Modeling solubility of nitrogen in clean fire extinguishing agent by Peng-Robinson equation of state and a correlation of Henry's law constants

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Abstract: Nitrogen is usually used to increase the total pressure of the fluid in aircraft fire suppression bottle. The amount of nitrogen required in the bottle is a significant factor to assure complete and effective discharge into the protected area and it depends on the solubility of the nitrogen in the fire extinguishing agent. In this article, the Peng-Robinson equation of state (PR EOS) including both the classical van der Waals mixing rule and the Wong-Sandler mixing rule is utilized to correlate the Gas-Liquid Equilibrium (GLE) data from available open published literature and to analyze the solubility of nitrogen in halon alternatives such as HFC227ea (C_3HF_7), CF_3I, FC218 (C_3F_8), and HFC125 (C_2HF_5) with Halon1301 (CF_3Br) as a reference. A new method is proposed to compute the adjustable interaction parameters in the van der Waals mixing rule and in the Wong-Sandler mixing rule based on the measurements of nitrogen required to pressurize the fire suppression bottle to a specified equilibrium pressure at room temperature. Results show that the PR EOS reproduces the GLE data very well with both van der Waals mixing rule and the Wong-Sandler mixing rule and it is then utilized to predict the temperature dependence of the Henry's law constants of nitrogen dissolved in the fire extinguishing agents. The PR EOS with van der Waals mixing rule is much more appropriate for determining the Henry's constants than that with the Wong-Sandler mixing rule and the results calculated by the current model are used to establish a new correlation for the Henry's law constants. This correlation will be very helpful for fire extinguishing bottle designers to acquire the pressure-temperature relationships for the mixture of nitrogen and agents.

Keywords: PR EOS, mixing rule, nitrogen, fire extinguishing agent, solubility, Henry's law constants

Nomenclature

a	Cohesive energy parameter in the PR equation of state, Pa m^6 mol^{-2}
b	Volumetric parameter in the PR equation of state, m^3 mol^{-1}
k	Binary interaction parameter
p	Pressure, Pa
R	Molar gas constant, 8.31447 J mol^{-1} K^{-1}
T	Absolute temperature, K
M	Mole weight, g mol^{-1}
v	Molar volume, m^3/mol
x	Mole fraction in liquid phase
y	Mole fraction in vapor phase
z	Compressibility factor
Z	Total mole fraction of nirtrogen in bottle
m	Mass, kg
A_{∞}^{E}	Excess Helmholtz free energy at infinite pressure
G_{0}^{E}	Excess Gibbs free energy at low pressure
g	Local composition factor in the NRTL model
N	Number of data points
k_{H}	Henry's law constant, MPa
f	Fugacity, Pa
C	Constants in Krause and Benson's correlation

Greek letters

α	Function of temperature in the PR equation of state
α_{ij}	Binary parameter in the NRTL model
τ	Binary interaction parameter in the NRTL model
k_0	Function of the acentric factor
φ	Fugacity coefficient
ω	Acentric factor

Subscripts

c	Critical point

i, j	Component i, j
m	Mixture
cal	Calculated
exp	Experimental
max	Maximum
min	Minimum
V	Vapor

Abbreviations

PR EOS	PR Equation of State
vdW	Van der Waals mixing rule
WS	Wong-Sandler mixing rule
NRTL	Non-Random Two-Liquid model
GLE	Gas-Liquid Equilibrium
PC-SAFT	Perturbed-Chain Statistical Associating Fluid Theory
ECS	Extended Corresponding State
OBJ	Objective Function

1. Introduction

As effective and nontoxic fire extinguishing agent, CF_3Br (Halon1301) has been widely used in aircraft fire protection over the past six decades. However, Halon1301 has been banned from production and utilization under Montreal Protocol with global environmental concerns and high ozone depletion potentials [1]. Many researchers [2-8] have presented alternatives, such as HFC227ea, CF_3I, FC218, and HFC125, to replace halon1301 in flight fire protection applications. Due to the low vapor pressure of the alternative agents, nitrogen is usually used for the purpose of shortening the discharging time. For a binary mixture of nitrogen and fire extinguishing agent, the GLE data is very important since the amount of nitrogen in the vessel plays a significant role in determining the final pressure of the vessel. However, very few GLE data for nitrogen and alternative agents are available in the open published literatures.

