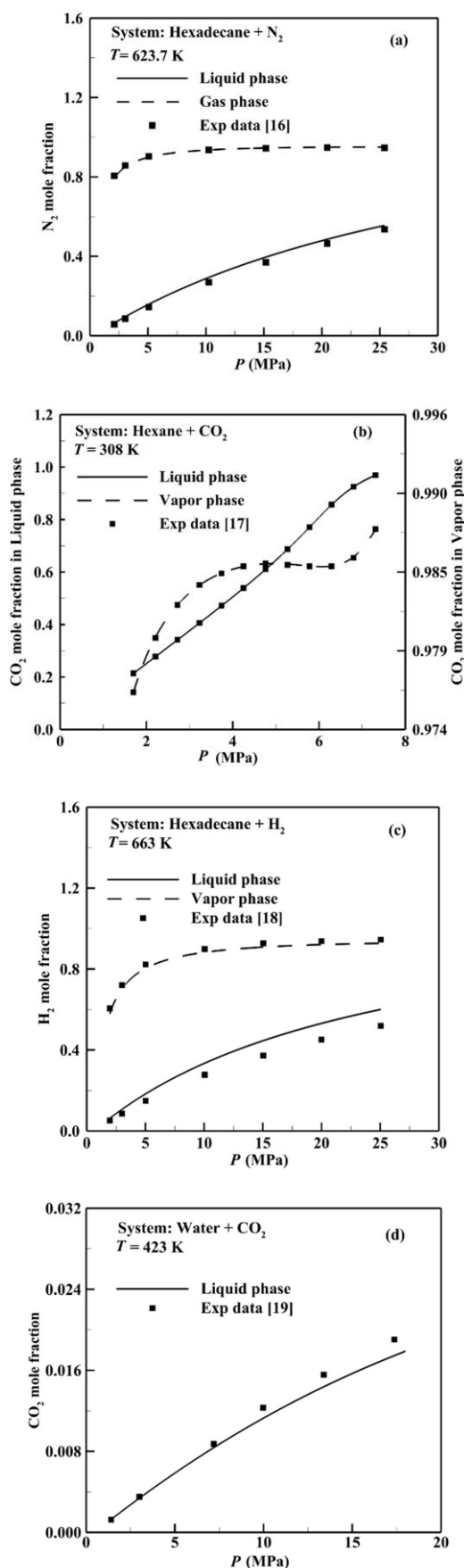


Fig. 2. Comparison results of the presented model for binary systems with experimental data: (a) hexadecane-nitrogen, (b) hexane-carbon dioxide, (c) hexadecane-hydrogen, (d) water-carbon dioxide.

systems, from light gases like hydrogen to heavy gases such as carbon dioxide, and from liquids with small molecules like water to those containing larger molecules like hexadecane.

Figure 2 shows a comparison of the predicted values and measured data reported by Lin et al. [16] for the hexadecane-nitrogen system (Fig. 2a), – Lay et al. [17] for the hexane-carbon dioxide system (Fig. 2b), – Lin et al. [18] for the hexadecane-hydrogen system (Fig. 2c), and – Søreide et al. [19] for water-carbon dioxide system (Fig. 2d). The predicted values agree with the experimental data in binary systems.

Experimental data from Uribe-Vargas et al. [20] for the hexane-decane-nitrogen system and Dima et al. [21] for the water-methane-carbon dioxide system have been employed to validate the numerical model for ternary systems. According to Fig. 3, the current model demonstrates good agreement with experimental data in ternary systems.

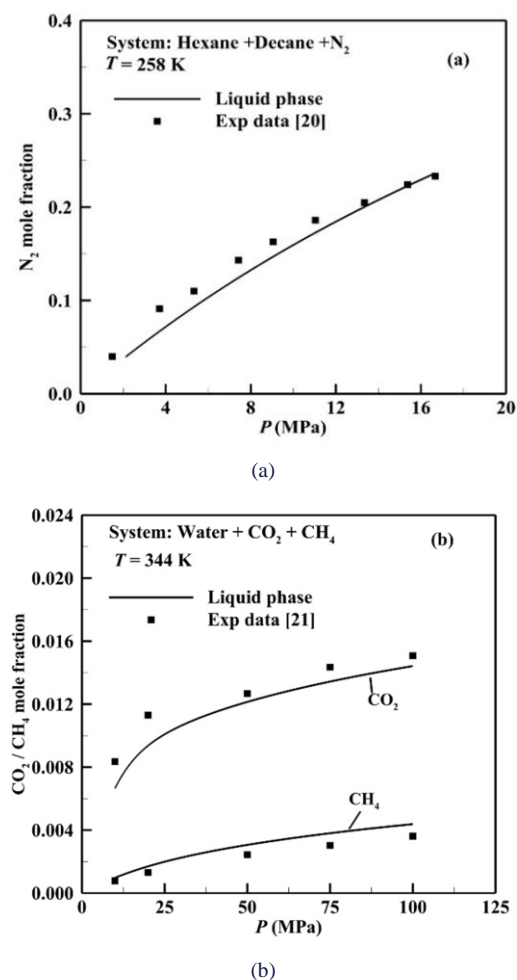


Fig. 3. Comparison of the presented model results with experimental data: (a) hexane-decane-nitrogen, (b) water-methane-carbon dioxide.

