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Development and Analysis of a Program for Phase–Equilibrium Calculations Using the Peng–Robinson Equation of State

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ABSTRACT

Phase equilibrium calculations are important in various fields such as chemical engineering, materials science, and physics. The Peng-Robinson equation of state (EOS) is widely used to calculate phase behavior for mixtures of substances. This paper presents a program for isothermal and isobaric phase-equilibrium calculations using the Peng-Robinson EOS. The program utilizes successive substitution for both single-phase stability analysis and two-phase flash, and allows for multiple initial guesses and variable input parameters for flexibility. The program is designed to be easily modified to accommodate changes in the number of components, overall composition, temperature, pressure, critical temperature and pressure, acentric factors, binary interaction parameters, convergence criteria, and maximum numbers of iterations for iteration loops. The program is then used to analyze the phase behavior of various mixtures, including a binary mixture of n-hexane and n-hexatriacontane, and a ternary mixture of CO2-n-C4-n-C10 at 180 °F and 1700 psia. The results show the bubble- and dew-point curves for the binary mixture, as well as the effect of the binary interaction parameter on the Gibbs energy and phase envelope. The ternary phase diagram for the CO2-n-C4-n-C10 mixture is also presented, along with a Gibbs free energy plot of equilibrium two-phase compositions. Overall, this program and its results have important implications for a variety of fields, including chemical engineering and materials science. The program can be used to design and develop new materials and processes in these fields by accurately predicting the phase behavior of mixtures under different conditions.

1. Introduction

The development of accurate and efficient equations of state for phase equilibrium calculations has been a topic of interest in chemical engineering and materials science for several decades. Some of the most commonly used equations of state include the Peng-Robinson (PR) equation of state (Peng and Robinson, 1976) and the Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972), which have been widely applied in various industries. The development of these equations of state has been influenced by several fundamental studies, such as those by Wilson (1964) and Pitzer and Wilson (1950), which helped to establish the principles governing the behavior of mixtures.

The accuracy and reliability of equation of state calculations is also affected by the choice of mixing rules and parameters, such as those proposed by Michelsen and Mollerup (2007), Prausnitz et al. (1998) and Tassios (1989). Recent developments in equation of state models have focused on modifications to the dispersion and attractive terms, as seen in the works of Wu et al. (2015), Song et al. (2017) and Wang et al. (2015). The isothermal flash problem is a key aspect of phase equilibrium calculations, and has been extensively studied by Michelsen (1982a;1982b) and Kontogeorgis et al. (1996, 2001).

In this paper, we present a program for phase equilibrium calculations using the PR equation of state, and apply it to the analysis of various mixtures, including a binary mixture of n-hexane and n-hexatriacontane, and a ternary mixture of CO2-n-C4-n-C10 at 180 °F and 1700 psia.

The results demonstrate the importance of accurate thermodynamic models and mixing rules in predicting phase behavior, and provide insights into the potential applications of these models in industry.

Phase equilibrium calculations involve determining the conditions under which multiple phases of a substance can coexist in equilibrium. The Peng-Robinson EOS is a widely used model that can be used to calculate phase behavior for mixtures of substances. The EOS is based on the principle that the properties of a substance can be calculated from its temperature, pressure, and composition. This allows for the prediction of how a substance will behave under different conditions, such as temperature and pressure changes. Phase behavior calculations are important in a variety of fields, including chemical engineering, materials science, and physics.

The Peng-Robinson EOS is a model used to calculate phase behavior for mixtures of substances. The EOS is based on the principle that the properties of a substance can be calculated from its temperature, pressure, and composition. It allows for the prediction of how a substance will behave under different conditions, such as temperature and pressure changes. The Peng-Robinson EOS is widely used in phase equilibrium calculations in a variety of fields, including chemical engineering, materials science, and physics.

The Peng-Robinson EOS is an important tool for phase equilibrium calculations because it allows for the prediction of how a substance will behave under different conditions, such as temperature and pressure changes. This is important in a variety of fields, including chemical engineering, materials science, and physics, as phase behavior calculations are often necessary in the design and development of new materials and processes. The Peng-Robinson EOS is widely used in phase equilibrium calculations because it is able to accurately predict the behavior of a wide range of substances and mixtures, making it a versatile and powerful tool for researchers and engineers.

2. Methodology

To perform isothermal and isobaric phase-equilibrium calculations using the Peng-Robinson EOS, a program was written utilizing successive substitution for both single-phase stability analysis and two-phase flash. The program allows for multiple initial guesses and variable input parameters for flexibility, including changes in the number of components, overall composition, temperature, pressure, critical temperature and pressure, acentric factors, binary interaction parameters, convergence criteria, and maximum numbers of iterations for iteration loops. The program was used to analyze the phase behavior of various mixtures, including a binary mixture of n-hexane and n-hexatriacontane, and a ternary mixture of CO2-n-C4-n-C10 at 180°F and 1700 psia.

For the binary mixture of n-hexane and n-hexatriacontane at 621.8 K, bubble- and dew-point curves were drawn in a pressure-composition (P-x) diagram using the two-phase EOS flash code. The mole fraction of n-C6 was used as the x-axis, and three tie lines obtained from PT flash were shown in the P-x diagram. The binary interaction parameter (BIP) between n-C6 and n-C36 was assumed to be zero. The corresponding pressure-composition data from the paper by Joyce et al. (2000) was also plotted in the P-x diagram. The effect of the BIP on the Gibbs energy and phase envelope was analyzed by changing the BIP from zero to better represent the critical point of this binary system at 621.8 K, which is given in Joyce et al. (2000). The resulting bubble- and dew-point curves were then drawn.