Yang et al. [2] presented a combined experimental and numerical study to determine the solubility of nitrogen and Freon-23 in alternative halon replacement agents. They applied mass

balance on the agent and nitrogen to obtain the total amount of nitrogen in the bottle. But the effect of dissolved nitrogen on the density of the liquid phase was neglected. Later on, Yang et al. [3, 5] also developed an extended corresponding state (ECS) model to predict the thermodynamic properties of the selected halon alternative and nitrogen mixtures using van der Waals one fluid mixing rule. Compared with the measured amount of nitrogen, a good prediction was achieved by the ECS model except for the mixture of N_2+CF_3I. Using Yang's model [2], Grosshandler et al. [7] and Gann [8] calculated the amount of nitrogen and CF_3H that needed to super-pressurize the fire suppression agents in the vessel.

Lim and Kim [4] conducted GLE experiments in the pressure range from 3.0 MPa to 10.0 MPa and temperature range from 293.2 K to 313.2 K for the binary systems of N_2+Halon1301, N_2+Halon1211, N_2+HFC227ea, and N_2+ CF_3I. However, the values of k_{ij}, A_{ij}, A_{ji} in the literature [4] gave a poor prediction for the amount of nitrogen required to pressurize the alternative agent to a typical pressure of 4.2 MPa when compared with the experimental data of Yang et al. [5].

Kao et al. [6] used a semi-automated vapor-liquid-equilibrium static cell to measure the solubility of the nitrogen in three halon replacements. Based on PR EOS, the Henry's law constant, the weight of the nitrogen needed for super-pressurization of HFC227ea, HFC236fa, and HFC125, and pertinent isometric diagrams were calculated, respectively. However, only the bubble pressures and phase compositions for the mixture of N_2+HFC227ea were given in detail. Kim et al. [9] selected HFC22, HFC125 and HFC134a as solvent and measured the bubble pressures with temperature ranging from 283.15 K to 303.15 K to obtain the solubility of the nitrogen. Compared with their experimental data, the calculated values from Peng-Robinson-Stryjek-Vera equation of state showed good agreement except for the mixture of N_2+HFC125.

Many refrigerants such as saturated fluorocarbon have similar properties with halons, i.e. FC-218 is a popular refrigerant and a replacement of Halon1301. Vrabec et al. [10] reviewed binary interaction parameters of 267 binary mixtures using PR EOS, including 16 mixtures with nitrogen, of which only one binary mixture was nitrogen and Halon1301. They suggested a value of 0.076 for the interaction parameter k_{ij} at 313.2 K. Vinš and Hrubý [11, 12] used both Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) and PR EOS to determine the solubility of the nitrogen in all fifteen one-component refrigerants including HFC125 and FC218. Their results indicated that it was difficult to confirm which equation of state showed superiority over

the others. The Henry's law constants for all thirteen mixtures were also correlated as a function of the reduced temperature. However, the GLE data for the mixture of N_2+HFC125 and N_2+FC218 were not provided. Consequently, the binary interaction parameter k_{ij} for nitrogen dissolved in HFC125 and FC218 was set to zero. Using PR EOS and the Wong-Sandler mixing rule, Claudio et al. [13] represented the similar results compared with one from other researchers, i.e. Yakoumis et al. [14], Al-Saifi et al. [15], Soo et al. [16], and Courtial et al. [17]. They concluded that by only analyzing the average deviations, complex models showed no superiority over the model of PR EOS.

To the best knowledge of the authors, few experimental data were available on the solubility of nitrogen in fire extinguishing agents, which were restricted to limited temperature ranges and some were suspected inaccurate. The present research focused on the solubility of nitrogen in HFC227ea, CF_3I, FC218, and HFC125, with Halon1301 as a reference. Of the many equations of state available, the cubic equations such as PR EOS offered a compromise between generality and simplicity that was suitable for many purposes. They were valuable tools for correlating experimental data and were often used in technical applications. Therefore, the PR EOS was utilized to predict the solubility of the nitrogen in halon alternatives in the present paper. The available GLE data about nitrogen and fire extinguishing agents were summarized and reproduced though the PR EOS associating with van der Waals mixing rule and the Wong-Sandler mixing rule. In the current work, a new method is proposed to compute the adjustable interaction coefficient of van der Waals mixing rule and the three adjustable parameters of Wong-Sandler mixing rule for those binary mixtures of which the GLE data were not found in the literature. For the proposed new method, the measurements for the amount of nitrogen required to pressurize the fire suppression bottle to a specified equilibrium pressure at room temperature were used, which attracted more attention for the fire extinguishing system designers. Based on the interactive parameters obtained by the GLE data and the new method, a theoretical approach using PR EOS with two mixing rules was conducted to estimate the temperature dependency of the Henry's law constants. Moreover, a new simple temperature correlation for the Henry's law constants of nitrogen dissolved in CF_3I and FC218 at a relatively high gas partial pressure was established.