3.2. Results

The study further investigates the effect of pressure and temperature on the solubility of ambient gases in the liquid phase. For this purpose, liquid hydrocarbons, including heptane, dodecane, and hexadecane, were used in the presence of nitrogen,

Table 1. Properties of considered substances.

Substance	Chemical formula	Critical temperature (K)	Critical pressure (MPa)	Molecular mass (g/mol)	Acentric factor
Liquid					
Hexane	C ₆ H ₁₄	507.50	3.025	86.177	0.300
Heptane	C ₇ H ₁₆	540.20	2.740	100.202	0.350
Decane	C ₁₀ H ₂₂	617.70	2.110	142.285	0.490
Dodecane	C ₁₂ H ₂₆	658.00	1.820	170.338	0.576
Hexadecane	C ₁₆ H ₃₄	723.00	1.400	226.446	0.718
Water	H ₂ O	647.14	22.064	18.015	0.344
Gas					
Hydrogen	H ₂	32.98	2.016	2.016	-0.217
Nitrogen	N ₂	126.20	28.014	28.014	0.037
Oxygen	O ₂	154.58	31.999	31.999	0.000

oxygen, and carbon dioxide. The properties of these substances are listed in Table 1. In this study, heptane was chosen as a light hydrocarbon with high volatility, while hexadecane was selected as a heavy hydrocarbon with low volatility. Dodecane, on the other hand, represents a hydrocarbon with average molecular mass.

3.2.1. Binary systems

The effect of pressure and temperature on the solubility of nitrogen, oxygen, and carbon dioxide in heptane, dodecane, and hexadecane in a binary system has been investigated using the presented model.

Figure 4 shows the equilibrium concentrations for nitrogen in the heptane-nitrogen system at seven different reduced temperatures ($T_r = T/T_c$). It is evident that at a constant reduced temperature, the dissolved gas in the liquid phase increases almost linearly with increasing pressure. In the gas phase, the nitrogen mole fraction experiences an upward trend and gradually diminishes as it approaches the heptane boiling point or critical mixing point. This behaviour is because, with increasing pressure, some heptane in the vapour enters the liquid phase and condenses, resulting in an increase in the nitrogen mole fraction. However, as the condition approaches the boiling point or mixing point, the heptane in the liquid phase turns into vapour, and the nitrogen mole fraction in the gas phase decreases. Finally, nitrogen mole fractions in liquid- and vapour-phase meet at the boiling and critical mixing points in subcritical and supercritical regions, respectively.

Figure 5 presents the variation of nitrogen mole fraction in the heptane-nitrogen system as a function of reduced temperature in five different reduced pressures ($P_r = P/P_c$). In subcritical regions where heptane reduced pressure is less than one, as the temperature of the liquid phase increases, the amount of gas dissolved in the liquid phase generally decreases and vanishes at the liquid's boiling point. In this case, the attraction between molecules decreases as the temperature increases.

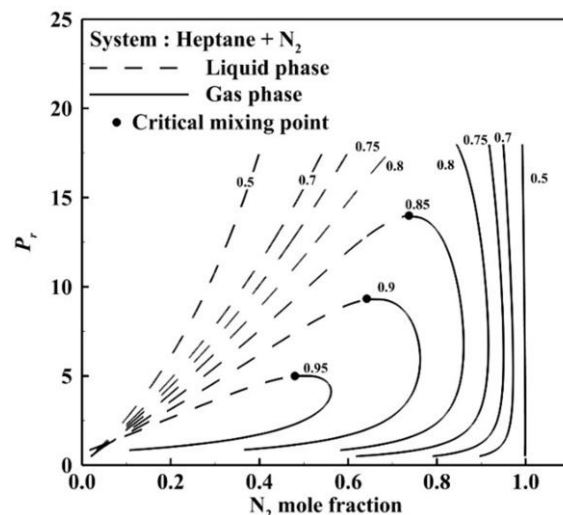


Fig. 4. Phase equilibrium diagram of the heptane-nitrogen system at constant reduced temperature using presented model. Numbers on the graph are heptane reduced temperature.

