สมดุลวัฏภาคของสารผสมปิโตรเลียมและน้ำโดยใช้สมการสภาวะแบบคิวบิก

นางสาวศศิธร รมลี

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PHASE EQUILIBRIUM OF PETROLEUM AND WATER MIXTURES USING THE CUBIC EQUATION OF STATE

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ศศิธร รมลี: สมดุลวัฏภาคของสารผสมปิโตรเลียมและน้ำโดยใช้สมการสภาวะแบบคิวบิก.(PHASE EQUILIBRIUM OF PETROLEUM AND WATER MIXTURES USING THE CUBIC EQUATION OF STATE) อ.ที่ปรึกษา : รศ.ดร.เกริกชัย สุกาญจนัจที, 95 หน้า. ISBN 974-03-0343-9

วัตถุประสงค์ของงานวิจัยฉบับนี้ต้องการศึกษาถึงการนำสมการสภาวะเพียงสมการเดียวมาใช้ในการคำนวณสมดุลวัฏภาคระหว่างสารผสมปิโตรเลียมและน้ำ พบว่าการใช้สมการ Peng Robinson และใช้สมการของผสมแบบ Huron-Vidal-NRTL สามารถทำให้บรรลุวัตถุประสงค์ได้

พารามิเตอร์ k_{ij} (interaction parameter) τ_{ij} และ τ_{ji} (พารามิเตอร์ในสมการ NRTL) ที่ปรากฏในสมการของผสมแบบใหม่ที่จะนำมาใช้ในการคำนวณสมดุลวัฏภาคระหว่างสารผสมปิโตรเลียมและน้ำนั้นได้นำค่าดังกล่าวมาจาก การหาความสัมพันธ์ระหว่างค่าพารามิเตอร์กับอุณหภูมิวิกฤตของสารประกอบไฮโดรคาร์บอนที่ได้สร้างขึ้นจากข้อมูลในเอกสารที่ทำการตีพิมพ์เกี่ยวกับค่าการละลายของของผสมระหว่างสารประกอบไฮโดรคาร์บอนกับน้ำหลายคู่

พบว่าค่าการละลายที่หาได้จากการคำนวณมีค่าตรงกับค่าการละลายของน้ำที่ได้ทำการทดลองขึ้นของระบบน้ำมันเบนซิน/น้ำ และ ระบบน้ำมันดีเซล/น้ำ

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ____________________
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KEY WORD: PETROLEUM FRACTION/WATER MIXTURE , PENG ROBINSON EQUATION ,
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The objective of this research is to determine a model consisting of a single equation of state for predicting the mutual solubility of petroleum fraction/water system. It was found that the Peng Robinson equation with the Huron-Vidal-NRTL mixing rule could achieve the objective.

Correlations with critical temperature of hydrocarbon for the interaction parameter, k_{ij}, as well as the parameters τ_{ij} and τ_{ji} of the NRTL equation were constructed based on published mutual solubility data of various hydrocarbon/water pairs. Then, these correlations were used to supply the values of these parameters for light oil/water system in phase equilibrium calculation.

Solubility in gasoline/water and diesel/water systems was also measured experimentally. The calculated solubility water in light oil matches rather well with that of experiment.