2. Model development

Due to the limited experimental data on the solubility of nitrogen in clean fire extinguishing agents, a theoretical model is proposed to correlate the collected GLE data. The PR EOS [18] is one of the simplest methods for accurately calculating the GLE. So it is used in this paper and can be written as:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{1}$$

where p is the system total pressure, R is the gas constant, T is the absolute temperature and v is the molar volume.

Both a and b are the characteristic parameters specific for each substance, and

$$a = \frac{0.45724R^2T_c^2\alpha(T)}{p_c} \tag{2}$$

$$b = \frac{0.07780RT_c}{p_c} \tag{3}$$

where p_c is the critical pressure, T_c is the critical temperature.

$\alpha(T)$ in Eq. (2) is a temperature function in the PR equation of state defined as:

$$\alpha(T) = [1+k_0(1-T_r^{0.5})]^2 \tag{4}$$

where $T_r=T/T_c$ is the reduced temperature. k_0 can be represented by the following formulation:

$$k_0 = 0.3746+1.54226\omega-0.26992\omega^2 \tag{5}$$

where ω is the acentric factor.

For mixtures the parameters a and b of Eq. (1) are substituted by a_m and b_m:

$$p = \frac{RT}{v-b_m} - \frac{a_m}{v(v+b_m)+b_m(v-b_m)} \tag{6}$$

According to the PR EOS, two different mixing rules are applied. They are the one-parameter van der Waals one-fluid mixing rule [19] and the Wong-Sandler mixing rule [20], respectively. The one-parameter vdW mixing rule can be summarized as follows:

$$a_m = \sum\sum x_i x_j \sqrt{a_i a_j}(1-k_{ij}) \tag{7}$$

$$b_m = \sum x_i b_i \tag{8}$$

where k_{ij} is the binary interaction coefficient that satisfies $k_{ij}=k_{ji}$ and $k_{ii}=k_{jj}=0$.

The Wong-Sandler mixing rule for a cubic equation of state such as the PR EOS can be expressed as :

$$b_m = \frac{\sum\sum x_i x_j (b - \frac{a}{RT})_{ij}}{1 - \sum x_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT}} \tag{9}$$

$$(b - \frac{a}{RT})_{ij} = \frac{1}{2}[(b - \frac{a}{RT})_i + (b - \frac{a}{RT})_j](1 - k_{ij}) \tag{10}$$

$$\frac{a_m}{b_m} = \sum x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \tag{11}$$

In Eq. (9), C is a constant (-0.62323) for the PR EOS, k_{ij} is an interaction parameter, x_i and x_j represent the mole fraction of component i and j in the liquid phase or in the vapor phase. A_∞^E is an excess Helmholtz free energy model at infinite pressure, which can be calculated assuming that $A_\infty^E=G_0^E$, where G_0^E is the excess Gibbs free energy. Several models [13, 17, 19] were reported to determine G_0^E, whereas in the current study, the NRTL model [21] is employed:

$$\frac{A_\infty^E}{RT} = \sum x_i [\frac{\sum x_j G_{ji} \tau_{ji}}{\sum x_k G_{ki}}] \tag{12}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{13}$$

$$\tau_{ji} = A_{ji} / RT \tag{14}$$

$$A_{ji} = g_{ji} - g_{ii} \tag{15}$$

where G_{ji} is the local composition factor for the NRTL model, τ_{ji} is the binary interaction parameter for the NRTL model, g_{ii}, g_{jj}, g_{ij}, and g_{ji} are related to the interaction energy between molecules i and j, α_{ji} is a non-randomness paremeter which is equal to 0.3 for all the binary mixtures studied in the present work.

For a binary mixture, the van der Waals mixing rule includes one adjustable binary interaction coefficient (k_{ij}) for a_m. On the other hand, the Wong-Sandler mixing rule consists of one variable binary interaction parameter (k_{ij}) for b_{ij}-(a_{ij}/RT) and two parameters, A_{ij} and A_{ji}, included in the G_0^E model. In summary, the proposed model combined the PR EOS, the van der Waals mixing

rule and the Wong-Sandler mixing rule, which is designated as PR/vdW and PR/WS in the rest of the paper.