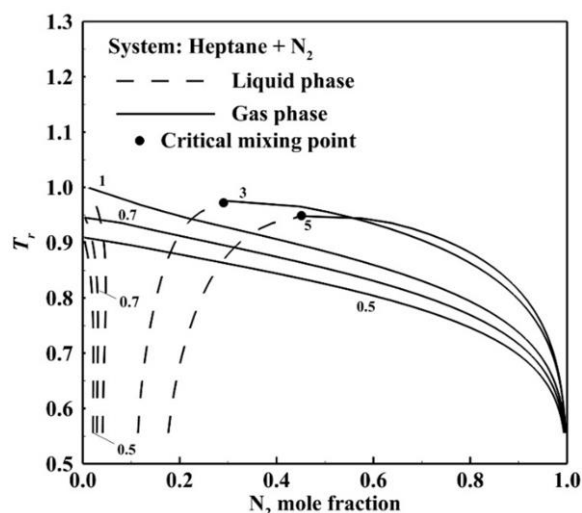


Fig. 5. Phase equilibrium diagram of the heptane-nitrogen system at constant reduced pressure using presented model. Numbers on the graph are heptane reduced pressure.

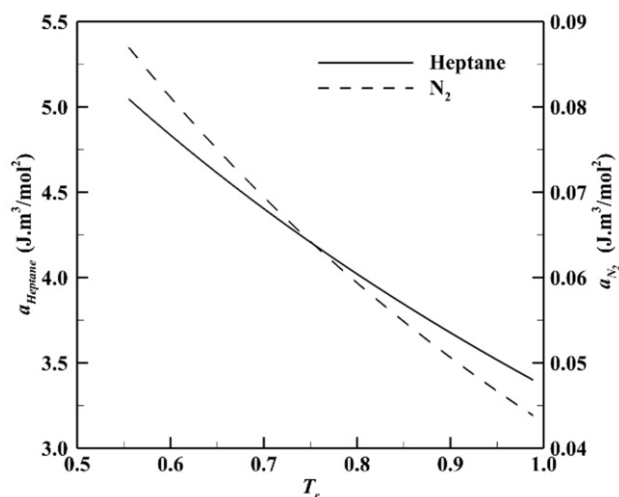


Fig. 6. Variation of parameter a for heptane and nitrogen.

As mentioned earlier, parameter a in the Peng-Robinson equation of state represents the intermolecular attractive force. The variation of this parameter with respect to temperature is shown in Fig. 6. Results indicate that increasing temperature decreases the attractive force between molecules in both heptane and nitrogen. However, this mitigation notably impacts the liquid phase at lower temperatures, resulting in easier dissolution of gas molecules. With a further increase in temperature, the attractive force between gas molecules also decreases. Consequently, a smaller amount of gas dissolves in the liquid. In addition (look back at Fig. 5), vaporization becomes dominant as the temperature of heptane approaches its boiling point. Within an isolated system, where the total mass remains constant, the evaporation of heptane is anticipated to result in an elevation of nitrogen mole fraction. However, contrary to expectations, this elevation does not occur. Accordingly, it can be concluded that nitrogen escapes from the liquid phase to the gas phase with the evaporation of heptane. In fact, with increasing temperature, decreasing attractive force between nitrogen molecules (parameter a) plays a controlling role in determining the equilibrium mole fraction. When the pressure exceeds the critical liquid pressure, an increase in temperature continuously increases the amount of gas solubility and reaches its maximum at the critical mixing point. The liquid phase exhibits gas-like characteristics with increasing temperature and approaching the critical state. Hence, nitrogen dissolves into the liquid phase more easily. It is apparent that even at relatively low temperatures, for example, 300 K (reduced temperature of about 0.55), the nitrogen mole fraction in the liquid phase increases with increasing pressure. For example, at a reduced pressure of 0.5, the amount of nitrogen dissolved in the liquid phase is approximately 0.025, while at a reduced pressure of 5, it is about 0.2, which emphasizes the importance of considering gas solubility in models such as droplet evaporation at high pressures.

Figure 7 compares nitrogen solubility in three hydrocarbons: heptane, dodecane, and hexadecane, at various reduced pressures. Figures 7a and b show the nitrogen mole fractions in subcritical pressures. According to these figures, with an increase in a reduced temperature, nitrogen solubility gradually increases, reaching local maximum values and decreasing rapidly. It can be seen that as the molecular weight of the liquid increases, the amount of dissolved gas decreases. In other words, with the reduction in the volatility of hydrocarbons, less nitrogen dissolves into the liquid phase. Specifically, in all cases, nitrogen exhibits the lowest solubility in hexadecane as a heavy hydrocarbon, whereas it demonstrates the highest solubility in heptane as a representative of light hydrocarbons. The difference vanishes for reduced temperature near unity, and dissolved nitrogen sharply drops to zero. Figures 7c and d depict the solubility of nitrogen in different liquids against reduced temperatures at two supercritical pressures. Similar to subcritical conditions, the solubility of nitrogen is higher for lighter liquids. However, in contrast, the solubility monotonically increases as temperature increases.

