

NUMERICAL ASPECT OF EQUATION OF STATE IN FLASH CALCULATIONS

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Abstract

In the present work a formulation of equation of state (EoS) was used to evaluation the phase equilibrium ratios.

Two constant Equation of state, such as the Piench Ropenson, Soave modification of the Redlich Kwong equation can not be highly accurate in the whole range of temperature, pressure, and composition, but they have the advantage that they require relatively little computer time and Soave Redlich Kwong (SRK) equation seldom gives rise to large errors when its applied to mixtures of lower hydrocarbon, nitrogen, carbon monoxide, carbon dioxide, and hydrogen sulphide.

Vapor-liquid equilibrium calculations were run on PC using QuickBasic V4.5 language.

The Soav Redlich Kwong Equation is stated in a form particularly useful for computer applications of complex and undefined mixtures calculations, such as crude oil and petroleum fractions.

Introduction

vapor liquid equilibrium (vle) calculations represent an important field in chemical engineering simulation or design calculations. Distillation is probably the most important separation and purification process used in the chemical industry, and reliable vle data are required for estimating the munmer of theoretical stages required in distillation column design. The many articles published on this theme may be classified in two groups. The equation of state approaches tries to estimate equilibria at high pressure but for a limited amount of compounds, and the activity coefficient approach estimates equilibria for a wide spectrum of compounds at normal pressure levels. Most of the articles on the EoS method present modified and new equations. Edmister⁽¹⁰⁾ has presented an analytical solution for driving charts for compressibility factors and fugacity coefficient. He does not, however. Because the solution strategy is deferent depending upon discuss the problem when the actual phase (Vapor or liquid) and the fact that the maximum or minimum points instead of the actual roots are accepted in some cases, the numerical method has been chosen and its governed by parameter check.

Prasnitz and Chueh⁽¹¹⁾ have developed a procedure for high pressure systems employing a modified Redlich-Kwong equationfor the vapor phase and for liquid-phase compressibility together with a modified Wohl-equation model for liquid phase activity coefficients

design and operation of fluid phase processes dependent most fundamentally on knowledge of phase operation of phase equilibrium. That is at any given temperature and pressure we must be able to predetermine the compositions of equilibrium phases : liquid-vapor, liquid-liquid, or liquid-liquid-vapor equilibrium.

It is convenient to define an equilibrium ratio as the ratio of mole fractions of a species into two phases in equilibrium. For the vapor liquid case the constant is refer to the K-value or vapor liquid equilibrium ratio.

For isothermal flash calculations, Rashfords and Rice⁽⁹⁾ have suggested that the vapor to feed ratio $\zeta=V/F$, may be computed by iteration from the equation :

$$f(\zeta) = \sum_{i=1}^{N_C} \frac{z_i(K_i - 1)}{z_i K_i + 1 - \zeta}$$

The function has two implement advantages:

(i) $f(\zeta)$ is monotonically decreasing as ζ increase. (the first derivative w.r.t the vapor to feed ratio is always negative). There is, therefore just one solution possible in the region $0 \leq \zeta \leq 1$ and this makes the computational safe.

(ii) $f(\zeta)$ can be solved in (4)-(6) iteration by a second order Newton method:

$$\Delta\zeta = -f/f'$$

Or in (4)-(6) iteration by a third order method presented by Asbjornsen

$$\Delta\zeta = \frac{f}{f' \left(1 - \sqrt{1 - 2f'' \cdot f / (f')^2} \right)}$$

To an accuracy of 0.001 for a given set of z_i K_i ($i=1, N_C$). The number of iterations depends on the linearly of $f(\zeta)$. At conditions close to critical, may have such a shape that the limited numerical resolution of the computer prevents proper solution.

In these cases, $f(\zeta)$ is very close to zero in the main part of the region $0 \leq \zeta \leq 1$

The third order method was chosen and maximum (for most off critical conditions) of 4 iteration were satisfactory.

Mathematical formulation

The basic condition for thermodynamic equilibrium between two phases states that

$$f_i^L = f_i^V \quad (1)$$

Where f_i represent the fugacity of component i .

Rewrite eq.1 in term of fugacity coefficient as

$$\phi_i^L x_i P^L = \phi_i^V y_i P^V \quad (2)$$

At equilibrium $P^L = P^V$, so eq. 2 becomes

$$\frac{\phi_i^L}{\phi_i^V} = \frac{y_i}{x_i} = K_i \quad (3)$$

Eq.3 is well known vapor-liquid equilibrium ratio, K-value or distribution coefficient.