Department Chemical Engineering Student's signature ____________________

Field of study Chemical Engineering Advisor's signature ____________________

Academic year 2001 Co-advisor's signature ____________________

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NOTATION

a	energy constant
b	volume constant
A,B,C,D	empirical constants
Cij	characteristic binary constant
k_{ij}	interaction coefficient
h	molar enthalpy
$\overline{h}_i$	partial molar enthalpy of component *i*
H_i	Henry's constant for component *i*
P	total pressure
R	gas constant
T	temperature(absolute)
Z	compressibility factor
S_1,S_2	pure component parameters
SG	specific gravity
v	molar volume
$\overline{v}_i$	partial molar volume of component *i*
x_i	liquid mole fraction of component *i*
y_i	vapor mole fraction of component *I*
g	Gibbs function
G^E	excess Gibbs function
M_F	mole fraction off on TBP assay of feed
M_L	mole fraction of on TBP assay of equilibrium liquid
M_V	mole fraction of on TBP assay of equilibrium vapor
γ_i^∞	infinite-dilution activity coefficient of component *i*
$\Delta\bar{c}_{pi}$	molar heat capacity of solution of component *i*
$\Delta\bar{h}_i$	molar heat (enthalpy) of solution of component *i*
$\Delta\bar{v}_i$	molar volume of solution of component *i*
α_{ij}	temperature constant for ij pair
ϕ_i^N	fugacity coefficient of component *i* in phase N

NOTATION (Cont.)

$\overline{f}_i^N$	fugacity of component *i* in phase N
ω	acentric factor

Subscripts

c	critical property
hc,*h*	hydrocarbon property
i,*j*(1,2)	property of component *i*,*j*(1,2)
hw	property of component hydrocarbon-water
wh	property of component water-hydrocarbon
m	mixture property
w	water property
3	three-phase equilibrium property
3c	three-phase critical end point property
r	reduced property
b	normal boiling point
pc	pseudocritical

Superscripts

E	excess property
V	vapor-phase property
L	liquid-phase property
s	saturated pure - component property

CHAPTER 1
PREFACE

1.1 Introduction

Petroleum is an important sort of energy source in nowadays, because it's easy to be used or transformed to other useful products. As we know, petroleum is a limited source, so many scientists have been trying to develop the transformed processes to be the most efficiency, the lowest cost, and the most safety processes.

Petroleum come from fossil placed over and over for a long time ago underground. There are two forms of petroleum, which are liquid and gas, in which they are called crude and natural gas respectively. However, they can't be used without good transformations. The most important transformation process is distillation. At this process, we found that there was few water mixed with crude or few vapor mixed with natural gas, which may cause danger to the process.

This thesis is considering only crude and this thesis will study to find the correlation of solubility water in crude. In the distillation process, we need to use high temperature and high pressure conditions. If there is too much water in crude, that will cause combustion or it will damage the equipment.

In this thesis, application of Equation of State in Light oil - Water phase equilibrium will be studied. Light oil will be used for study instead of crude, because Light oil's structure is more simple than crude's structure, but they are similar structure. That's mean, the prediction of solubility water in Light oil can be refer to the correlation of solubility water in crude.

Knowledge of Light oil - Water equilibrium is required in Petroleum distillation calculation or simulation. It is also useful in the field of environment concerning pollution.

Hydrocarbon – Water equilibrium were studied by various researchers. Mr.Economou I G. and C.Tsonopoulos found that modified Redlich – Kwong equation can be used to predict Hydrocarbon – Water equilibrium.

The prediction of Water/Light oil phase equilibrium or solubility of water in Light oil will be convenient if the calculation can be performed using only one question. Nowadays, the calculation of phase equilibrium in Water/Light oil system usually use an equation of state in vapor phase and Henry's constant in liquid phase which is obtained by experiment data. The calculation by cubic equation of state succeed in some cases because of choosing proper parameters and mixing rule.

In this research emphasize studying about proper choosing equations and mixing rule for cubic equation of state to predict solubility of Water in Light oil.

The result of this research is expected to be useful to the refinery, and related field. This thesis will be helpful and will encourage other people to further study about the correlation of water solubility in crude in the future.

1.2 Motivation

1.2.1 I am working for a organization in the petroleum industry. I want to apply the knowledge gained from this thesis to solve problem for the organization.

1.2.2 Many countries are facing water pollution problem, which cause by ships leaking oil to sea. This thesis maybe useful or can be applied to solve this problem.

1.3 Objective

To evaluate the cubic equation of state in predicting mutual solubilities of petroleum(Light oil) and water.