Figure 8 compares the solubility of different gases (nitrogen, oxygen, and carbon dioxide) in dodecane as a function of the reduced pressure. The findings reveal a positive correlation

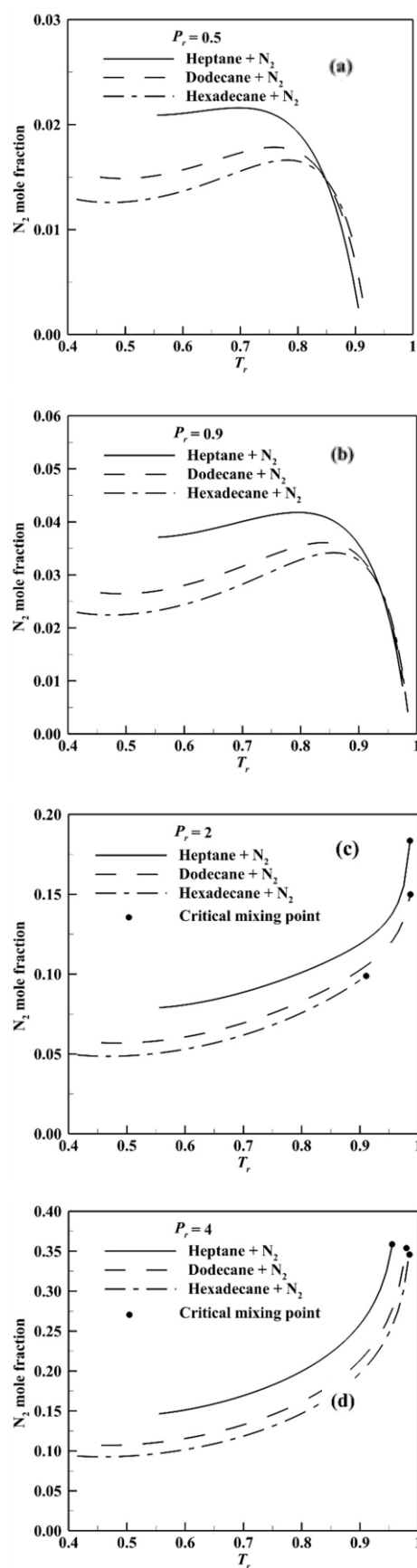


Fig. 7. Comparison of nitrogen solubility in three hydrocarbons, heptane, dodecane, and hexadecane at different hydrocarbon's reduced pressures: (a) $P_r = 0.5$, (b) $P_r = 0.9$, (c) $P_r = 2$, (d) $P_r = 4$.

between the molecular mass of the gas and its solubility. The solubility of carbon dioxide is approximately 5 to 6 times greater than nitrogen at lower temperatures. With rising temperatures, the solubility of carbon dioxide experiences a sharp decline, whereas the variations in the mole fractions of nitrogen and oxygen occur at a slower pace. The results indicate that the lighter gas dissolves less in a liquid, regardless of pressure.