The equilibrium ratio (K_i) of a component i in a multi component mixture of liquid and vapor phases is defined as the ratio of the mole fraction of that component in the vapor phase to that in the liquid phase.

K-Value correlations

Numerous procedures have been devised to predict K-values. These include equations of state (EOS), combinations of equations of state with liquid theory or with tabular data, and corresponding states correlations. It does not purport to be all-inclusive or comparative. Equations of state have appeal for predicting thermodynamic properties because they provide internally consistent values for all properties in convenient analytical form. Two popular state equations for K-value predictions are the Benedict-Webb-Rubin (BWR) equation and the Redlich-Kwong equation. The original BWR equation uses eight parameters for each component in a mixture plus a tabular temperature dependence for one of the parameters to improve the fit of vapor-pressure data. This original equation is reasonably accurate for light paraffin mixtures at reduced temperatures of 0.6 and above 0.8. The equation has difficulty with low temperatures, non-hydrocarbons, non-paraffin, and heavy paraffin.

Equation of state(EoS)

The equation of state is the most common method to estimate the fugacities through two phases vapor and liquid, and finding the widest applications for multicomponent multistage separation process calculations. consist of the modified various of the benedict-Webb-Rubin⁽⁵⁾ EoS.

A method of prediction liquid vapor equilibria is to estimate the fugacities of the multicomponent in the both phases and compare them until their difference is smaller than prescribed value.

Soave Redlich Kwong (SRK) equation

The Soave Redlich-Kwong⁽¹⁾(SRK) is a modified version of the Redlich-Kwong equation. One of the parameters in the original Redlich-Kwong equation, a , is modified to a more temperature dependent term. It is expressed as a function of the acentric factor. The SRK correlation has improved accuracy in predicting the saturation conditions of both pure substances and mixtures. It can also predict phase behavior in the critical

region, although at times the calculations become unstable around the critical point. Less accuracy has been obtained when applying the correlation to hydrogen-containing mixtures. Peng and Robinson⁽²⁾ similarly developed a two-constant Redlich-Kwong equation of state in 1976. In this correlation, the attractive pressure term of the semi-empirical van der Waals equation has been modified. It accurately predicts the vapor pressures of pure substances and equilibrium ratios of mixtures. In addition to offering the same simplicity as the SRK equation, the Peng-Robinson equation is more accurate in predicting the liquid density. In applying any of the above correlations, the original critical/physical properties used in the derivation must be inserted into the appropriate equations. One may obtain slightly different solutions from different computer programs, even for the same correlation. This can be attributed to different iteration techniques, convergence criteria, initial estimation values, etc. Determination and selection of interaction parameters and selection of a particular equation of state must be done carefully, considering the system components, the operating conditions, etc.

The SRK EoS is recommended for computing the thermodynamic properties of both liquid and vapor phases for a certain pure components and mixtures, the SRK equation is the most popular method among chemical engineers for estimating K-value of hydrocarbon mixture at moderate and high pressures.

For a mixture the EoS is :

$$Z = \frac{PV}{RT} = \frac{V}{V-b} - \frac{(a\alpha)}{RT(V+b)} \quad (4)$$

Where

$$(a\alpha) = \sum_j \sum_k x_j x_k a_j a_k \alpha_j \alpha_k (1 - k_{kj}) \quad (5)$$

$$b = \sum_j x_j b_j \quad , \quad b_j = 0.08664RT_{cj} / P_{cj} \quad (6)$$

$$b_j = (0.4274R^2 T_{cj}^2 / P_{cj})^{0.5} \quad (7)$$

For non-polar compounds, the α_j is related to the acentric factor ω ⁽¹²⁾ :

$$\alpha_j = 1 + (0.48 + 1.574\omega_j - 0.176\omega_j^2)(1 - T_{rj}^{0.5}) \quad (8)$$

The acentric factor of hydrocarbons is evaluated using equation suggested by Grayson and Streed⁽⁴⁾

$$\omega_i = \frac{3}{7} \left(\frac{\log(p_{ci}/14.7)}{T_{ci}/T_{bi} - 1} \right) - 1 \quad (9)$$

The necessary critical constants and binary interaction parameters k_{ij} are given by Reid et al.⁽⁷⁾. For hydrocarbon- hydrocarbon interaction k_{ij} is zero.