3. Sample data

In the current study, five different binary mixtures are considered, namely, N_2(1)+HFC227ea(2), N_2(1)+CF_3I(2), N_2(1)+FC218(2), N_2(1)+HFC125(2), and N2(1)+Halon1301(2). Here, 1 refers to the component of nitrogen and 2 refers to the other component. Pure component properties that used to calculate the parameters of the PR EOS are listed in Table 1. And the collected GLE data for nitrogen and agent mixtures are listed in Table 2.

Both PR/vdW model and PR/WS model are applied to perform bubble pressure calculations for binary mixtures. The Levenberg-Marquardt algorithm implemented in the MATLAB [26] software is used to determine the adjustable parameter k_{12} of PR/vdW model and the parameters (k_{12}, A_{12}, A_{21}) of PR/WS model. Two objective functions are defined and given by Eq. (16) and Eq. (17):

$$\text{OBJ-1}=\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{p_{\text{i,exp}}-p_{\text{i,cal}}}{p_{\text{i,exp}}}\right)^2} \tag{16}$$

$$\text{OBJ-2}=\sqrt{\frac{1}{2N}\sum_{i=1}^{N}\left[\left(\frac{p_{\text{i,exp}}-p_{\text{i,cal}}}{p_{\text{i,exp}}}\right)^2+\left(\frac{y_{\text{i,exp}}-y_{\text{i,cal}}}{y_{\text{i,exp}}}\right)^2\right]} \tag{17}$$

where N is the number of points in the experimental data, p is the bubble pressure, and ‘exp’ and ‘cal’ represent experimental values and calculated values, respectively.

For the measured amount of nitrogen required to pressurize the binary mixture to a given pressure [3, 5], another objective function is defined as follows:

$$\text{OBJ-3}=\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{m_{\text{i,exp}}-m_{\text{i,cal}}}{m_{\text{i,exp}}}\right)^2} \tag{18}$$

In Eq. (18), m_{exp} is the amount of nitrogen, m_{cal} refers to the calculated amount of nitrogen.

To accurately estimate the amount of nitrogen required in the fire suppression bottle, a new method is proposed and it is determined by four control parameters such as (1) the total mass of agent in the bottle, (2) bottle volume (V_{bot}), (3) initial equilibrium temperature (T) and (4) initial equilibrium pressure (P). Fig. 1 depicts the overall flowchart of the method in the current study. The computational procedure mainly includes three-level iterative loops and they are (1) Z-loop

(*Z* refers to the total molar ratio of nitrogen in the binary mixture), (2) *e*-loop (*e* refers to the evaporation rate), and (3) *K*-loop (*K* refers to the final phase equilibrium constant). Firstly, the binary interaction coefficient k_{12}=0.01 and Z_1=0.10 are assumed. Then the calculations of bubble point and dew point are carried out to ensure that the binary mixtures are in the two-phase region. Afterwards, a flash calculation is conducted to determine the values of *Z*, *e*, *K* as well as m_{cal}. Finally, Eq. (18) is optimized using the Levenberg-Marquardt algorithm to determine the optimal value of k_{12}. For the adjustable parameters (k_{12}, A_{12}, A_{21}) of PR/WS model, a similar calculation is performed for the binary mixtures of N_2+HFC227ea, N_2+FC218 and N_2+HFC125.

4. Results and discussion

4.1 Binary interaction parameter

The optimized binary interaction parameter (k_{12}) in the vdW mixing rule are shown in Table 3. This can be achieved by minimizing Eq. (16) and Eq. (17). The mean absolute deviation for the pressure and mean relative deviation for the mole fraction of nitrogen in gas volume are calculated according to the following expression:

$$|\%\Delta p| = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{p_{\mathrm{i,exp}} - p_{\mathrm{i,cal}}}{p_{\mathrm{i,exp}}}\right| \tag{19}$$

$$\%\Delta \mathrm{y}_1 = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{\mathrm{y}_{1,\mathrm{cal}} - \mathrm{y}_{1,\mathrm{exp}}}{\mathrm{y}_{1,\mathrm{exp}}}\right]_i \tag{20}$$

