International Journal of Management, IT & Engineering
Vol. 7 Issue 1, January 2017,
ISSN: 2249-0558 Impact Factor: 7.119
Journal Homepage: http://www.ijmra.us, Email: editorijmie@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

Calculation of Thermo Physical Properties of a mixture using Vapour Liquid Equilibrium

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Abstract

To determine the specific heat and thermal conductivity of n-heptane and nitrogen mixture, a vapour liquid equilibrium thermodynamic analysis was developed to calculate the composition of different components in different phases. The analysis was based on Peng-Robinson equation of state and it has been found that specific heat and thermal conductivity of the gas mixture increases with increase in temperature. The model was validated by comparing the computational results with the experimental values.

Keywords:

n-heptane;
nitrogen;
EOS;
VLE;

1. Introduction

In most of the engineering applications involving the multi-component mixtures, it is essential to estimate the thermodynamic properties of the mixtures. Sometimes it is very difficult to predict the properties at a particular temperature and pressure experimentally. The properties of multi-component mixtures depend on the composition as well as the temperature and pressure. If compositions of different components in different phases are known, it is very easy to predict the other thermodynamics properties.

During the past 20 years, great interest has developed in the properties of fluids and fluid mixtures [1,2]. This has evolved from numerous applications of Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), and Peng-Robinson (PR) equations of state in Oil and Gas industry [3], in calculation of volumetric and thermodynamic properties of pure refrigerants and refrigerant mixtures [4], determination of thermodynamic properties of nitric acid plant [5], in storage and transportation of hydrocarbons amongst others. These equations are used to predict the thermodynamic properties such as pressure, internal energy, density, viscosity, enthalpy, entropy etc. for the pure compounds and the non associating mixtures [6,7].

A recent survey on the accuracy of 10 different cubic equations of state (EOS) for 75 pure components [8] showed that Peng-Robinson EOS is one of the best methods for the prediction of vapour volumes at and near saturation. For the 75 compounds tested, Peng-Robinson equation predicted the vapour pressure to within an absolute average deviation of 1.39% (best equation 1.27%) and the saturated vapour volume to within 5.34% (best equation 5.08%); deviations for hydrocarbons even lower than worse. The work of Adachi et. al. [9] also shows the superiority of the PR EOS for predicting the saturated vapour volume of paraffin hydrocarbons.

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In the present study, for non associating bi-component system (nitrogen and n-hepate), PR EOS has been used to model the vapour-liquid equilibrium (VLE). The main aim is to calculate the composition of n-heptane and nitrogen in liquid and vapour phase, consequently other thermodynamic properties can be easily determined.

2. Specific Heat Calculation of Gas Mixture

For the estimation of low pressure (ideal gas) specific heats, a number of polynomial of other functional form are available in literature, one form is given as :

$$C_{pg}^{o} = \left(a_o + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4\right) xR \quad \text{....(1)}$$

where C_{pg}^{o} is ideal gas specific heat in $J\ mol^{-1}K^{-1}$ and R is universal gas constant in $J\ mol^{-1}K^{-1}$.

$$C_{pg\,m}^{o} = \sum \left(y_{igs} C_{pg_i}^{o}\right) \quad \text{....(2)}$$

For high pressure gaseous mixtures, Lee-Kesler method [10] is employed:

$$\left(C_p - C_p^o\right)_m = \left(\Delta C_p\right)_m = \left(\Delta C_p\right)_m^o + \omega\left(\Delta C_p\right)_m^1 \quad \text{....(3)}$$

where $\left(\Delta C_p\right)_m^o$ is simple fluid contribution, $\left(\Delta C_p\right)_m^1$ is the deviation function. The mixing rules used for Lee- Kesler method are :

$$T_{cm} = \frac{1}{V_{c_m}^{1/4}} \sum_i \sum_j x_i x_j V_{c_{ij}}^{1/4} T_{c_{ij}} \quad \text{....(4)}$$

$$V_{c_m} = \sum_i \sum_j x_i x_j V_{c_{ij}} \quad \text{....(5)}$$

$$\omega_m = \sum_i x_i \omega_i \quad \text{....(6)}$$

$$T_{c_{ij}} = \left(T_{c_i} T_{c_j}\right)^{1/2} k_{ij}^{'} \quad \text{....(7)}$$

$$V_{c_{ij}} = \frac{1}{8}\left(V_{c_i}^{1/3} + V_{c_j}^{1/3}\right)^3 \quad \text{....(8)}$$

$$P_{c_m} = \left(0.2905 - 0.085\omega_m\right) RT_{c_m} / V_{c_m} \quad \text{....(9)}$$