The double sum appears in Eq.5 is time consuming to evaluate on the computer .It is reduced to a single sum as follows:

$$(a\alpha) = \sum_j x_j^* z_j^* \quad (10)$$

Where

$$x_j^* = x_j a_j \alpha_j \quad (11)$$

and

$$z_j^* = \sum_k x_k^* (1 - k_{jk}) \quad (12)$$

The SRK equation can be written in a third degree polynomial of compressibility factor terms as follow:

$$Z^3 - Z^2 + (A - B - B^2).Z - A.B = 0 \quad (13)$$

Noting that the definitions of Z, A, and B are

$$Z = \frac{PV}{RT}, \quad A = \frac{(a\alpha)P}{(RT)^2}, \quad B = \frac{bP}{RT}$$

The coefficient A and B are evaluated depending upon the actual phase either vapor or liquid.

Solution of cubic EoS

The usual cubic equations of state all be expressed in the same form

$$Z^3 - Z^2 + \beta Z + \gamma = 0 \quad (14)$$

For the SRK EoS the parameters are:

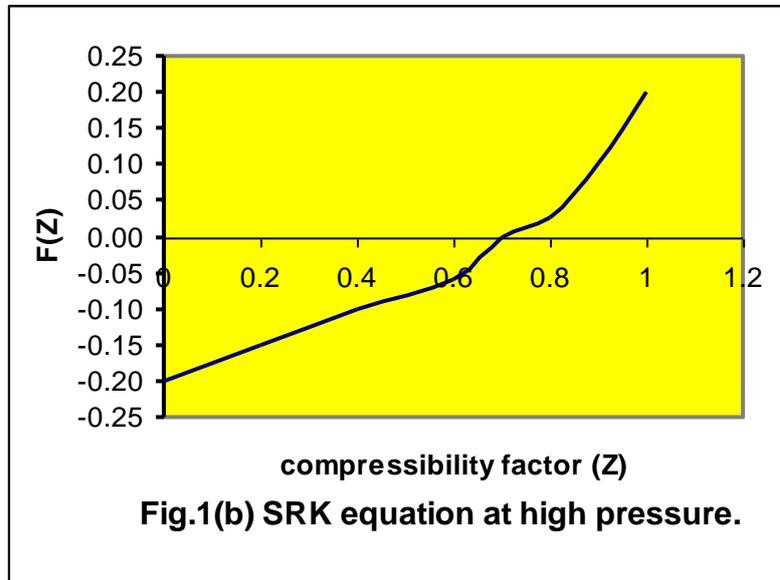
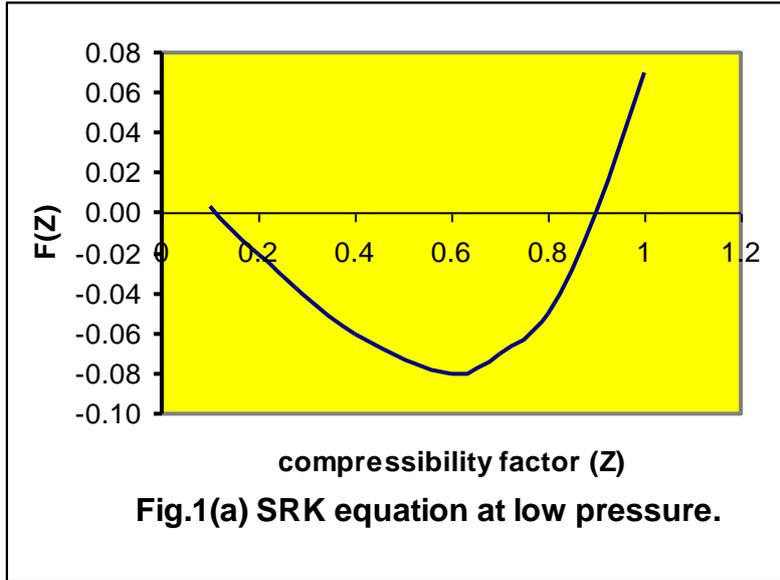
$$\beta = A - B - B^2, \quad \gamma = -A.B$$

Depending upon the coefficients β and γ the cubic equation has one or three real roots. Since it is the composition of one of the phases and not the total composition of the system that is used to determine the coefficients β and γ , the number of roots no relation to the number of phases in the system. The correct interpolation at the existence of three roots is that the actual composition can exist both as a vapor and as a liquid, but not necessarily in equilibrium. The strategy is therefore is to pick up the largest root when the cubic equation is solved for the vapor phase compressibility and the smallest root when the cubic equation is solved for the liquid phase compressibility.