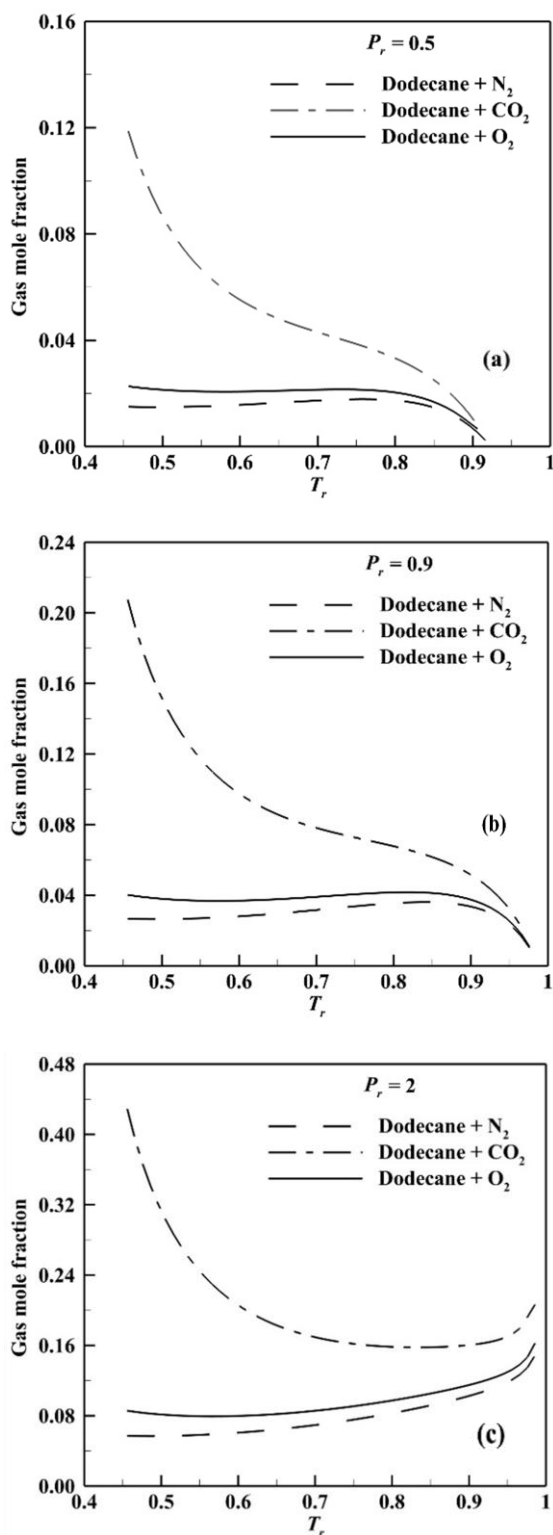


Fig. 8. Comparison of nitrogen, carbon dioxide, and oxygen solubility in dodecane at different reduced pressures: (a) $P_r = 0.5$, (b) $P_r = 0.9$, (c) $P_r = 2$.

It contrasts with the previous finding that a gas dissolves less in heavier liquid at a given pressure. It is also worth mentioning that the results of the dodecane- CO_2 system are in agreement with the experimental data of Camacho-Camacho [22].

The disparity in gas solubility can be attributed to the attractive force between molecules. Figure 9 shows the value of the parameter a for substances studied in this paper. Figure 9a presents the value of attractive force for nitrogen, oxygen, and carbon dioxide. It can be seen that the value of this parameter for carbon dioxide is about four times higher than nitrogen in 300 K. Indeed, the attractive force between carbon dioxide molecules is much higher than that of nitrogen. Consequently, carbon dioxide demonstrates substantially higher solubility than nitrogen, particularly under low-temperature conditions. The value of this parameter for oxygen is approximately 1.3 times greater than that of nitrogen. As a result, the solubility levels of nitrogen and oxygen in Fig. 8 demonstrate a similar magnitude. Figure 9b illustrates the liquids studied in this work. Through a comparison between this figure and Fig. 7, it becomes evident that with an increase of molecular attractive force in the liquid phase, the amount of gas dissolved in the liquid decreases, with nitrogen gas demonstrating the highest amount of solubility in heptane and the least amount of solubility in hexadecane. Parameter a depends on the critical temperature and pressure. Since the critical temperature and pressure depend on the molecular mass, parameter a also depends on the molecular mass. Therefore, it can

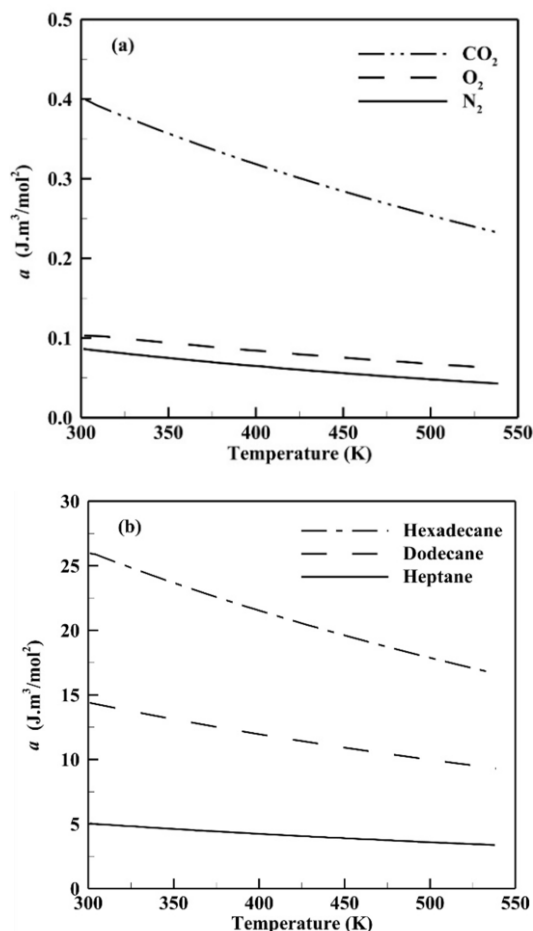


Fig. 9. Value of parameter a in different substances: (a) gas substances, (b) liquid substances.

be claimed that an increase in the molecular mass of the gas leads to an increase in its solubility within the liquid phase. However, gas solubility decreases in the liquid by increasing the molecular mass. As the density of liquids and gases decreases with increasing temperature, it could be claimed that parameter a and density are directly associated with each other, and the density of the species subsequently impacts gas solubility.