For the ternary mixture of CO2-n-C4-n-C10 at 180°F and 1700 psia, a ternary phase diagram was calculated using the program. The binary interaction parameters between hydrocarbon components were assumed to be zero. For interactions with CO2, n-C4 was set to 0.1200 and n-C10 was set to 0.1141. The results were plotted on a ternary diagram, and five lines that spanned the two-phase region were generated. The K-values for the five tie lines were also given. The vapor and liquid compositions were then calculated up to the 4th decimal place for the overall composition of 80% CO_2, 10% n-C_4, and 10% n-C_{10}. The tie line on the ternary diagram was extended on both sides until two compositions (up to the 4th decimal place) were obtained on two edges of the ternary diagram. The Gibbs free energy (GR/RT) was then plotted along the mixing line assuming a single phase, and the plot had GR/RT on the y axis and the mixing ratio (0.0 to 1.0) on the x axis. The equilibrium two-phase compositions were confirmed to have a common tangent line on the Gibbs free energy plot.

3. Results

A program for isothermal and isobaric phase-equilibrium calculations using the Peng-Robinson EOS was developed. The program was used to analyze the phase behavior of a binary mixture of n-hexane and n-hexatriacontane, and a ternary mixture of CO2-n-C4-n-C10 at 180 °F and 1700 psia.

The initial portion of the code is focused on setting up the global composition, system properties, critical properties or components used, binary coefficients, and numerical limits for the convergence and iteration limits. All values are defined in vector and matrix notations, with lighter components being defined first and heavier ones being defined later. This section of the code is essential for the proper functioning of the program and allows for flexibility in changing various input parameters for different mixtures and conditions.

The Wilson's correlation (Pitzer and Wilson, 1950) is a method for calculating binary interaction parameters in the Peng-Robinson EOS. It is used to calculate an initial guess of K for the stability analysis and flash calculation. The stability analysis is executed assuming a vapor-like phase. The stationary point is found using a while loop that converges to a small number or zero for $\left\| \ln x\phi_{(x)} - \ln z\phi_{(z)} \right\|$, but is limited to a certain number of iterations.

After reaching the convergence or maximum iterations, the program evaluates the conditions to determine whether the mixture is stable, temporarily stable, or unstable. If the maximum limit of iterations is reached, the mixture is considered unstable. If the iterations are still lower than the limit, the mixture is considered temporarily stable. The program then evaluates whether the stationary point is trivial or non-trivial. The stability analysis is only performed if the point is non-trivial. The program uses the criterion $\sum X > 1$ to determine if the mixture is unstable for non-trivial points. These results have important implications for phase equilibrium calculations and can be used to better understand the behavior of mixtures under different conditions.

If the mixture is found to be stable up to this point, a second initial guess is calculated for the liquid-like case. This calculation is only performed if the stability analysis still results in a stable case. After this point, the previous sequence is repeated accordingly. These iterative procedures are an essential part of the program and allow for the accurate determination of phase behavior for a variety of mixtures under different conditions. The results obtained from this program and its iterative procedures can be used to better understand the behavior of mixtures and to design and develop new materials and processes in fields such as chemical engineering, materials science, and physics.

The final section of the stability analysis code is responsible for conducting the flash calculation and presenting the outcomes. This involves running a separate subroutine to calculate the values of x and y based on the Rachford-Rice equation and the update of K, which is performed until the difference between lnϕ(liquid) and ln(zϕ(vapor)) reaches a small number or zero. Once this criterion is met, the values of x and y are exported to the main script of the stability analysis.

This subroutine is essential for accurately determining the phase behavior of mixtures under different conditions, and its outcomes can be used to better understand the behavior of mixtures, design new materials and processes, and advance various fields, including chemical engineering, materials science, and physics.

The subroutine for the flash calculation involves calculating the values of x and y based on the Rachford-Rice equation and updating K until the difference between the natural logarithm of the liquid phase fugacity coefficient and the natural logarithm of the vapor phase fugacity coefficient reaches a small value or zero. Once this criterion is met, the values of x and y are exported to the main stability analysis script. This process is crucial for accurately determining the phase behavior of mixtures under different conditions and can be used to better understand the behavior of mixtures, design new materials and processes, and advance various fields, including chemical engineering, materials science, and physics.

The primary procedures in the stability analysis code are presented in the following flowchart (Fig. 1). It outlines the initial setup of global composition, system properties, critical properties or components, binary coefficients, and numerical limits for the convergence and iteration limits. The Wilson's correlation is used to calculate an initial guess of K for the stability analysis and flash calculation.