Eq.14 can be solved analytically or by numerical iterative method.

Analytical solution

At low pressure $F(Z) = Z^3 - Z^2 + (A - B - B^2).Z - A.B$ (eq. 13) will make a form as given by Fig. 1(a)⁽¹³⁾, while increasing pressure will make the function monotonically increasing as shown in Fig. 1(b).



Three real roots are obtained, the largest value of Z corresponding to the vapor phase and the smallest value due to the liquid phase.

If we examine the following forms, It is roots can be obtained:

$$q = \frac{1}{3}\beta - \frac{1}{9}, \quad r = \frac{1}{6}(\beta - 3\gamma) - \frac{1}{27}$$

If $q^3 + r^2 > 0$ there will be one real root and a pair of complex conjugate roots.

If $q^3 + r^2 = 0$ all roots are real and at least two will be equal.

If $q^3 + r^2 < 0$ all roots are real and unequal (irreducible case i.e. no analytical solution)

Case (i) solution for $q^3 + r^2 \geq 0$

In this case the roots can be expressed using the following definitions:

$$s_1 = \left(r + 3\sqrt{q^3 + r^2} \right)^{1/3}, \quad s_2 = \left(r - 3\sqrt{q^3 + r^2} \right)^{1/3}$$

And the roots are:

$$Z_1 = s_1 + s_2 - \frac{1}{3} \quad (15)$$

$$Z_{2,3} = -s_3 \pm \frac{i\sqrt{3}}{2}(s_1 - s_2) \quad (16)$$

Where $s_3 = \frac{(s_1 + s_2)}{2} + \frac{1}{3}$

You should be some interesting and useful properties of the roots
 $Z_1 + Z_2 + Z_3 = -1$, $Z_1Z_2 + Z_3Z_1 + Z_2Z_3 = \beta$, and $Z_1Z_2Z_3 = -\gamma$

Case (ii) solution for $q^3 + r^2 < 0$.

The roots are given by

$$Z_1 = \pm 2\sqrt{-q} \cos\left(\frac{\theta}{3}\right) - \frac{\alpha}{3} \quad (17)$$

$$Z_2 = \pm 2\sqrt{-q} \cos\left(\frac{\theta}{3} + \frac{2\pi}{3}\right) - \frac{\alpha}{3} \quad (18)$$

$$Z_3 = \pm 2\sqrt{-q} \cos\left(\frac{\theta}{3} + \frac{4\pi}{3}\right) - \frac{\alpha}{3} \quad (19)$$

Where $\theta = \arccos \sqrt{\frac{r^2}{(-q)^3}}$ (θ is in degree)

In Eqs.17 - 19 the upper sign applies if r is positive, the lower sign applies if r is negative.

Three real roots are obtained, the largest value of Z corresponding to the vapor phase and the smallest value due to the liquid phase.

A fugacity coefficient can be estimated for both phases due to the value of Z as follow:

$$\ln \phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{B} \left(\frac{2a_i \alpha_i z_i^*}{a\alpha} - \frac{b_i}{b} \right) \ln \left(1 + \frac{B}{Z} \right) \quad (20)$$

When the equilibrium ratios are evaluated using Eq.3, the same equation of state is used for both phases.

Gardan's method

Gardan's method is an iterative numerical solution which used to solve polynomial of third degree equation, the details of this method is described as algorithm in Fig.(2).