Figure 10 illustrates the effect of pressure on the solubility of nitrogen at 300 K in three hydrocarbons: heptane, dodecane, and hexadecane. It is evident in Fig. 10a that with an increase in pressure, nitrogen solubility increases in all cases. As mentioned earlier, the attractive force in the Peng-Robinson equation of state for a pure substance only depends on the temperature. Therefore, at a constant temperature, its value remains constant with increasing pressure. Hence, in this case, this variable does not play any role in the difference between gas solubility in the liquid phase. With increasing pressure, gas density increases, and more gas is placed in a particular volume. As shown in the figure, hexadecane dissolves more nitrogen than heptane. Differences in the solubility of liquids at a given temperature and pressure are related to their different reduced states. For example, 4 MPa corresponds to reduced pressure of 1.46 and 2.86 for heptane and hexadecane, respectively. Therefore, hexadecane experiences more pressure for dissolving the nitrogen. Figure 10b shows the nitrogen solubility with respect to the reduced pressure of liquids. Compared to Fig 10a, an utterly reverse dependency on the pressure is seen. For a given reduced pressure,

heptane can dissolve more gas into itself. It is dependent on the real state of the liquid; $T = 300$ K corresponds to a reduced temperature of 0.55, while the reduced temperature for hexadecane is 0.42. In the first case, the dissolution should be more.

3.2.2. Ternary system

The subsequent discussion encompasses three ternary systems: heptane-hexadecane-nitrogen, dodecane-heptane-nitrogen, and dodecane-hexadecane-nitrogen. The initial mole fraction of each component in the liquid phase is tabulated in Table 2. In the presented model, the temperature was considered 300, 350, and 500 K, and the pressure was changed from 0.5 MPa to 10 MPa.

Table 2. Initial mole fraction of liquid components.

System	C_7H_{16}	$C_{16}H_{34}$	$C_{16}H_{34}$	N_2
$C_7H_{16} + C_{16}H_{34} + N_2$	0.7	0.3	–	–
$C_{12}H_{24} + C_7H_{16} + N_2$	0.3	–	0.7	–
$C_{12}H_{24} + C_{16}H_{34} + N_2$	–	0.3	0.7	–

Figure 11 illustrates the variation of liquid- and vapour-phase mole fractions as a function of pressure at a constant temperature of 350 K. Figure 11a shows that the mole fraction of

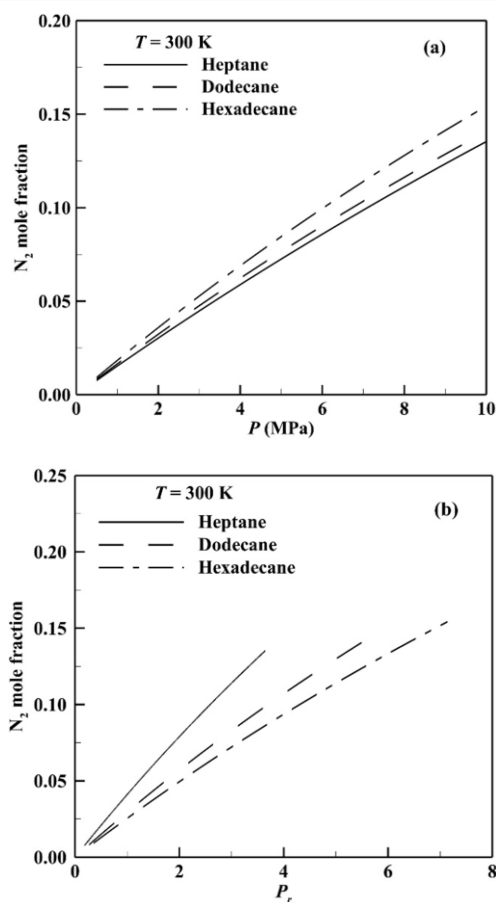


Fig. 10. Effect of pressure on nitrogen solubility at 300 K vs. (a) pressure and (b) reduced pressure.

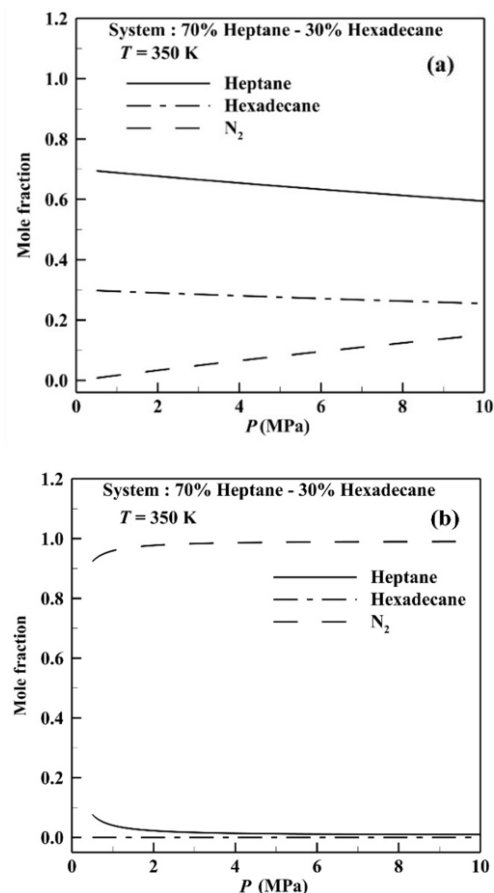


Fig. 11. Mole fractions in 70% heptane-30% hexadecane-nitrogen system using presented model: (a) in the liquid phase and (b) in the gas phase.