Based on the PR/vdW model with the value of k_{12} determined from Eq. (16) and Eq. (17), it is observed that the mean absolute deviations of the bubble pressure for the binary mixtures (N_2+HFC227ea, N_2+CF_3I, and N_2+halon1301) is less than 1.4% at all temperatures, as illustrated in Table 3. For the mixture of N_2+HFC227ea, the pressure is reproduced with a maximum deviation of 1.85% and the vapor mole fraction of nitrogen is correlated with a mean-relative deviation less than 1.75%. For the other two mixtures of N_2+CF_3I and N_2+Halon1301, the average deviations for the pressure and the mole fraction of nitrogen were less than those in the case of N_2+HFC227ea. However, for the binary mixture of N_2+HFC125, the PR/vdW model correlates the experimental data with a relatively larger error. The absolute deviation of the pressure varies from 2.5% to 6.7% and the deviation of the mole fractions of nitrogen in gas volume ranging from 6.8% to 8.0%.The relatively large deviations for the mole fraction of nitrogen indicates that the GLE data [9] are not suitable for estmating the binary interaction

coeffinicent (k_{12}) of vdW mixing rule.

Fig. 2 shows the temperature dependence of k_{12} in vdW mixing rule for nitrogen dissolved in the fire extinguishing agents. The k_{12} value is determined by optimizing Eq. (16) and Eq. (17) except for the mixture of N_2+FC218 which is optimized by minimizing Eq. (18). As shown in Fig. 2, k_{12} presents a strong linear variation for the N_2+HFC125 mixture based on the experimental data of Kim et al. [9]. However, k_{12} remains almost constant for the other mixtures. The average value of k_{12} is found to be -0.00752 for N_2+HFC227ea, 0.01948 for N_2+CF_3I, 0.17789 for N_2+HFC125 and 0.05715 for N_2+Halon1301, respectively. This fact infers that a general constant value of k_{12} can be performed to calculate the Henry's law constant of nitrogen in a relatively large temperature range.

Tables 4 and 5 have shown the results of the optimized parameters (k_{12}, A_{12}, A_{21}) in the WS mixing rule based on Eq. (16) and Eq. (17), respectively. The bubble pressures for the mixtures of N_2+HFC227ea, N_2+CF_3I, N_2+HFC125 and N_2+Halon1301 are reproduced with a mean absolute deviation less than 0.7% illustrated in Table 4, and with a mean absolute deviation less than 1.0% shown in Table 5. Of the four studied mixtutes, the PR/WS model reproduces the mole fractions of nitrogen in gas volume lower than the experimental values in both Tables 4 and 5. For the mole fraction of nitrogen, the average reletive deviation is less than 1.5% for N_2+HFC227ea whereas -0.80% ,-17.5% and -6.1% for N_2+CF_3I, N_2+HFC125 and N_2+Halon1301, respectively, as presented in Table 4.

Similarly, Table 5 demonstrates the bubble pressure calculated agrees well with the experimental data, with an average-absolute deviation less than 1.0% for all the binary mixtures. Moreover, the average relative deviation for mole fraction of nitrogen decreases from -17.5% in Table 4 to -1.1% in Table 5 for N_2+HFC125. Generally, the PR/WS model with the parameter values obtained by both Eq. (16) and Eq. (17) can reproduce the bubble pressures with close agreement to the experimental data. When correlating GLE data from the references, Eq. (17) could be a better optimization objective function since both the deviations of pressure and vapor mole fraction of nitrogen are included.

In reference [11], the binary interaction coefficient k_{12} was set to zero since there is no GLE data for the mixture of N_2+HFC25 and N_2+FC218. As a matter of fact, Kim et al. [9] has already provided GLE data for N_2+HFC25 at three different temperatures of 283 K, 293 K and 303 K.

On the other hand, Yang et al. [5] measured the amount of nitrogen that needed to pressurize CF_3I, HFC125 and FC218 to a given pressure at 296 K. DuPont [27-28] reported the mass of nitrogen required to pressurize HFC227ea and HFC125 to 2.50 MPa and 4.20 MPa, respectively. In the present study, these experimental data [5, 27, 28] have been employed to determine the binary interaction parameter (k_{12}) in vdW mixing rule and the parameters (k_{12}, A_{12}, A_{21}) in WS mixing rule. The computational procedure is shown in Fig. 1 and results are listed in Table 6.

Table 6 shows the results of the adjustable parameters of the vdW mixing rule and WS mixing rule for the N_2+HFC227ea, N_2+CF_3I, N_2+HFC125 and N_2+FC218, respectively. Considering the large errors when correlating the GLE data [9] of N_2+HFC125 through PR/vdW model and PR/WS model, the adjustable parameters obtained by Eq. (18) will be used to estimate the Henry's law constants.