The correct interpolation at the existence of three roots is that the actual composition can exist both as a vapor and as a liquid, but not necessarily in equilibrium. The strategy is therefore is to pick up the largest root when the cubic equation is solved for the vapor phase compressibility and the smallest root when the cubic equation is solved for the liquid phase compressibility. In particular the first and second derivative of the function $F(Z)$,

$$F'(Z) = 3Z^2 - 2Z + \beta$$

$F''(Z) = 6Z - 2$ Will indicate the possibility of one or more roots in the region $0 \leq Z \leq 1$ the point of inflection $F''(Z) = 0$ for the SRK equation is at $Z=1/3$ for all values of x_i, y_i, p and T . The Z value of the extreme points $F'(Z) = 0$ are given by:

$$Z_{1,2} = \frac{1}{3} \pm \frac{1}{3} \sqrt{1-3\beta}$$

Obviously, if $\beta=1/3$ the extreme points and the point of inflection, coincide at $Z=1/3$ then $F(Z)$ is monotonically increasing (Fig. 1(b)) and there is only one root possible.

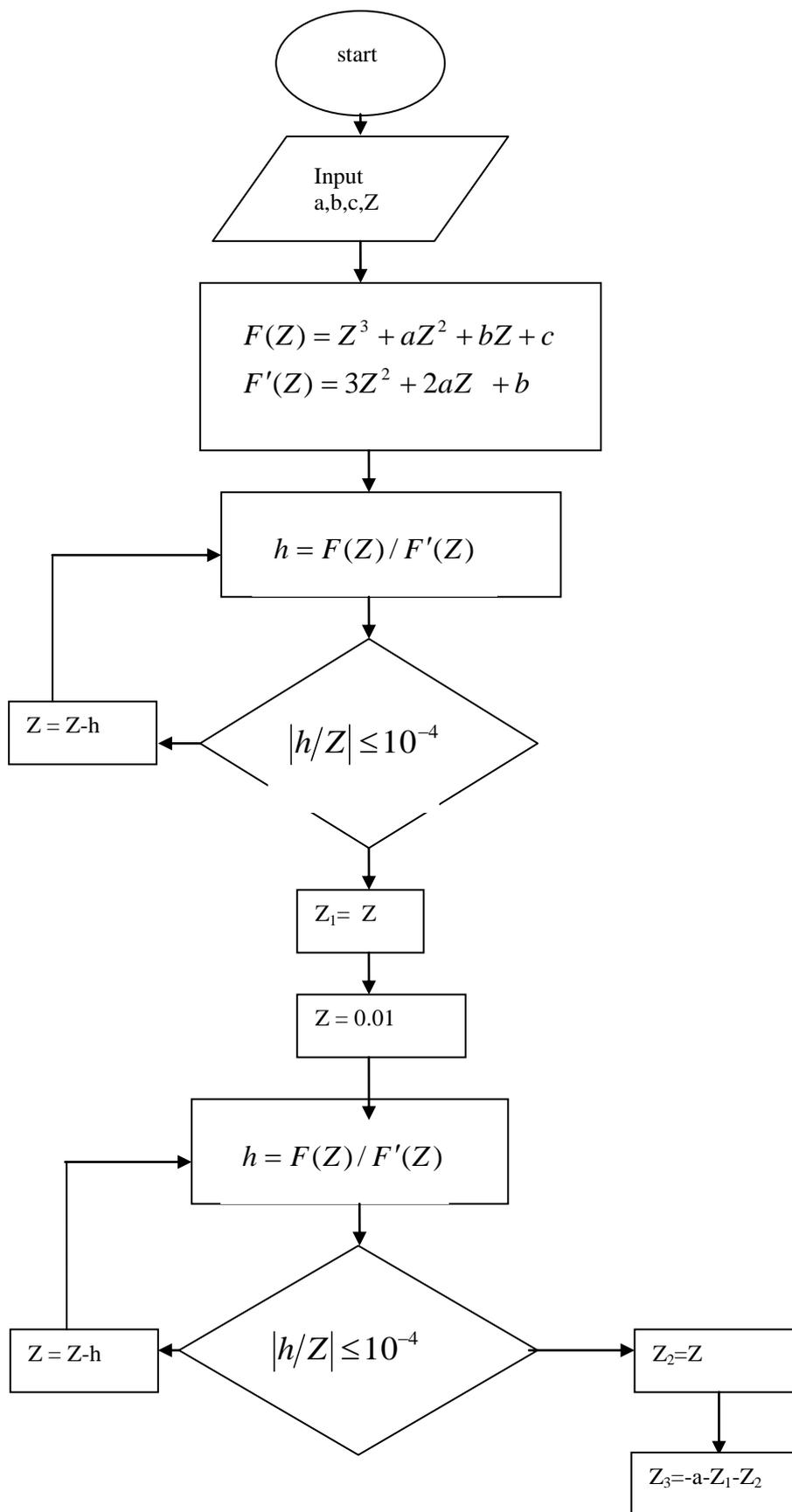


Fig.2 Flow chart of Gardan's method for the solution of the SRK equation of state.