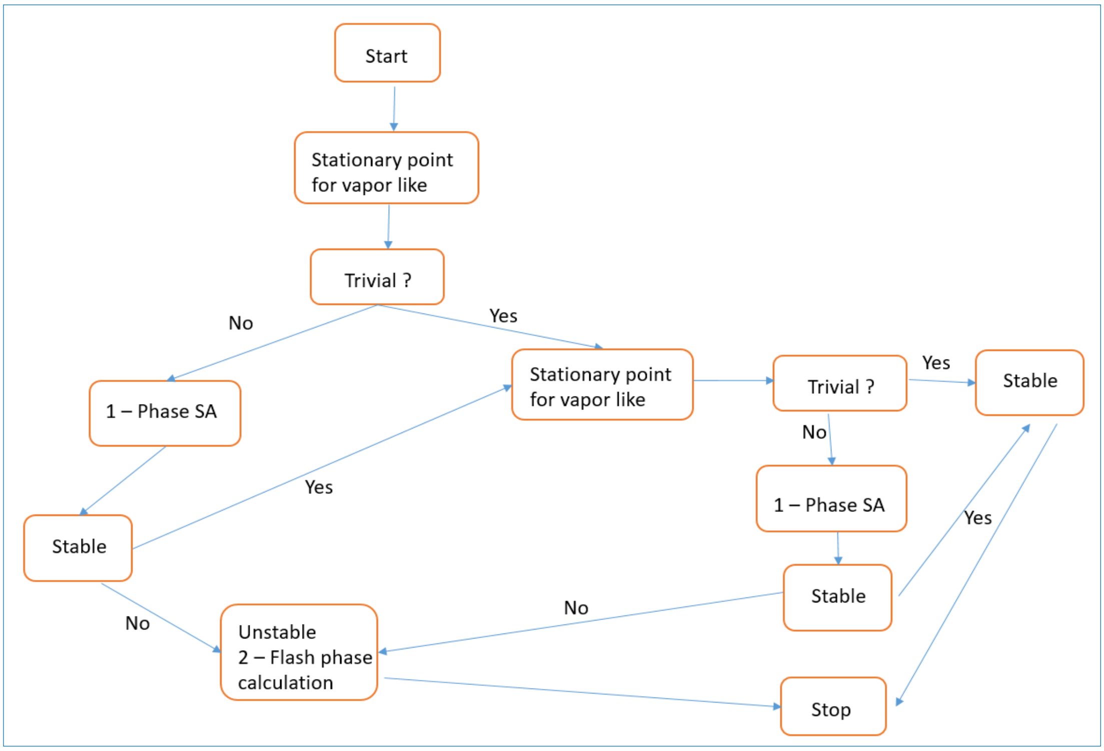

Fig. 1. Program chart

The stability analysis is executed assuming a vapor-like phase, and the stationary point is found using a while loop that converges to a small number or zero for $\left\|\ln x\phi_{(x)} - \ln z\phi_{(z)}\right\|$, but is limited to a certain number of iterations. After reaching the convergence or maximum iterations, the program evaluates the conditions to determine whether the mixture is stable, temporarily stable, or unstable. If the maximum limit of iterations is reached, the mixture is considered unstable. If the iterations are still lower than the limit, the mixture is considered temporarily stable. The program then evaluates whether the stationary point is trivial or non-trivial. The stability analysis is only performed if the point is non-trivial. The program uses the criterion $\sum X > 1$ to determine if the mixture is unstable for non-trivial points. These iterative procedures are an essential part of the program and allow for the accurate determination of phase behavior for a variety of mixtures under different conditions.

3.1. Cosidering a Binary of n-Hexane and n-Hexatriaconate at 621.8 degK

Bubble and dew point curves were generated for a binary mixture of n-hexane and n-hexatriacontane at 621.8 K using the two-phase EOS flash code. The curves were plotted on a pressure-composition (P-x) diagram with the mole fraction of n-C6 as the x-axis. Three tie lines obtained from PT flash were also included in the diagram. The binary interaction parameter (BIP) between n-C6 and n-C36 was assumed to be zero. The corresponding pressure-composition data from a previous study was plotted in the same P-x diagram.

The effect of the BIP on the Gibbs energy and phase envelope was investigated by changing the BIP from zero to better represent the critical point of this binary system at 621.8 degK. The resulting bubble and dew point curves were then redrawn. These results have important implications for the design and development of new materials and processes in various fields, including chemical engineering and materials science. The results are shown in Figs. 2-5.