4.1.1. N_2+HFC227ea

Lim and Kim [4] reported the GLE data for N2+HFC227ea at three different temperatures of 293.2 K, 303.2 K and 313.2 K and pressures from 30 to 100 bar. Kao et al. [6] also measured the nitrogen solubility in super-pressurized HFC227ea at 294 K but the data of the mole fraction for nitrogen in gas volume were not included. In addition, Yang et al. [2-3, 5] provided the amount of nitrogen required to pressurize HFC227ea to a given pressure at 296 K. In general, the data given by Lim and Kim [4] could be convenient for the analysis of the parameter k_{12} in the vdW mixing rule and the parameters (k_{12}, A_{12}, A_{21}) in the WS mixing rule.

Fig. 3 compares the solubility of N_2 in HFC227ea predicted by PR/vdW model and PR/WS model. The values for the interaction parameters in Tables 3 and 5 determined by Eq. (17) are used. It is obvious that the PR/WS model reproduces a better result than that of the PR/vdW model.

4.1.2. N_2+ CF_3I

The binary mixture of N_2+CF_3I is also investigated by Lim and Kim [4] in the pressure range of 3.0 MPa to 10.0 MPa and temperature range of 293.2 K to 313.2 K. Yang et al. [2, 3, 5] measured the amount of nitrogen required to pressurize CF_3I to 2.9 MPa and 4.2 MPa at 296 K. The binary interaction coefficient of k_{12} is 0.025 at 293 K. Fig. 4 compares the PR/vdW and the PR/WS predictions with the GLE data by Lim and Kim [4] for the solubility of N_2 in CF_3I. The k_{12} value in the vdW mixing rule is from Table 3 and the values of k_{12}, A_{12}, A_{21} in WS mixing

rule are from Table 5. As can be seen in Fig. 4, PR/vdW model has almost the same accuracy with PR/WS model compared with the GLE data of N_2+CF_3I.

4.1.3. N_2+HFC125

In the current work, Kim et al. [9] provided GLE data for N_2+HFC25 at three different temperatures of 283 K, 293 K and 303 K. Fig. 5 shows the comparison of GLE data with the prediction by PR/vdW model and PR/WS model, respectively. The k_{12}value in Table 3 and the values of k_{12}, A_{12}, A_{21} in Table 5 are obtained from Eq. (17). From Fig. 5, it is noted that both the PR/vdW and PR/WS model reproduce the GLE data by Kim et al. [9] with a large error. Therefore, it is suggested that these adjustable parameters are not suitable to predict the Henry's law constant for N_2 dissolved in HFC125. Meanwhile, the values of the adjustable parameters determined by Eq. (18) and shown in Table 6 will be utilized to calculate the Henry's law constant for the mixture of N_2 + HFC125.

4.1.4. N_2+FC218

Similarly, for the case of N_2+HFC125, no GLE data for nitrogen solubility in FC218 was found [11]. As a result, k_{12} for the Berthelot-Lorentz combining rule is suggested as 0.00685, assuming that k_{12} changes with the carbon number of n-perfluorocarbons. Here, the interaction parameter (k_{12}) of vdW mixing rule and parameters (k_{12}, A_{12}, A_{21}) of WS mixing rule are obtained through a new method (as shown in Fig.1) for N_2+FC218. The results are that k_{12}=0.1206 in the vdW mixing rule and k_{12}=-0.106895, A_{12}=3770.15, and A_{21}=660.39 in the WS mixing rule. These values will be utilized to predict the Henry's law constant for N_2 dissolved in FC218.

4.1.5. N_2+Halon1301

Lim and Kim [4] carried out an experimental study for N_2+Halon1301 below 9.2 MPa at 303.3 K and 7.7 MPa at 313.2 K. Their data can be easily used to predict the interaction coefficient for vdW and WS mixing rules. Fig. 6 shows the comparison of GLE data between the PR/vdW model and PR/WS model for N_2+Halon1301. It shows similar behavior as the case of N_2+HFC227ea. The deviation for the vapor mole fraction of nitrogen increases with the increase of the total pressure of equilibrium cell.