Results and Discussion

The algorithm in Fig. 2 has shown the great influence that the choice of roots in the solution of the cubic equation of state has on flash calculations. The physical interpolation of the number of roots of the equation seems to vary in the literature. The author's experience with the SRK equation of state is that it's only at low pressure levels that the function $F(Z)$ is shaped as in Fig. 1(a) with three roots from both phases.

Numerical investigation of the 8 components system (Table (1)) showed that $F(Z)$ for the liquid phase become monotonic for pressures above 10 atm, while the vapor phase resulted in a monotonic $F(Z)$ for pressures above 145 atm. The number of phases in the system therefore has nothing to do with the number of roots of SRK equation of state.

Flash calculations were carried out for the mixture I in Table 1, based on the experimental data of Kurata and Katz ⁽⁸⁾. The experimental critical point is reported ⁽⁶⁾ to be at 172.6 atm and 316.1 K.

Table 1. Composition of test mixture I

component	mole%
Nitrogen	0.45
Methane	72.8
Ethane	5.46
Propane	3.02
n-Butane	3.07
n-Pentane	6.88
Hexane__	4.38
Heptane	3.75

The number of iterations increases as we approach the critical point:

1-100 atm: 2- 10iterations

100-150 atm: 10-14 iterations

150-170 atm: 14-35 iterations.

Vapor-liquid equilibrium calculations were run on PC using QuickBasic V4.5 language

In the following some of results are plotted to demonstrate that the proposed algorithm gives physically acceptable results.

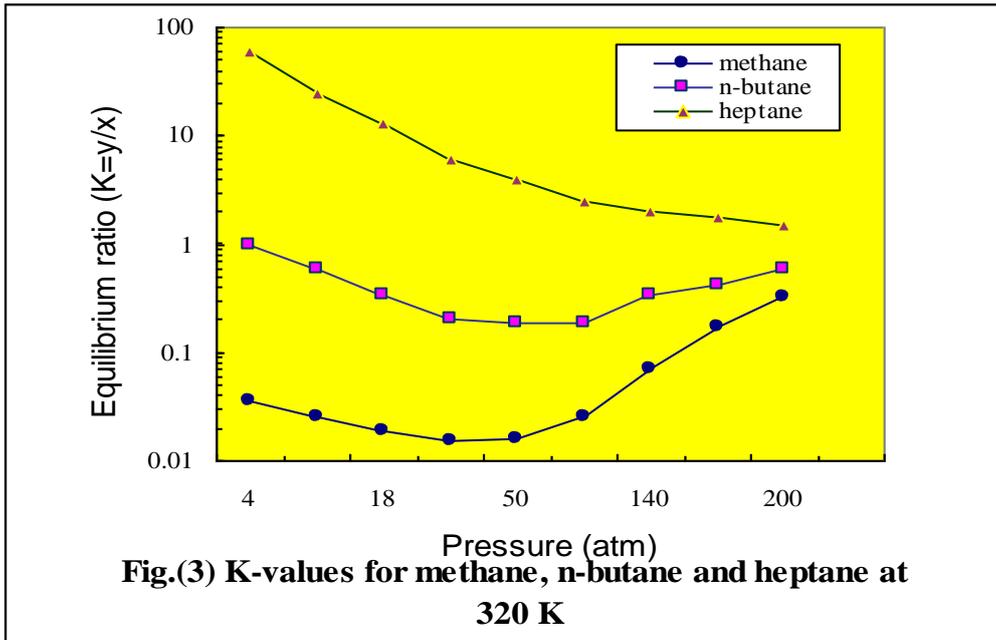
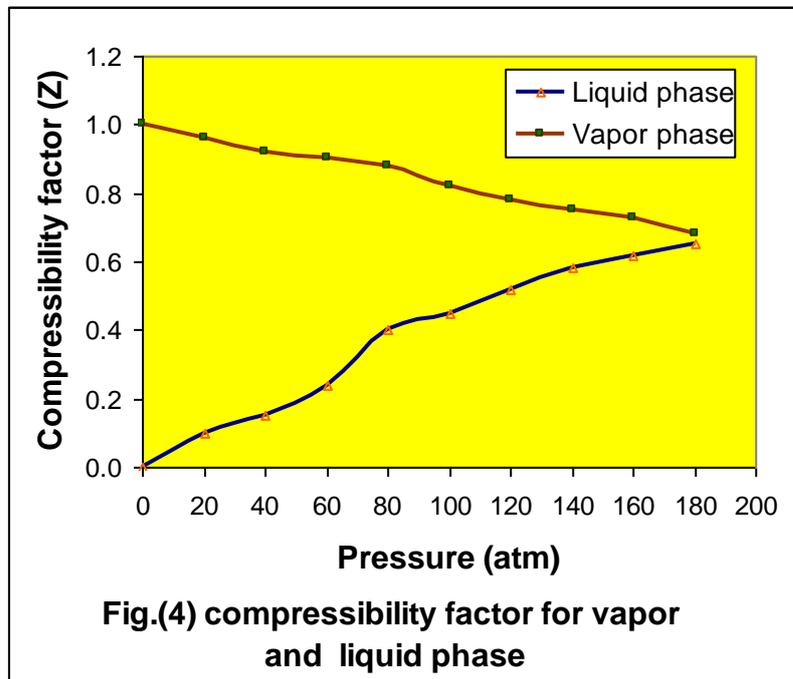