1.4 Scope

1.4.1 Search information about solubility of water in petroleum, and solubility of petroleum in water on journals and on internet.

1.4.2 Experimentally, determine the solubility data of water in oil and oil in water.

1.4.3 Develop computer program for calculating solubility of water in petroleum and solubility of petroleum in water and compare the results to the published information.

1.4.3.1 Correlate interaction parameter.

1.4.3.2 Find proper mixing rule for the calculation.

1.4.3.3 Demonstrate solubility of water in various petroleum fractions.

1.5 The benefit from this thesis

1.5.1 It can be used for the petroleum industry in quality control of oil or gas.

1.5.2 It can be useful to the petroleum production process.

1.5.3 It can be useful to the environment assessment.

1.5.4 We will have a computer program for the correlation between water and petroleum in equilibrium.

CHAPTER 2
THEORY

2.1 Phase Equilibria [6]

2.1.1 Vapor/Liquid Equilibrium (VLE) from Equations of State

Calculation of VLE from an equation of state is based on the equilibrium equations

$$y_i \hat{\phi}_i^v = x_i \hat{\phi}_i^l \qquad (i = 1, 2, \ldots N) \qquad (2.1.1.1)$$

Application of Equation (2.1.1.1) requires the availability of a single PVT equation of state suitable for both liquid and vapor mixtures. Experience shows that such an equation is invariably explicit in pressure, and thus expressions for the $\hat{\phi}_i$ are computed from Equation from:

$$\ln \hat{\phi}_i = \int_0^P \left\{ \left[\frac{\partial (nZ)}{\partial n_i} \right]_{T,\rho,n_j} - 1 \right\} \frac{d\rho}{\rho} - \ln Z \qquad (2.1.1.2)$$

The resulting expressions for the $\hat{\phi}_i$ are generally complicated, and the calculations involve considerable iteration. They are therefore done with a computer.

Such as, a schematic block diagram for case the liquid of known composition is at its bubble point, and pressure is one of the quantities sought; calculation is shown in Figure 2.1.1.

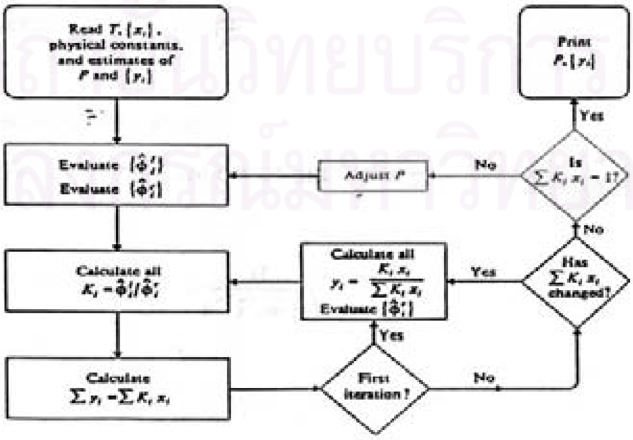


Figure 2.1.1 Block diagram for the calculation BUBL P [6]

2.1.2 Liquid/Liquid Equilibria

It is a matter of experience that some pairs of pure liquids, when mixed in appropriate proportions at certain temperatures and pressures, do not produce a single homogeneous liquid phase but instead form two liquid phases of different compositions. If the phases are at thermodynamic equilibrium, the phenomenon is an example liquid/liquid equilibrium, or " LLE."