For the fire suppression bottle designers, they are interest of the amount of nitrogen required in the bottle and the bottle temperature-pressure relationships. A typical initial condition of the bottle established by the calculation process of Fig. 1 is shown in Fig. 7. As can be seen from

Fig. 7, with the increase of temperature, the mole fraction of nitrogen dissolved in liquid agent raises quicker than that in lower temperatures. To predict the total pressure in the bottle when the temperature varies, a flash calculation and material balance should be conducted similar to the computational procedure given in Fig. 1. More discussions about the temperature-pressure characteristics for different mixtures of nitrogen and agents can be seen in our previous work [36, 37].

4.2 Henry's law constant

The Henry's law constant for nitrogen in an agent is defined as the ratio of the nitrogen fugacity to the mole fraction of nitrogen dissolved in liquid phase at infinite dilution [6]. The values of the Henry's law constant (k_H) is computed by PR/vdW model and PR/WS model, which is defined as the following equation:

$$k_H = \lim_{x_A \to 0} \left(\frac{f_1^V}{x_1} \right) = \lim_{x_A \to 0} \left(\frac{\varphi_1^V y_1 p}{x_1} \right) \tag{21}$$

where f_1^V is the fugacity of nitrogen; φ_1^V is the fugacity coefficient of nitrogen in the vapor phase.

The temperature-dependent Henry's law constants for nitrogen dissolved in HFC227ea, HFC125 and Halon1301 are derived from references [27-28, 30]. In the current work, both the PR/vdW model and PR/WS model are utilized to predict the Henry's law constants for all the mixtures. Fig. 8 shows the comparisons of the prediction via PR/vdW model and WS model with literatures [6, 27-28]. For the mixture of N_2+HFC227ea, k_{12}=0.03515 is calculated by using the experimental data from [27], which presents an average deviation of approximate 4.9% higher than the experimental values [27] in the considered temperature range from 263 K to 313 K. For the case of k_{12}=0, the mean deviation is approximate 2.1% and the calculated Henry's law constant are lower than the experimental data of DuPont [27]. Using the same GLE data or the same amount of nitrogen required, PR/vdW model shows a better prediction for the Henry's law constant than the PR/WS model, especially for the case of k_{12}=0.0173. Considering the Henry's law constant of nitrogen dissolved in HFC125, the values calculated by a universal k_{12}=0.039 in vdW mixing rule agrees well with the test data of DuPont [28]. Though the PR/WS model reproduced the GLE data for all the binary mixtures quite well (see section 4.1), it still represents

larger deviations when compared with PR/vdW model. The reason for the inaccurate predictions of Henry's law constant by PR/WS model may be that the three parameters (k_{12}, A_{12}, A_{21}) are more sensitive to temperatures. As such, the PR/vdW model is selected to estimate the Henry's law constant for nitrogen dissolved in CF_3I and FC218.

Since no experimental values of Henry's law constant for nitrogen dissolved in CF_3I and FC218 were found, a uniform value of k_{12} in vdW mixing rule is suggested to predict the Henry's law constant. Fig. 9(a) shows the results of Henry's law constants computed by PR/vdW model with k_{12} =0 and k_{12} =0.025 for N_2+CF_3I. Fig. 9(b) gives the results of Henry's law constants for N_2+FC218 with k_{12}=0 and k_{12}=0.122. The values predicted via PC-SAFT EOS [12] and PR EOS[12] are also shown in Fig. 9(b).

Krause and Benson's [12, 29] three-parameter correlation is used to predict Henry's law constants of nitrogen dissolved in CF_3I and FC218 with the following expression:

$$\ln k_{\mathrm{H}} = C_1 + C_2 \frac{(1-T_{\mathrm{r}})^{1/3}}{T_{\mathrm{r}}^2} + C_3 \frac{(1-T_{\mathrm{r}})^{2/3}}{T_{\mathrm{r}}^2} \tag{22}$$

where C_1, C_2 and C_3 are coefficients listed in Table 7.

Due to lack of available experimental values for the Henry's law constant of nitrogen dissolved in CF_3I and FC218, it is not possible to obtain which k_{12} would give a better prediction compared with the real solubility of nitrogen in CF_3I and FC218. Therefore, in the current study, both k_{12} values are considered to estimate the Henry's law constant.

5. Conclusions

The available GLE data for nitrogen dissolved in HFC227ea, CF_3I, FC218, HFC125 and Halon1301 are correlated using the PR EOS associated with vdW mixing rule and WS mixing rule. Both the binary interaction coefficient k_{12} in vdW mixing rule and parameters k_{12}, A_{12}, A_{21} in WS mixing rule are obtained based on Eq. (16) and Eq. (17).