Now $T_{r_m} = T/T_{c_m}$, $P_{r_m} = P/P_{c_m}$ Then $\left(\Delta C_p\right)_m^o$ and $\left(\Delta C_p\right)_m^1$ are taken from tabulated values [10] and finally C_{pg_m} at high pressure is evaluated.

3. Thermal conductivity Calculations

For gas phase, at low to moderate pressure gas mixtures, thermal conductivity is calculated using Wassiljewa equation [11]:

$$\lambda_m = \sum_{i=1}^{n} \frac{y_i \lambda_i}{\sum_{j=1}^{n} y_i A_{ij}} \quad \text{....(10)}$$

where

$$A_{ij} = \frac{\left[1 + \left(\eta_i/\eta_j\right)^{1/2} \left(M_j/M_i\right)^{1/4}\right]^2}{\left[8\left(1 + M_i/M_j\right)\right]^{1/2}} \quad \text{....(11)}$$

and

$$\lambda_m = \sum_{i=1}^{n} \frac{y_i \lambda_i}{\sum_{j=1}^{n} y_i A_{ij}} \quad \text{....(12)}$$

where

$$A_{ji} = (\eta_i / \eta_j)(M_i / M_j) A_{ij} \quad \text{....(13)}$$

η_i and η_j are the pure component gas viscosities, M_i and M_j are molecular weights. For pure, low pressure non-polar gases, Steil and Thodos[20] suggested :

$$\lambda = \left[1.15 + \frac{2.03}{(C_v / R)}\right] \frac{\eta C_v}{M} \quad \text{....(14)}$$

Where C_v is in $kJ/kmol - K$, η is in Ns/m^2, M is in kg/mol.

$$C_v = C_p - R_{sp} \quad \text{....(15)}$$

$$R_{sp} = R / M \quad \text{....(16)}$$

4. Results and Discussion

PR EOS equation of state has been solved using the computer programme in FORTRAN. The results obtained are compared with the experimental values, and it has been found that results obtained are in good agreement with experimental values.

Specific Heat of gas mixture

At any particular composition, the specific heat of gas mixture is calculated using equation (1). In addition, the specific heat for the mixture composition at VLE conditions is also plotted (Fig 1) in temperature range of 300K to 492 K at 13.7 bar. It has been observed that specific heat of the gas mixture increases with increase in temperature. The model used in this work is validated using the data provided by National Institute of Standards and Technology, USA (NIST) [12]. The results in this work are closely matching with the NIST as shown in Fig 2 for pure nitrogen thereby validating the calculation procedure.

Thermal Conductivity of gas mixture

Thermal conductivity of the gas mixture is calculated using Wassiljewa Equation (10) and it has been observed that with increase in temperature thermal conductivity increases for a given composition. The result is plotted in Fig 3 . In addition, the specific heat for the mixture composition at VLE conditions is also plotted in temperature range of 300K to 492 K at 13.7 bar. The model used in this work is validated using the data provided by National Institute of Standards and Technology, USA (NIST). The results in this work are closely matching with the NIST as shown in Fig 4 for pure nitrogen thereby validating the calculation procedure.

5. Conclusion

The phase equilibrium between fuel and gas phase govern the combustion characteristics of the fuel. The PR EOS is used for VLE of n-heptane and nitrogen mixture and the results obtained by the computational techniques are matching the experimental results. The VLE data thus obtained is used to calculate the specific heat and thermal conductivity of the mixture. Specific heat of the gas mixture as well as thermal conductivity at a particular composition increases with increase in temperature.