The thermodynamic description of LLE is based on the same critiria used for VLE, namely uniformity of *T,P* and of the fugacity $\hat{f}_i$ for each chemical species in both phase. Designating the equilibrium liquid phases by the symbols α and β , we therefore write the criterion for LLE in an *N*-component system of uniform *T* and *P* as

$$\hat{f}_1^{\alpha} = \hat{f}_1^{\beta} \qquad (i = 1, 2, \ldots . N)$$

2.2 <u>Equation of state</u> [5]

Most of the simple equations that evolved from the vander Waals' equation are in cubic form, the simplest from for representing *P-V-T* relations of both vapor and liquid phases. But the simple equations are not accurate enough for the many *P-V-T* representations, and a more complex form of equation such as Benedict-Webb-Rubin equation is required to describe accurately the *P-V-T* relations of real fluids. However ,simple equations of state have found extremely valuable applications in phase equilibrium predictions, as demonstrated by Soave and by Peng and Robinson in their modifications of the Redlich-Kwong equation of state.

2.2.1 Redlich - Kwong Equation

The Redlich-Kwong equation of state may be written in the following general form:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \qquad (2.2.1.1)$$

As will be evident in the following derivation, it is convenient to express the parameter *a* as a product of a temperature-independent parameter, *a'*, and a temperature dependent term, *f(T)*, as follows:

$$a = a' f(T) \tag{2.2.1.2}$$

In the original Redlich-Kwong equation *f(T)* = $T^{-1/2}$

Expressing Equation 2.2.1.1 in cubic form in terms of molar volume ,*V*, gives

$$V^3 - \left(\frac{RT}{P}\right)V^2 + \left(\frac{a}{P} - \frac{bRT}{P} - b^2\right)V - \frac{ab}{P} = 0 \tag{2.2.1.3}$$

The adjustable parameters *a'* and *b* may be determined from the characteristics of critical point.

$$3V_c = \frac{RT_c}{P_c} \tag{2.2.1.4}$$

$$3V_c^2 = \frac{a_c}{P_c} - \frac{bRT_c}{P_c} - b^2 \tag{2.2.1.5}$$

$$V_c^3 = \frac{a_c b}{P_c} \tag{2.2.1.6}$$

where $$a_c = a' f(T_c) \tag{2.2.1.7}$$

From the definition of compressibility factor and Equation 2.2.1.4, the Z_c of the Redlich-Kwong equation becomes a universal constant of 1/3 for all fluids. Because of this shortcoming, the Redlich-Kwong equation is inaccurate around critical region. Now Equations 2.2.1.4, 2.2.1.5, and 2.2.1.6 will be solved for a_c and *b.* The three equations are combined to give

$$b^3 + (3V_c)b^2 + (3V_c^2)b - V_c^3 = 0$$

Rearranging this equation gives

$$\left(b^3 + 3b^2V_c + 3bV_c^2 + V_c^3\right) = 2V_c^3$$

or $$(b + V_c)^3 = 2V_c^3$$

or $$b = \left(2^{1/3} - 1\right)V_c \tag{2.2.1.8}$$

Combining Equations 2.2.1.4 and 2.2.1.8 gives

$$b = \frac{\left(2^{1/3} - 1\right)RT_c}{3P_c} = 0.08664\frac{RT_c}{P_c} \tag{2.2.1.9}$$

Combining Equations 2.2.1.4, 2.2.1.6, and 2.2.1.9 gives

$$a_c = \frac{(RT_c)^2}{9(2^{1/3}-1)P_c} = 0.42748\frac{(RT_c)^2}{P_c} \qquad (2.2.1.10)$$

For convenience the numerical constants in Equations 2.2.1.9 and 2.2.1.10 are often denoted by

$$\Omega_b = 0.08664$$

$$\Omega_a = 0.42748$$

From Equations 2.2.1.2 and 2.2.1.7

$$a = a_c\frac{f(T)}{f(T_c)}$$

From this point on the ratio, $f(T)/f(T_c)$ will be denoted by α following the Soave notation. Thus, the above equation becomes