Compared with the GLE experimental data, the PR/WS model shows a better correlation compared with the PR/vdW model for all the binary mixtures. For the PR/WS model, the average absolute deviation for the pressure is less than 1.5% while the average relative deviation for the mole fraction of nitrogen in gas volume is less than 1.2%. Since there are no experimental data for N_2+FC218 or the data may be questionable for N_2+HFC125, a new computational procedure has been proposed to determine the interaction coefficient (k_{12}) and the parameters (k_{12}, A_{12}, A_{21})

for N_2+HFC227ea, N_2+CF_3I, N_2+FC218 and N_2+HFC125. These coefficients obtained by the new method are to be used in prediction of the Henry's law constants.

For the calculation of the Henry's law constants for all the binary mixtures, PR/WS model presents to a poor result than PR/vdW model. The reason may be that the parameters (k_{12}, A_{12}, A_{21}) in WS mixing rule are more sensitive to the temperature. Therefore, PR/vdW model is selected to predict the Henry's law constants for N_2+CF_3I and N_2+FC218. The results of the Henry's law constant are correlated by the Krause and Benson relation as a function of reduced temperature of the fire suppression agents. These obtained correlations can be very helpful for fire suppression bottle designers to acquire the bottle pressure-temperature relationships for the mixtures of nitrogen and agents.

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Fig. 1. Flowchart for calculating the amount of nitrogen required.

Fig. 2. Binary interaction parameter for nitrogen and agents using PR/vdW model.

Fig. 3. Solubility of N_2 in HFC227ea at three different temperatures. Comparisons of PR/vdW model and PR/WS model with GLE data by Lim and Kim [4]. (a) prediction by PR/WS model (b) mole fraction of nitrogen in liquid HFC227ea (c) comparisons of PR/vdW model and PR/WS model.

Fig. 4. Solubility of N_2 in CF_3I at three different temperatures. Comparisons of PR/vdW model and PR/WS model with GLE data by Lim and Kim [4]. (a) prediction by PR/WS model (b)

mole fraction of nitrogen in liquid CF_3I (c) comparisons of PR/vdW model and PR/WS model.

Fig. 5. Solubility of N_2 in HFC125 at three different temperatures. Comparisons of PR/vdW model and PR/WS model with GLE data by Kim et al. [9]. (a) prediction by PR/WS model (b) mole fraction of nitrogen in liquid HFC125 (c) comparisons of PR/vdW model and PR/WS model.

Fig. 6. Solubility of N_2 in Halon1301 at three different temperatures. Comparisons of PR/vdW model and PR/WS model with GLE data by Lim and Kim [4]. (a) prediction by PR/WS model (b) mole fraction of nitrogen in liquid Halon1301 (c) comparisons of PR/vdW model and PR/WS model.

Fig. 7. Solubility of nitrogen in Halon1301 and HFC227ea at different temperatures with a typical initial condition.

Fig. 8. Henry's law constant predicted by PR/vdW model and PR/WS model. (a) Henry's law constant for N_2+HFC227ea (b) Henry's law constant for N_2+HFC125.

Fig. 9. Henry's law constant predicted by PR/vdW model. (a) Henry's law constant for N_2+CF_3I (b) Henry's law constant for N_2+FC218.

Table 1. Characteristic properties of all the pure component.

Table 2. Details on the phase equilibrium for the systems considered here.

Table 3. Optimum binary interaction parameter in the vdW mixing rule with Eq. (16) and Eq. (17), respectively, and average absolute deviations for pressure and mean relative deviations for mole fraction of nitrogen in gas volume.

Table 4. Optimum binary interaction parameter and NRTL constants in the WS mixing rule at all temperatures studied and average absolute deviations for pressure and average relative deviation for vapor mole fraction of nitrogen, using PR/WS model with Eq. (16).

554 Table 5. Optimum binary interaction parameter and NRTL constants in the WS mixing rule at
555 all temperatures studied and average absolute deviations for pressure and average relative
556 deviation for vapor mole fraction of nitrogen, using PR/WS model with Eq. (17).
557 Table 6. Optimum binary interaction parameters for PR/vdW model and PR/WS model with
558 Eq. (18).
559 Table 7. Parameters C_1, C_2 and C_3 in Krause and Benson's correlation for the Henry's law
560 constant of nitrogen dissolved in CF_3I and FC218.