nitrogen dissolved in the liquid phase increases with increasing pressure. In this case, the gas solubility behaviour in the ternary system is identical to that of binary systems. Meanwhile, the mole fraction of heptane and hexadecane has constantly decreased due to the nitrogen mole fraction increase. Figure 11b presents mole fractions in the gas phase. It can be observed that the mole fraction of heptane and hexadecane in the gas phase decreases with increasing pressure. Because the volatility of heptane is higher than that of hexadecane, the mole fraction of heptane in the gas phase is continuously higher.

Figure 12a depicts the variations in the nitrogen mole fraction in the liquid phase in a 70% heptane-30% hexadecane mixture as a function of pressure at 350 K and 500 K. The results show that the amount of nitrogen dissolved in the liquid phase has increased with an increase in temperature. Figure 12b displays the attractive force between the mixture's molecules in the liquid phase in terms of pressure. It can be seen that similar to binary systems, this parameter's value has decreased with an increase in temperature. The reduction in the parameter a within the liquid phase has increased the gas solubility in the liquid phase. An important observation is the decrease in nitrogen solubility as the temperature increases at lower pressure. In this

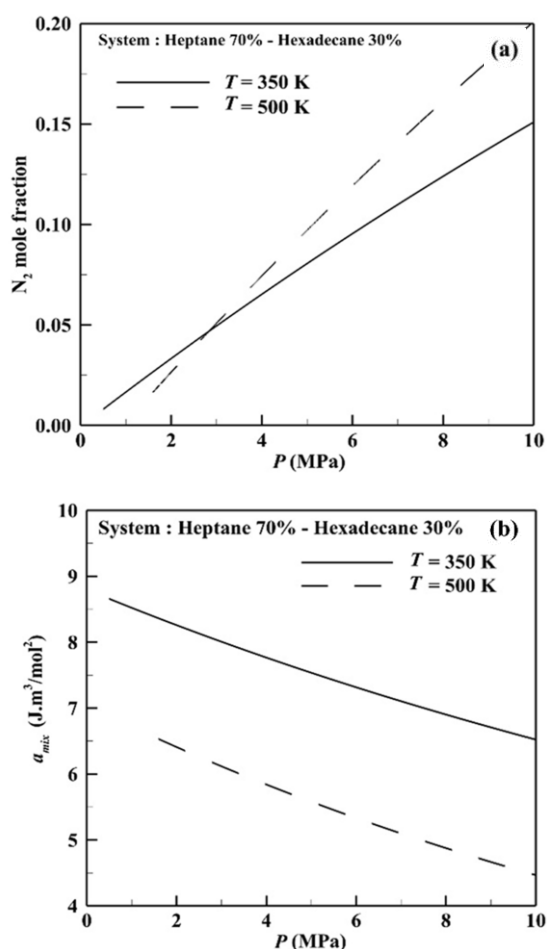


Fig. 12. Model predictions of (a) dissolved nitrogen mole fraction and (b) attractive force, in 70% heptane-30% hexadecane-nitrogen system at 350 K and 500 K.

case, with the increase in temperature, the liquid mixture is closer to its boiling temperature, and the solubility decreases like the binary system. As the pressure increases and moves further away from the boiling point of the mixture's lighter component, the gas solubility at 500 K is higher than at 350 K, which can be attributed to the parameter a . As Fig. 12b shows, the attractive force in the liquid mixture decreases by pressure, and the slope is more acute at higher temperatures. Here, it is worth noting that the density of the mixture is lower at higher temperatures. Therefore, the solubility of the gas encounters less resistance at higher temperatures. This figure depicts that the sensitivity of the solubility to the pressure is higher at higher temperatures.

Figure 13 compares nitrogen solubility in different concentrations of heptane and hexadecane mixture at 300 K. It is evident that nitrogen solubility increases at a constant reduced pressure by increasing heptane concentration (lighter hydrocarbon). For instance, at reduced pressure 2, the mole fraction of nitrogen in pure hexadecane is approximately 0.05. By adding heptane to hexadecane and increasing heptane concentration to 30%, the nitrogen mole fraction changes to 0.06. At this reduced pressure, nitrogen solubility in a 70% heptane-30% hexadecane mixture is about 0.07, while in pure heptane, it is approximately 0.08. These results accentuate the use of this comprehensive model to calculate species concentration, especially for light hydrocarbon mixtures at high pressures.