$$a = a_c\alpha \qquad (2.2.1.11)$$

As obvious from $f(T)/f(T_c)$, α must be unity at $T = T_c$

Replacing V in Equation 2.2.1.1 with ZRT/P and rearranging gives

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \qquad (2.2.1.12)$$

where

$$A = \frac{aP}{(RT)^2} \qquad (2.2.1.13)$$

$$B = \frac{bP}{RT} \qquad (2.2.1.14)$$

It should be noted that Redlich and Kwong have originally denoted $a/(RT)^2$ as A^2 , b/RT as B, and b/V as h to express Equation 2.2.1.1 as follows:

$$Z = \frac{1}{1-h} - \left(\frac{A^2}{B}\right)_{RK}\frac{h}{1+h}$$

However, the Soave notation, as given by Equation 2.2.1.13 and 2.2.1.14, is simpler to use for Equation 2.2.1.12. Combining Equation 2.2.1.13 with 2.2.1.10 and 2.2.1.11, and 2.2.1.14 with 2.2.1.9 gives

$$A = 0.42748\left(\frac{P_r}{T_r^2}\right)\alpha \tag{2.2.1.15}$$

$$B = 0.08664\frac{P_r}{T_r} \tag{2.2.1.16}$$

The only difference in the original Redlich-Kwong, the Wilson, and the Soave equations is the expression for α .At $T = T_c$, where α=1, the three equations become identical.

In the original Redlich-Kwong equation, the α expression is

$$\alpha = T_r^{-0.5} \tag{2.2.1.17}$$

Redlich and Kwong determined the α expression as an integral part of their equation of state development, without considering the variation of individual fluids, but Wilson and Soave included the variation by expressing α as a function of acentric factor and also using additional information on the *P-V-T* relations of real fluids. This will be discussed next. Note, however, that Redlich and Kwong developed their equation six years before the acentric factor was proposed.

2.2.2 Soave Equation

Soave also defined the α as a function of T and ω, but in a much different way than Wilson. Soave calculated the values of α at a series of temperatures for a number of pure hydrocarbons, using the equality of vapor and liquid fugacities along the saturation curve. The fugacity of each component in a mixture is identical in all phases at equilibrium. This is equally true for a single component system having vapor and liquid phases at equilibrium.

$$f_i^V = f_i^L \tag{2.2.2.1}$$

where f_i^V and f_i^L are the pure component fugacities of vapor and liquid respectively. This equation is valid at any point on the saturation curve, where the vapor and liquid coexist in equilibrium.

The pure component fugacity expression is derived from Equations of Redlich-Kwong in the fugacity coefficient form.Equation 2.2.1.1 in the fugacity coefficient form, as follow :

$$\ln\left(\frac{f}{P}\right) = Z - 1 - \ln Z + \int_{\infty}^{V}\left[\frac{b}{V(V-b)} - \frac{a}{RTV(V+b}\right]dV$$

Integrating the last term of this equation and combining with *b/V = B/Z* from Equation 2.2.1.14, *a/(bRT) = A/B* from Equations 2.2.1.13 and 2.2.1.14, results in

$$\ln\left(\frac{f}{P}\right) = Z - 1 - \ln(Z - B) - \left(\frac{A}{B}\right)\left(1 + \frac{B}{Z}\right) \qquad (2.2.2.2)$$

As is obvious from Equations 2.2.1.12 , 2.2.1.13 , and 2.2.1.16 the solution of Equation 2.2.2.2 requires the knowledge of T_r ,P_r , and α, and prior solution of Equation 2.2.1.12 for Z Writing Equation 2.2.2.2 for both vapor and liquid, subtracting the two expressions and combining with Equation 2.2.2.1 gives

$$\ln\left(\frac{f^V}{f^L}\right) = 0 = Z_v - Z_L - \ln\left(\frac{Z_v - B}{Z_L - B}\right) - \frac{A}{B}\ln\left(\frac{Z_V + B}{Z_V + B}\right) \qquad (2.2.2.3)$$

Equation 2.2.2.3 is valid for pure fluids along the saturation curve where the vapor and liquid phases coexist in equilibrium. Mathematically, Equation 2.2.2.3 is still a function of T_r ,P_r and α as is Equation 2.2.1.16 . Along the equilibrium curve, P_r is no longer independent, but is dependent upon T_r . Therefore, at the vapor-liquid equilibrium condition, α is the only adjustable variable to satisfy Equation 2.2.2.3 for a given value of T_r.