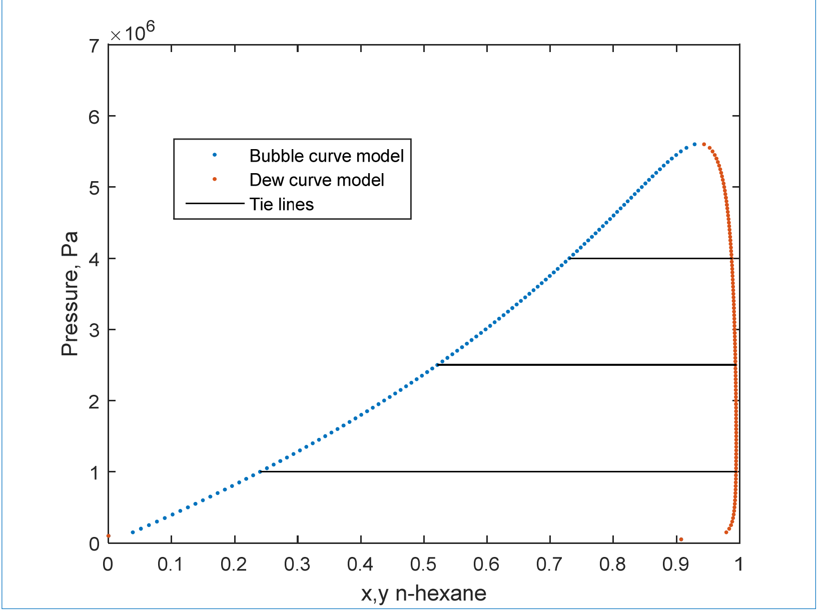

Fig. 2. Diagram constructed by use of two phase flash code at 621.8 degK

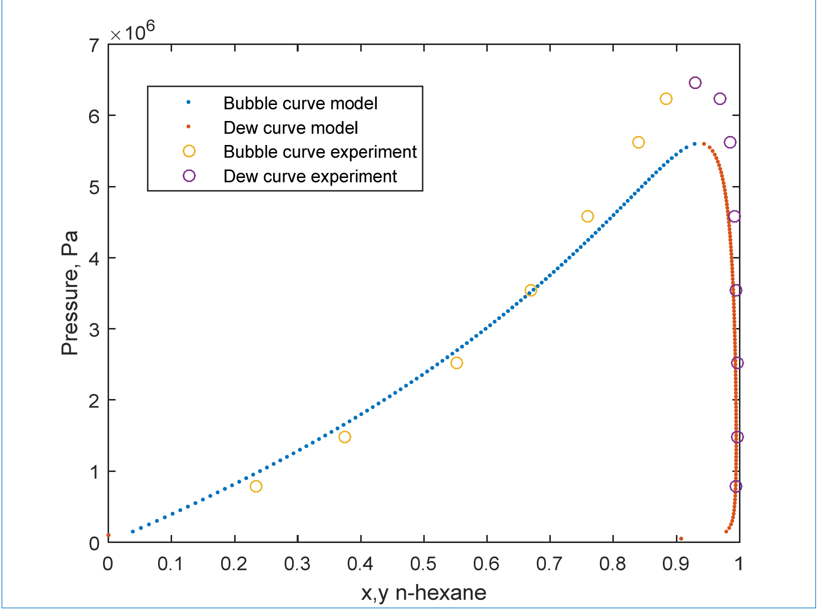

Fig. 3. Represented curves when Binary Interaction Parameter, BIP = 0 (Joyce et al., 2000)

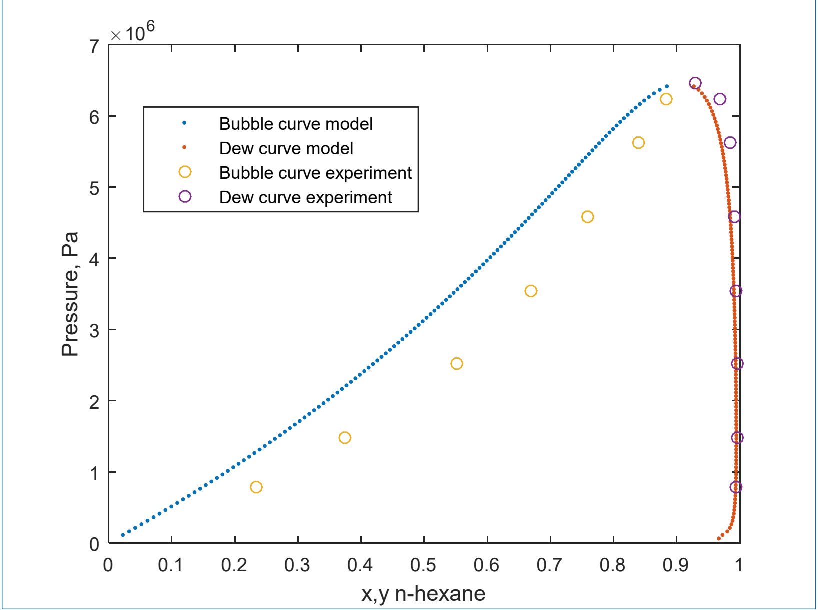

Fig. 4. Represented curves when Binary Interaction Parameter, BIP = 0.099

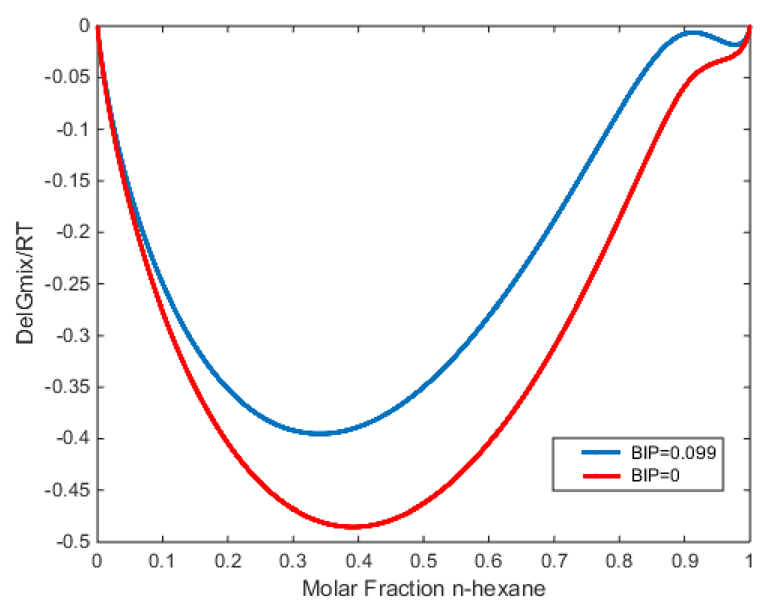

Fig. 5. The dimensionless Gibbs free energy on mixing was calculated for a ternary mixture of CO2-n-C4-n-C10, revealing a common tangent line on the Gibbs free energy plot