Nomenclature

C_p	Specific Heat at Constant Pressure
C_v	Specific Heat at Constant Volume
C_{pg}^o	Ideal gas specific heat at constant pressure
f	Fugacity
h, H	Enthalpy
k_{ij}	Binary Interaction Parameter
g	Gram
mol	Mole
M	Molecular weight of pure species
M'	Molecular weight of mixture
N,n	Mole Number
P	Pressure
P_c	Critical Pressure
P_r	Reduced Pressure
P^s	Saturation Pressure
R	Universal Gas Constant
T	Temperature
T_c	Critical Temperature
T_r	Reduced Temperature
V,v	Volume
W	Molecular Weight (g / mol)
x	Mole fraction of species in liquid phase
y	Mass fraction of species in gas phase
Z	Compressibility Factor

Greek Letters

ω	Acentric Factor

Subscripts and superscripts

g	gas
l	Liquid
i, j	Particular species

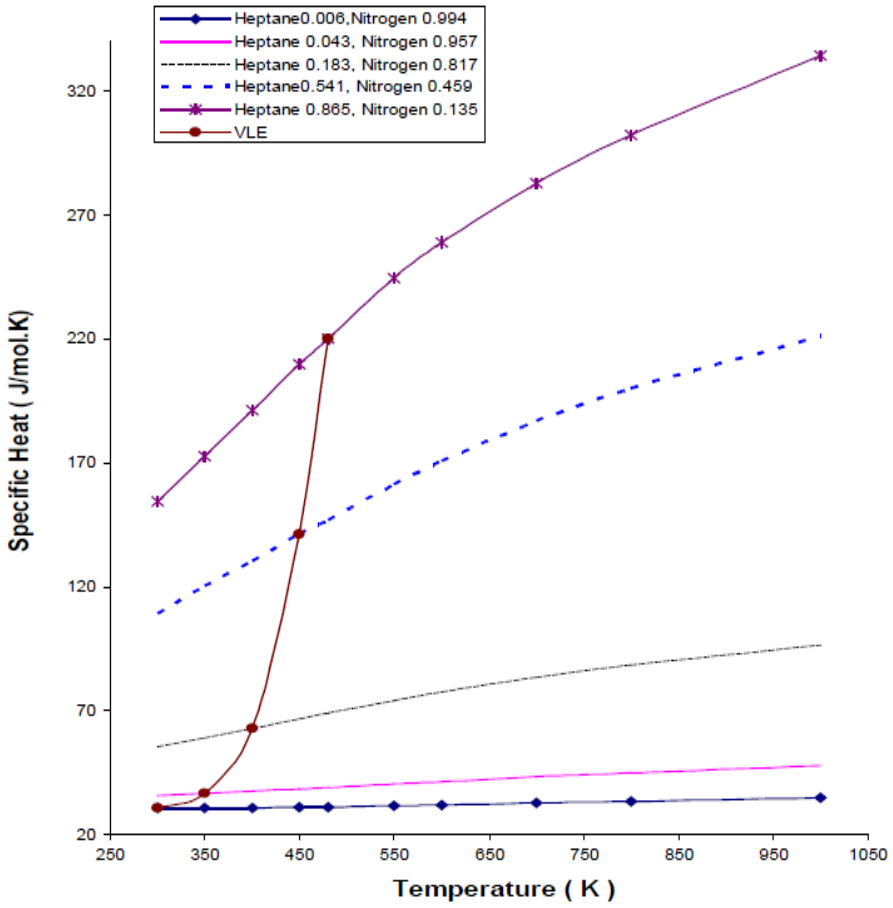

Fig 1: Specific heat of n-heptane and nitrogen gas mixture at 13.7 bar