The solution of Equation 2.2.2.3 for α may be carried out by an iterative solution method such as Newton-Raphson or Wegstein method. The main emphasis on the solution of cubic equations.

Soave calculated the values of α over a temperature range of T_r = 0.4 to 1 for a number of light hydrocarbons and found that $\alpha^{0.5}$ was a linear function of $T_r^{0.5}$ with a negative slope for each fluid studied, i.e.,

$$\alpha^{0.5} = c - mT_r^{0.5}$$

Because α = 1 at T = 1, by definition, the above equation may be rewritten as follows:

$$\alpha^{0.5} = 1 - m(1 - T_r^{0.5}) \qquad (2.2.2.4)$$

After establishing the linear relationship of Equation 2.2.2.4, Soave calculated the slope m directly from Equations 2.2.2.3 and 2.2.2.4, without using any experimental data, as follows:

1. A value of acentric factor, ω, was assumed to calculate $P_r = 10^{-(1+\omega)}$ at T_r =0.7. This equation, by definition, is valid at T_r = 0.7

2. Using these values of ω, P_r , and T_r =0.7, Equation 2.2.2.3 was solved for α.

3. The slope m was calculated by Equation 2.2.2.4, using T_r =0.7 and the α value from step 2, as follows:

$$m = \left[\left(\alpha_{T_r=0.7}\right)^{0.5} - 1\right] / \left(1 - 0.7^{0.5}\right)$$

In this manner the values of m were calculated for a series of ω values from 0 to 0.5 with an interval of 0.05, and then correlated as a quadratic function of ω, the acentric factor, as follows:

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \qquad (2.2.2.5)$$

combining Equations 2.2.2.4 and 2.2.2.5 gives,

$$\alpha^{0.5} = 1 + \left(0.48 + 1.574\omega - 0.176\omega^2\right)\left(1 - T_r^{o.5}\right) \qquad (2.2.2.6)$$

Particularly for predicting vapor-liquid phase equilibria for hydrocarbon systems, both pure and mixture fluids. Equation 2.2.1.12 has made a tremendous contribution to the wide spread use of simple equations of state in hydrocarbon industries. Peng and Robinson used an analogous correlation in the development of their equation of state.

2.2.3 Peng-Robinson Equation

The original Redlich-Kwong equation and the modifications by Wilson and by Soave have a common shortcoming, i.e., they predict poor liquid densities and an unrealistic universal critical compressibility factor of 1/3 for all substances. To alleviate this shortcoming, Peng and Robinson modified Equation 2.2.1.1 as follows:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \qquad (2.2.3.1)$$

or

$$P = \frac{RT}{V-b} - \frac{a}{\left[V + \left(2^{0.5}+1\right)b\right]\left[V - \left(2^{0.5}-1\right)b\right]} \qquad (2.2.3.1a)$$

where a is of the same form as Equation 2.2.1.2. The parameters a and b are obtained by the same procedure used previously for the Redlich-Kwong equation, i.e., Equation 2.2.1.1 Rearranging Equation 2.2.3.1 in cubic form in terms of V gives

$$V^3 - \left(\frac{RT}{P} - b\right)V^2 + \left(\frac{a}{P} - \frac{2bRT}{P} - 3b^2\right)V - b\left(\frac{a}{P} - b - b^2\right) = 0 \qquad (2.2.3.1b)$$