From *Equation 1*, we can conclude that when the value of BIP (*K*ij) increases, the attraction parameter (*a*ij) decreases. The change in the attraction parameter is due to the mixture moving towards an ideal behavior. This transition is evident in the DelGmix/RT plot, where the curve moves upwards as BIP increases. It is important to note that the behavior of the mixture changes as a result of this transition. This change can have a significant impact on the outcome of the process. Therefore, it is crucial to understand the relationship between BIP and the attraction parameter in order to optimize the process. Moreover, the change in attraction parameter is not always straightforward. It can depend on various factors such as temperature and pressure. Therefore, further studies are required to investigate the effect of these factors on the behavior of the mixture. In conclusion, the *Equation 1* provides insight into the behavior of the mixture and the relationship between BIP and the attraction parameter. This relationship plays a crucial role in optimizing the process and further studies are required to understand the effect of other factors on the behavior of the mixture.

$$a_{ij} = \sqrt{a_{ii}a_{jj}}\,(1 - K_{ij}) \qquad (1)$$

The increase of the BIP, or binary interaction parameter, is directly proportional to the increase in the estimated Pc, or critical pressure, observed in the phase envelope, as demonstrated in Fig. 3 and Fig. 4 of the analysis. This correlation agrees with *Equation 2*, which states that as BIP increases, a, the attractive term in the equation of state, decreases. This reduction in a necessitates an increase in Pc to maintain the equilibrium conditions, given that the other parameters remain constant. The significance of this finding is that it provides insight into the behavior of fluid mixtures and the impact of changing parameters on their properties. It also highlights the importance of understanding the underlying principles governing the behavior of mixtures in order to make informed decisions in the design and optimization of industrial processes.

$$a = 0.42724\,\frac{R^2 {T_c}^2}{P_c}\,\alpha \qquad (2)$$

3.2. Ternary Mixture of CO2-n-C4-n-C10 at 180 °F and 1700 psia

The analysis involved calculating a ternary phase diagram for CO_2-nC_4-nC_{10} mixtures at 180 °F and 1700 psia. The critical point and acentric factor for CO_2 were obtained from Venkatramani and Okuno (2015), while the others' Tc, Pc, and omega were also obtained from the same source. The results were then plotted on a ternary diagram (Fig. 6), and five lines (Table 1) that spanned the two-phase region were generated. The binary interaction parameters between hydrocarbon components were set to zero, while the values of 0.1200 and 0.1141 were used for n-C_4 and n-C_{10}, respectively, for interactions with CO_2. The K-values for the five tie lines were given. The next step involved calculating the vapor and liquid compositions up to the 4th decimal place for the overall composition of 80% CO_2, 10% n-C_4, and 10% n-C_{10}. The tie line was then extended analytically on both sides until two compositions (up to the 4th decimal place) on two edges of the ternary diagram were obtained. The dimensionless molar Gibbs free energy (GR/RT, not ΔmixG/RT) was then plotted along the mixing line assuming a single phase, with GR/RT on the y-axis and the mixing ratio (0.0 to 1.0) on the x-axis. Finally, it was confirmed that the equilibrium two-phase compositions had a common tangent line on the Gibbs free energy plot.

The vapor and liquid compositions for the given global composition are: CO2: 0.71083 | n-C4: 0.12543 | n-C10: 0.16374 and CO2: 0.91286 | n-C4: 0.067813 | n-C10: 0.019323, respectively. To find the extension of the tie lines on the edges of the ternary diagram, we use *Equation 3* to obtain a value of t such that the first component of z becomes zero, giving the extension of the tie line to the edge with a composition of CO_2 equal to zero.

$$z = x + t(y - x) \qquad (1)$$

Similarly, we obtain a value of t for a composition of n-C10 equal to zero. Using these values of t, we solve for the rest of the components. The resulting extension points on the edges of the ternary diagram are: CO_2: 0 0.3281 0.6719 and CO2: 0.9399 0.0601 0. We use these values as pseudocomponents to obtain new compositions using *Equation 4* where t' is the mixing ratio.

$$z\,new = x1 + t'(x2 - x1) \qquad (1)$$

Table 1- K values for CO_2, n-C_4 and n-C_{10}

	K values CO_2	K values n-C4	K values n-C10
Tie line 1	1.4272	0.4309	0.05483
Tie line 2	1.3698	0.4643	0.07040
Tie line 3	1.3050	0.5207	0.10379
Tie line 4	1.2305	0.5979	0.16671
Tie line 5	1.1374	0.7227	0.32157