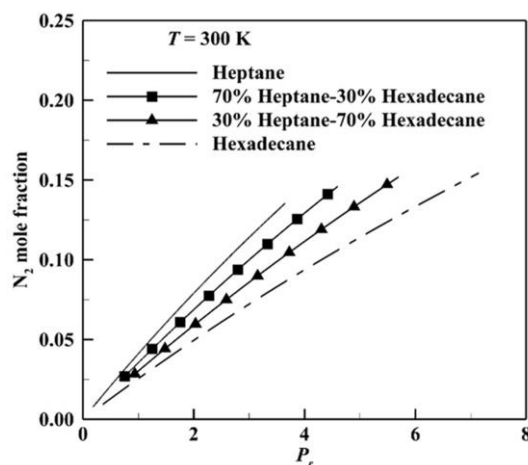


Fig. 13. Effect of pressure on nitrogen solubility in different concentrations of heptane and hexadecane mixture at 300 K using the presented model. The mixture reduced pressure is calculated from [14].

Figure 14 shows how adding heptane and hexadecane to dodecane affects nitrogen solubility. Nitrogen dissolution is compared in two systems of 70% dodecane-30% heptane and 70% dodecane and 30% hexadecane. Adding heptane as a light and volatile hydrocarbon to dodecane increases nitrogen dissolution compared to the dodecane-hexadecane mixture. As the reduced pressure increases, this difference becomes noticeable. For example, at reduced pressure 5, the amount of nitrogen dissolved in the dodecane-heptane mixture is about 11% more than in the dodecane-hexadecane mixture.

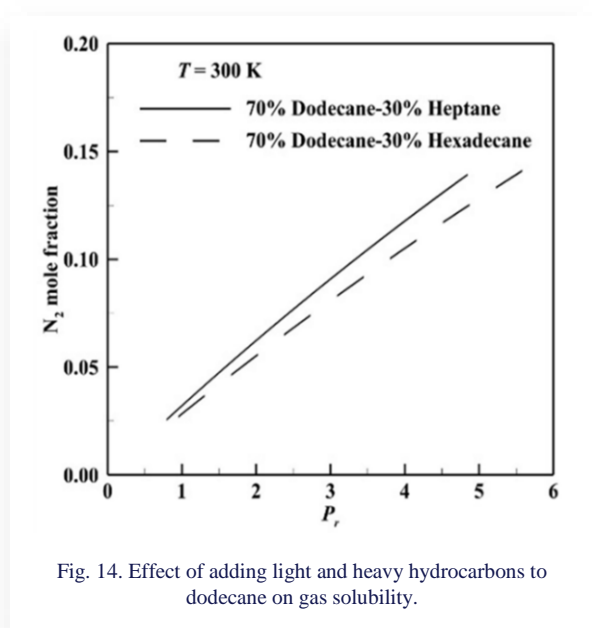


Fig. 14. Effect of adding light and heavy hydrocarbons to dodecane on gas solubility.

6. Conclusions

For studying the evaporation of droplets at high pressures, accurately estimating equilibrium mole fractions is crucial for determining droplet lifetime and evaporation rate. An iterative process using the fugacity coefficients of all species in both phases is employed to estimate phase equilibrium. This model accounts for all effects related to high pressure, including gas solubility in liquids, high-pressure phase equilibrium, and gas-phase non-idealities. The procedure of solving related equations, which is not covered in the literature, is described in detail. A system of 4 and 6 equations for binary and ternary system, respectively, are set with appropriate initial conditions, accompanying with Peng-Robinson equation of state. Compared to experimental data published in the literature, the numerical model is quantitatively validated and shows satisfactory agreement. The presented model can investigate the solubility of different ambient gases in various liquid hydrocarbons under subcritical and supercritical conditions. The primary conclusions of this study are as follows:

- 1) The attractive force term within the Peng-Robinson equation of state significantly impacts solubility with temperature variations. In the liquid phase, reduction in the parameter a , which represents the intermolecular attraction force, improves gas dissolution. Hydrocarbons with lower molecular weights, exhibiting reduced attractive forces, display a propensity for higher gas solubility as temperature rises. Conversely, concerning gases, a heavier gas with a higher attractive force tends to dissolve more in a particular liquid.
- 2) Gas solubility declines as the temperature rises in the subcritical region, while dissolved gas rises and achieves its maximum value at the critical mixing point in the supercritical region. In both subcritical and supercritical regions, dissolved gas in the liquid phase increases as pressure rises.

- 3) Adding heptane as a light hydrocarbon to a mixture increases gas solubility at a given temperature, while heavy hydrocarbons like hexadecane reduce solubility.

Although the presented model is simple and can be used for a wide range of substances at different temperatures and pressures, it is unreliable near liquid critical points. Also, due to the complexities of polar molecules, there is a need to provide a comprehensive model for polar systems.

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