Applied Thermal Engineering 110 (2017) 457–468

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research Paper

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

Mengdong Chen [a], Yongqi Xie [a,*], Hongwei Wu [b,*], Shang Shi [a], Jianzu Yu [a]

[a] School of Aeronautic Science and Engineering, Beihang University, Beijing 100191, China
[b] Department of Mechanical and Construction Engineering, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, United Kingdom

HIGHLIGHTS

- Available GLE data for nitrogen and fire extinguishing agents are correlated by PR/vdW model and PR/WS model.
- The amount of nitrogen required to pressurize agents is utilized to determine the interaction parameter and NRTL constants.
- Solubility of nitrogen in five fire extinguishing agents is predicted.
- A correlation of Henry's law constants for nitrogen dissolved in CF_3I and FC218 is established.

ARTICLE INFO

Article history:
Received 1 December 2015
Revised 24 August 2016
Accepted 27 August 2016
Available online 29 August 2016

Keywords:
PR EOS
Mixing rule
Nitrogen
Fire extinguishing agent
Solubility
Henry's law constants

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.

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.

* Corresponding authors.
E-mail addresses: xyq@buaa.edu.cn (Y. Xie), hongwei.wu@northumbria.ac.uk (Hongwei Wu).

http://dx.doi.org/10.1016/j.applthermaleng.2016.08.179
1359-4311/

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 nitrogen in bottle
m	mass, kg
A^E_∞	excess Helmholtz free energy at infinite pressure
G^E_0	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

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 and Miller [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, Faúndez and Valderrama [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