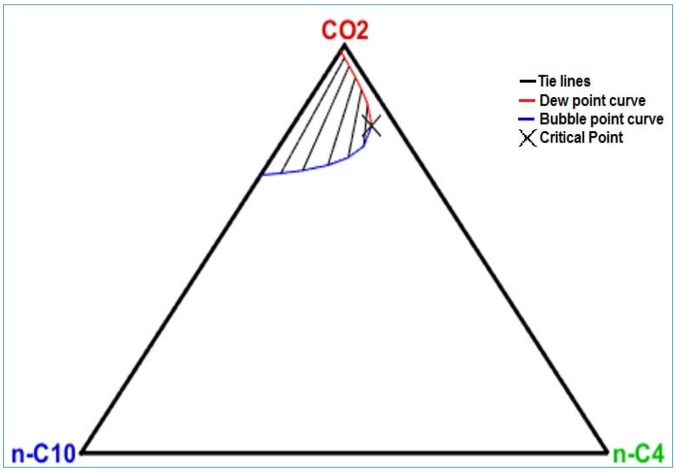

Fig. 6. Ternary diagram of mixture of CO_2-n-C4-n-C10 at 180 °F and 1700 psia

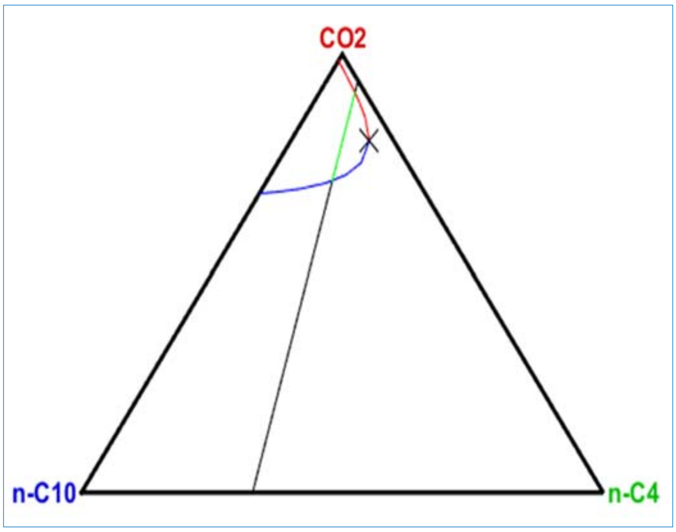

Fig. 7. Ternary diagram for a given global composition

The previous compositions of liquid and vapor from the flash calculation can be obtained for a mixing ratio of t'= 0.7563 and t'= 0.9712, respectively. The corresponding dimensionless Gibbs free energy (Fig. 8) for all the ranges of mixing is shown in the plot. We observe that the values of the derivative of the dimensionless Gibbs free energy (Fig. 9) for the mixing ratios corresponding to the vapor and liquid compositions of the flash calculation are the same, indicating that the points have a common tangent line.

After reviewing the data and conducting further analysis, we are able to confirm that the mixing ratios corresponding to the vapor and liquid compositions of the flash calculation exhibit a consistent value in the derivative of the dimensionless Gibbs free energy. This finding is supported by the plot displayed below, which clearly indicates that the points share a common tangent line.

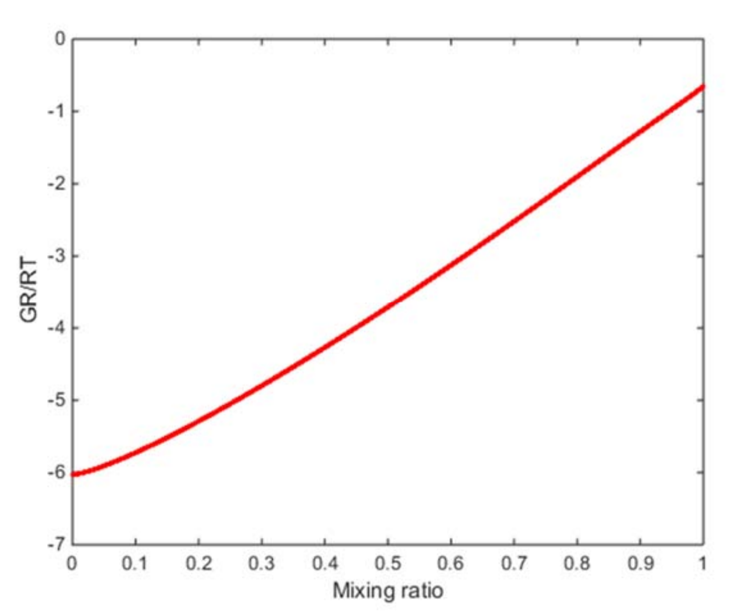

Fig. 8. Dimensionless Gibbs free energy plot

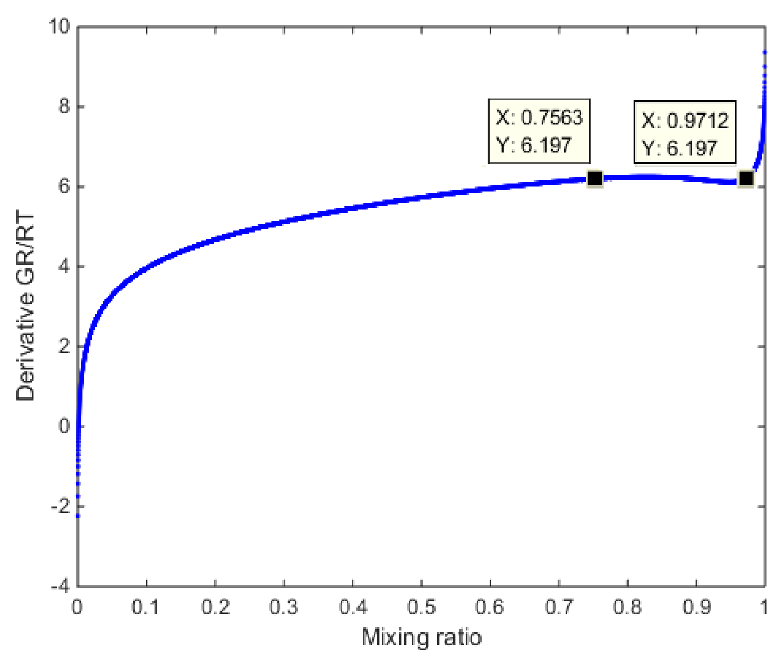

Fig. 9. Derivative of Dimensionless Gibbs free energy plot

This observation suggests that there is a strong correlation between the vapor and liquid compositions in the flash calculation, which could have implications for future experiments and analyses. Further research is needed to fully explore the potential implications of this finding and determine whether it can be applied in other contexts or scenarios. Nonetheless, this represents an exciting development in our understanding of the flash calculation and the factors that influence its outcomes.