Fig.3 shows K-values for methane, n-butane and heptane in mixture I at 320 K. The shapes of the curve agree well with theory, and the K-values approach 1.0 when the pressure comes close to it's critical value.

In Fig.4, compressibility factors of two phases are plotted against pressure at 320 K. When the pressure approach it's critical value, the two compressibility factors meet at a value of about 0.68.



At high pressure the K-values do not behave normally outside the two-phase region. At pressure exceeding 60% of the critical pressure, the iteration outside the two phase region fails ⁽¹³⁾. For example at temperature above the dew point, the mole fraction of the liquid phase and the K-values tend to continue changing until all K-values come

close to 1.0 and the composition of two phases become identical. It was found that the only possible way of reaching the critical region of the mixture was to do a sequential calculation, starting at low pressure (1 atm) and then increasing the pressure stepwise until the actual pressure was reached.

Nomenclatures

A, B	coefficients of cubic equation of state
K_i	equilibrium ratio for component i
k_{ij}	binary interaction parameter of the SRK equation
N_i	number of moles of component i
N_C	number of components $K =$ equilibrium ratio,
P	absolute pressure, kPa (abs)
R	universal gas constant, (kPa (abs) • m ³) / (kmol • K)
T	temperature, K or °C
V	ratio of moles of vapor to moles of total mixture
X	mole fraction of component in the liquid phase
y	mole fraction of component in the vapor phase
Z	compressibility factor

Subscripts

i,j,k	component
c	critical property
r	reduced property
b	boiling

Superscript

L	liquid
V	vapor

Greek letters

α	parameter of the SRK equation
β	parameter of the SRK equation
γ	parameter of the SRK equation
ζ	vapor to feed ratio
ω	acentric factor

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الخلاصة

في البحث المقدم تم صياغة معادلة الحالة لتقييم نسب توازن الاطوار لخليط متعدد المكونات. إن معادلات الحالة ذات الثابتان مثل بينتس روبينسون وريدليتش كونج المعدلة لا يمكن أن تكون دقيقة جدا في المدى الواسع لدرجات الحرارة، ضغوط وتراكيز، لذا أختيرت معادلة سواف ريدليك كونج Soav Redlich Kwong كونها سهلة التطبيق واسعة المدى ولاتسبب الأخطاء الكبيرة خصوصاً عند استخدامها لخليط هيدروكربوني معقد. استخدم الحل التحليلي والحل العددي بطريقة كاردن لأيجاد جذور المعادلة الثالث والمتمثلة بعامل الانضغاطية للانظمة غير المثالية باستخدام لغة البرمجة QuickBasic V4.5.

طرحت معادلة سواف ريدليك كونج بشكل مفيد جدا لتطبيقات الحاسوب لتحديد نسبة توازن الاطوار للخلائط المعقدة والغير المعروفة كالنفط الخام أو مشتقاته التي تتطلب وقت حاسوب كبير نسبيا لمزيج متعدد المكونات