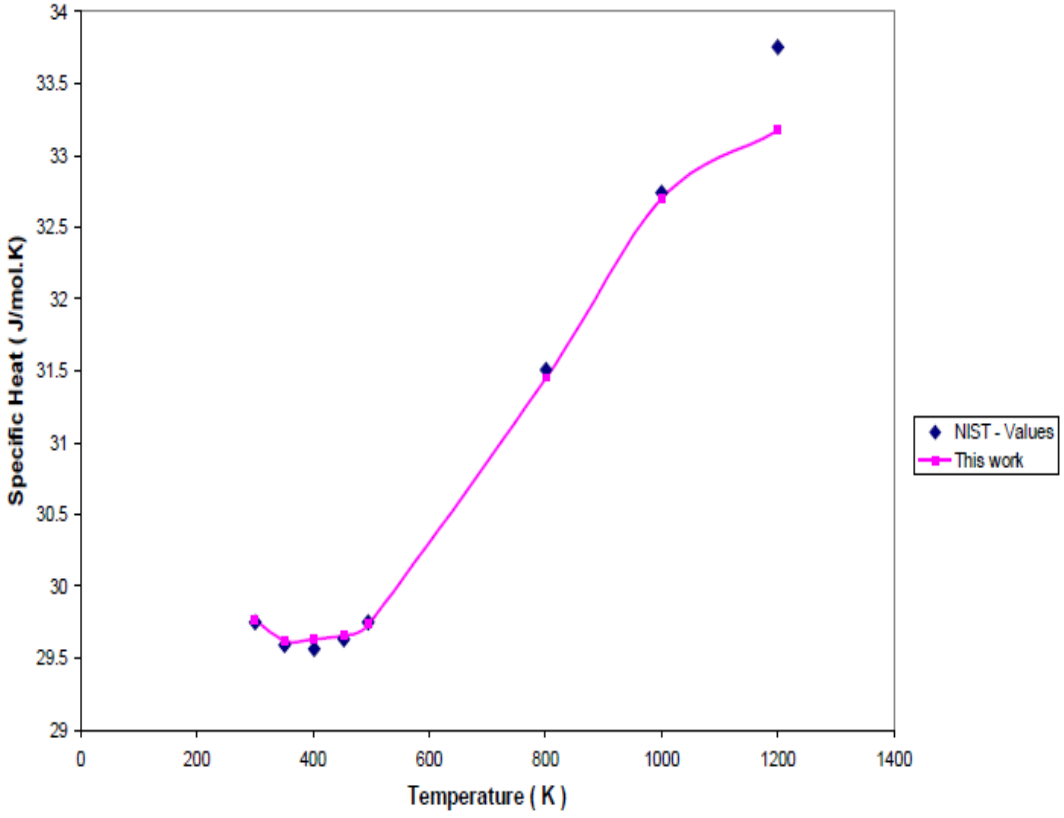

Fig 2: Specific heat of pure nitrogen gas mixture at 13.7 bar

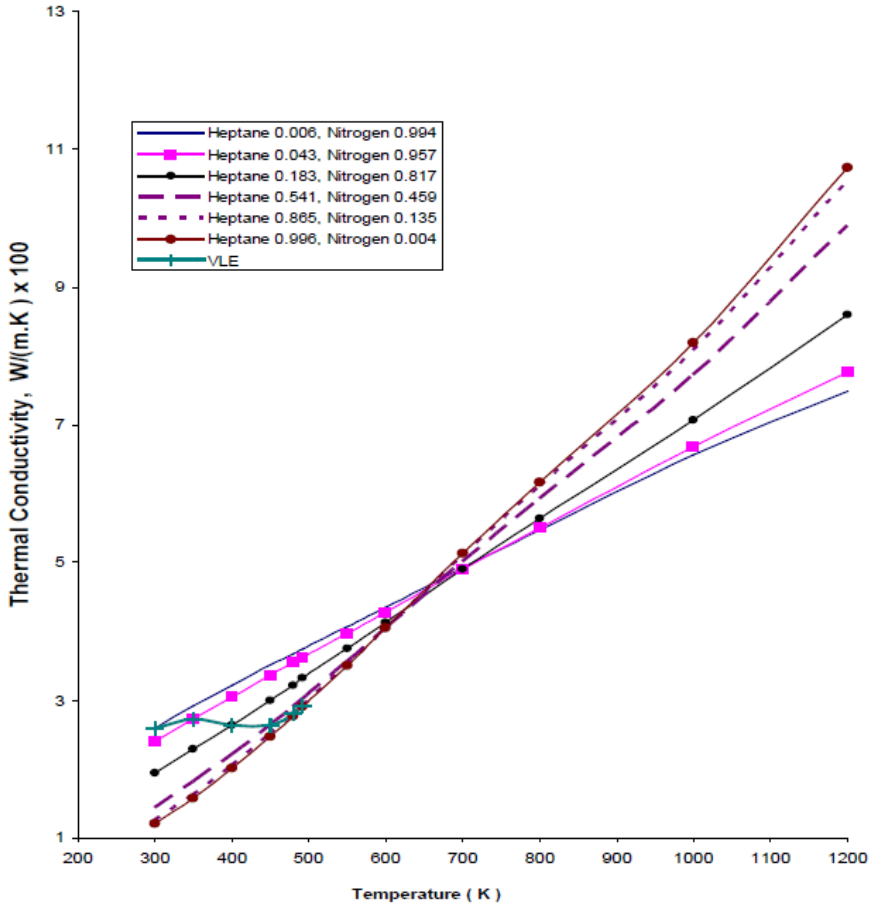

Fig 3: Variation of thermal conductivity of n-heptane and nitrogen mixture at 13.7 bar

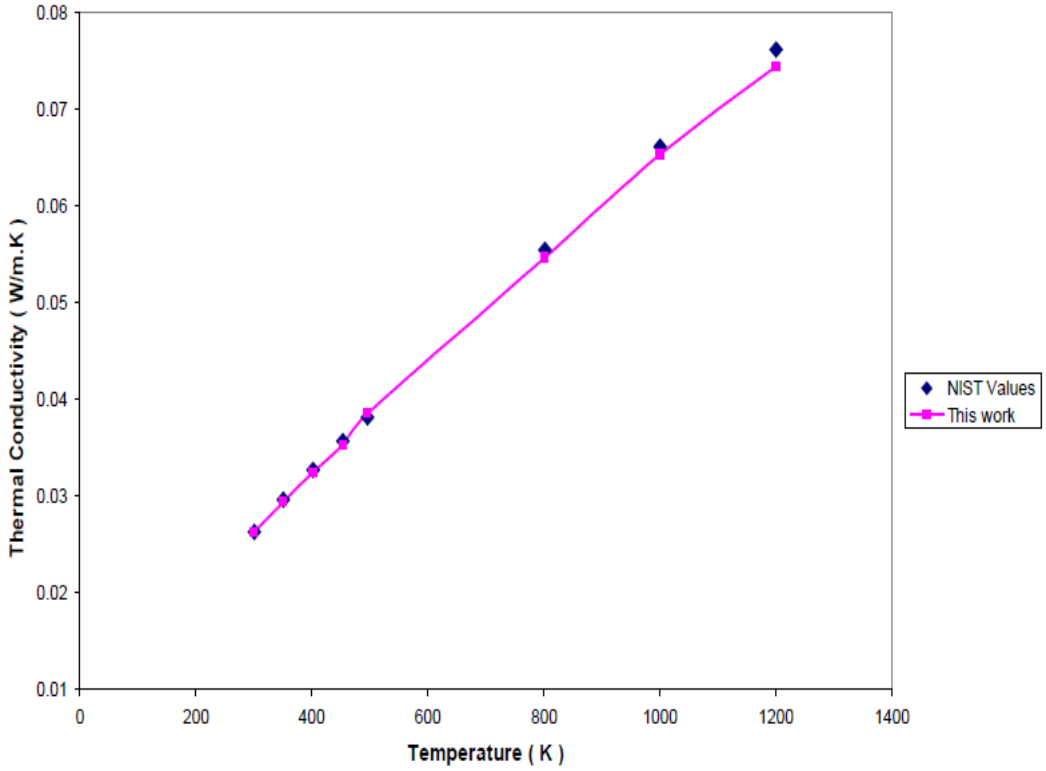

Fig 4: Variation of thermal conductivity of pure nitrogen mixture at 13.7 bar

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