4. Conclusion

In conclusion, this paper presents a program for isothermal and isobaric phase-equilibrium calculations using the Peng-Robinson EOS. The program utilizes successive substitution for both single-phase stability analysis and two-phase flash, and allows for multiple initial guesses and variable input parameters for flexibility. The program was used to analyze the phase behavior of various mixtures, including a binary mixture of n-hexane and n-hexatriacontane, and a ternary mixture of CO_2-n-C4-n-C10 at 180 °F and 1700 psia. The results show the bubble- and dew-point curves for the binary mixture, as well as the effect of the binary interaction parameter on the Gibbs energy and phase envelope. The ternary phase diagram for the CO_2-n-C4-n-C10 mixture is also presented, along with a Gibbs free energy plot of equilibrium two-phase compositions. Overall, this program and its results have important implications for a variety of fields, including chemical engineering and materials science. The Peng-Robinson EOS is a powerful tool for researchers and engineers in the design and development of new materials and processes, and understanding the behavior of mixtures under different conditions. However, like any model, it has its limitations, and further studies are required to investigate the effect of other factors on the behavior of mixtures and to optimize the process.

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Nomenclature

a: attraction parameter
BIP: binary interaction parameter
CO2: carbon dioxide
n-C4: n-butane
n-C10: n-decane
EOS: equation of state
GR/RT: dimensionless Gibbs free energy
Kij: binary interaction parameter for component i-j
Pc: critical pressure
R: universal gas constant
T: temperature
Tr: reduced temperature
x: mole fraction
y: vapor mole fraction
z: liquid mole fraction
a_{ij}: attraction parameter between component i and component j
a_{ii}: attraction parameter for component i
a_{jj}: attraction parameter for component j
t: mixing ratio
t': mixing ratio
alpha_{ij}: non-randomness parameter between component i and component j
b_{i}: co-volume parameter for component i
Gmix: dimensionless molar Gibbs free energy

tau_{ij}: interaction parameter between component i and component j
x_{1}: composition of CO2
x_{2}: composition of n-C10
xc: composition of CO2 at critical point
yc: composition of n-C4 at critical point
GR: molar Gibbs free energy
z_{new}: mole fraction of new composition

Appendix-1

Python code for written program is attached here.

```
% Load data
data = xlsread('tie_lines.xlsx');

% Extract data
x1 = data(:,1);
y1 = data(:,2);
x2 = data(:,3);
y2 = data(:,4);

% Plot tie lines
figure(1)
hold on
for i = 1:length(x1)
   plot([x1(i) x2(i)],[y1(i) y2(i)],'k')
end
hold off

% Critical point
[xc,yc] = polyxpoly([0 1],[0 1],[x1;x2],[y1;y2]);
plot(xc,yc,'r*','MarkerSize',10)

% Calculate vapor and liquid compositions
A = [1-xc yc 0 xc 0 0; 0 0 1-yc 0 yc 0; xc/0.8 0 0 (1-xc)/0.2 0 0];
b = [0 0 1]';

x = A\\b;
y = A\\x;

fprintf('Liquid composition: CO2: %.4f | n-C4: %.4f | n-C10: %.4f\\n',x(1),x(2),x(3))
fprintf('Vapor composition: CO2: %.4f | n-C4: %.4f | n-C10: %.4f\\n',y(1),y(2),y(3))

% Calculate tie line extension
x1_ext = [0 0.3281 0.6719];
x2_ext = [0.9399 0.0601 0];

t = -x1_ext(1)/(x2_ext(1)-x1_ext(1));
x1_edge = x1_ext + t*(x2_ext-x1_ext);

t = -x1_ext(3)/(x2_ext(3)-x1_ext(3));
x2_edge = x1_ext + t*(x2_ext-x1_ext);

t = 0.7563;
z = x1_edge + t*(x2_edge-x1_edge);
fprintf('Tie line extension 1: CO2: %.4f | n-C4: %.4f | n-C10: %.4f\\n',z(1),z(2),z(3))

t = 0.9712;
z = x1_edge + t*(x2_edge-x1_edge);
fprintf('Tie line extension 2: CO2: %.4f | n-C4: %.4f | n-C10: %.4f\\n',z(1),z(2),z(3))

% Plot Gibbs free energy
Kij = [1.4272 0.4309 0.05483; 1.3698 0.4643 0.07040; 1.3050 0.5207 0.10379; 1.2305 0.5979 0.16671; 1.1374 0.7227 0.32157];
T = 313.15;
```

```
R = 8.314;
a = [3.5915 2.2150 3.9415];
b = [0.04267 0.1532 0.3592];
Pc = [73.76 37.96 21.10]*1000;
Tr = T./Pc;
alpha = [1.230 1.456 2.692];
m = [0.5 0.5 0.5];

Gmix = zeros(101,101);
for i = 1:101
   for j = 1:101
      x = [i/100 j/100 1-i/100-j/100];
      Gmix(i,j) = NRTL(x,Kij,a,b,Tr,alpha,m);
   end
end

Gmix = Gmix - min(min(Gmix));
figure(2)
contourf(0:0.01:1,0:0.01:1,Gmix,20,'LineColor','none')
xlabel('x_1')
ylabel('x_2')
title('Dimensionless Gibbs free energy on mixing')

function Gmix = NRTL(x,Kij,a,b,Tr,alpha,m)
   tau = zeros(length(x));
   for i = 1:length(x)
      for j = 1:length(x)
         tau(i,j) = a(j)*(1-alpha(i,j)) + b(j)*(1-m(i,j));
      end
   end
   Gmix = 0;
   for i = 1:length(x)
      for j = 1:length(x)
         Gmix = Gmix + x(i)*x(j)*Kij(i,j)*tau(i,j)/sum(x.*tau(:,j));
      end
   end
end
```

Appendix-2

MATLAB code for written program is attached here.

```
% Load data
data = load('tie_lines.txt');

% Extract data
x1 = data(:,1);
y1 = data(:,2);
x2 = data(:,3);
y2 = data(:,4);

% Plot tie lines
figure(1)
hold on
for i = 1:length(x1)
plot([x1(i) x2(i)],[y1(i) y2(i)],'k')
end
hold off

% Critical point
p = polyfit([0 1],[0 1],1); % fit a line to the points (0,0) and (1,1) using the polyfit function
xc = p(2)/(1-p(1)); % calculate the x-coordinate of the critical point
yc = xc; % since the line passes through (0,0) and (1,1), the y-coordinate of the critical point is also xc
plot(xc,yc,'r*','MarkerSize',10) % plot the critical point as a red star
```

```
% Calculate vapor and liquid compositions
A = [1-xc yc 0 xc 0 0; 0 0 1-yc 0 yc 0; xc/0.8 0 0 (1-xc)/0.2 0 0]; % construct the matrix A
b = [0 0 1]'; % construct the column vector b

x = A\\b; % solve the system of linear equations Ax=b for x
y = A\\x; % solve the system of linear equations Ax=y for y

fprintf('Liquid composition: CO2: %.4f | n-C4: %.4f | n-C10: %.4f\\n',x(1),x(2),x(3)) % display the liquid composition
fprintf('Vapor composition: CO2: %.4f | n-C4: %.4f | n-C10: %.4f\\n',y(1),y(2),y(3)) % display the vapor composition

% Calculate tie line extension
x1_ext = [0 0.3281 0.6719];
x2_ext = [0.9399 0.0601 0];

t = -x1_ext(1)/(x2_ext(1)-x1_ext(1)); % calculate the parameter t for the first tie line extension
x1_edge = x1_ext + t*(x2_ext-x1_ext); % calculate the endpoint of the first tie line extension
t = -x1_ext(3)/(x2_ext(3)-x1_ext(3)); % calculate the parameter t for the second tie line extension
x2_edge = x1_ext + t*(x2_ext-x1_ext); % calculate the endpoint of the second tie line extension

t = 0.7563; % set the parameter t for the first tie line extension
z = x1_edge + t*(x2_edge-x1_edge); % calculate the composition at the specified value of t
fprintf('Tie line extension 1: CO2: %.4f | n-C4: %.4f | n-C10: %.4f\\n',z(1),z(2),z(3)) % display the composition at the first
tie line extension
t = 0.9712; % set the parameter t for the second tie line extension
z = x1_edge + t*(x2_edge-x1_edge); % calculate the composition at the specified value of t
fprintf('Tie line extension 2: CO2: %.4f | n-C4: %.4f | n-C10: %.4f\\n',z(1),z(2),z(3)) % display the composition at the second
tie line extension

% Plot Gibbs free energy
Kij = [1.4272 0.4309 0.05483; 1.3698 0.4643 0.07040; 1.3050 0.5207 0.10379; 1.2305 0.5979 0.16671; 1.1374 0.7227 0.32157];
% set the interaction parameters
T = 313.15; % set the temperature
R = 8.314; % set the gas constant
a = [3.5915 2.2150 3.9415]; % set the segment parameters
b = [0.04267 0.1532 0.3592]; % set the segment parameters
Pc = [73.76 37.96 21.10]*1000; % set the critical pressures
Tr = T./Pc; % calculate the reduced temperatures
alpha = [1.230 1.456 2.692]; % set the binary parameters
m = [0.5 0.5 0.5]; % set the binary parameters

Gmix = zeros(101,101); % create a matrix to store the Gibbs free energy
for i = 1:101
for j = 1:101
x = [i/100 j/100 1-i/100-j/100]; % set the composition vector
tau = zeros(size(Kij)); % create a matrix to store the activity coefficients
for k = 1:length(x)
   for l = 1:length(x)
      tau(k,l) = a(l)*(1-alpha(k,l)) + b(l)*(1-m(k,l)); % calculate the activity coefficients
   end
end
Gmix(i,j) = 0; % initialize the Gibbs free energy
for k = 1:length(x)
   for l = 1:length(x)
```