And solving the three resulting equations for V_c ,*b,* and *a*, and also using the definition of $\alpha = f(T)/f(T_c)$ gives the following:

$$V_c = 0.307\frac{RT_c}{P_c} \qquad (2.2.3.2)$$

$$b = 0.077796\frac{RT_C}{P_c} \tag{2.2.3.3}$$

$$a = a_c\alpha \tag{2.2.3.4}$$

where

$$a_c = 0.457235\frac{(RT_c)^2}{P_c} \tag{2.2.3.5}$$

As indicated by Equation 2.2.3.2, a universal critical compressibility factor of 0.307 is predicted by Equation 2.2.3.1. This is a marked improvement over the 1/3 that is predicted by the Redlich-Kwong equation or the Wilson and the Soave modifications. However, the value is still far from the actual critical compressibility factors of real fluids except for hydrogen and helium. Equation 2.2.3.1 also predicts the liquid density significantly better than does the Soave equation, except for simple fluids.

Rearranging Equation 2.2.3.1 into compressibility factor form gives

$$Z^3 - (1-B)Z^2 + \left(A - 2B - 3B^2\right)Z - \left(AB - B^2 - B^3\right) = 0 \tag{2.2.3.6}$$

where A and B are given by Equations 2.2.1.13 and 2.2.1.16 respectively, but with the *a* and *b* parameters being given by Equations 2.2.3.3 and 2.2.3.4. It is interesting to compare Equation 2.2.3.6 with Equation 2.2.1.12, the cubic form in Z for the Redlich-Kwong or the Soave equation.

Combining Equation 2.2.1.13 with 2.2.3.4, and Equation 2.2.1.16 with 2.2.3.3 gives,

$$A = 0.457235\left(\frac{P_r}{T_r^2}\right)\alpha \tag{2.2.3.7}$$

$$B = 0.077796\frac{P_r}{T_r} \tag{2.2.3.8}$$

The α expression for the Peng-Robinson equation may be obtained by the same procedure used previously for Soave equation, using the fugacity coefficient expression derived from Equations 2.2.3.1.

$$\ln\left(\frac{f}{P}\right) = Z - 1 - \ln(Z - B) - \frac{A}{2^{-1.5}B}\ln\left(\frac{Z + \left(2^{0.5} + 1\right)B}{Z - \left(2^{0.5} - 1\right)B}\right) \tag{2.2.3.9}$$

As discussed earlier, Soave used the vapor pressure data just to establish the functional relationship of α to T_r as given by Equation 2.2.2.4, then calculated the slope *m* from the definiton of acentric factor. In contrast to this, Peng and Robinson, who retained the same form as Equation 2.2.2.4 for α, found the slope m directly from vapor pressure data for a number of hydrocarbons from the normal boiling points to the critical points. The resulting m values were then correlated with ω to obtain the following.

$$m = 0.37646 + 1.54226\omega - 0.26992\omega^2 \tag{2.2.3.10}$$

Thus, for Peng-Robinson equation, the expression for α becomes

$$\alpha^{0.5} = 1 + \left(0.37646 + 1.54226\omega - 0,26992\omega^2\right)\left(1 - T_r^{0.5}\right) \tag{2.2.3.11}$$

Both the Soave and the Peng-Robinson equations are excellent in predicting the vapor pressures. This important capability stems from the remarkably good expressions for α, i.e., Equation 2.2.2.6. for the Soave modification, and Equation 2.2.3.11 for the Peng-Robinson equation, rather than from the formulations of the equations of state. But the form of the equation of state does affect the prediction of molar volumes in the dense phase region, where the Peng-Robinson equation, though not as accurate as desired, shows a marked improvement over the Soave equation.

2.2.4 RKJZ Equation

A modification of the Redlich-Kwong equation of state proposed by Zudkevitch and Joffe (1970). This equation of state, which will be refered to by the initials RKJZ, was recently used by Wilson et. al.(1981) in a study of the volatility of coal liquids.

Briefly, in the RK equation:

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)} \tag{2.2.4.1}$$

The temperature dependence of *a* and *b* is determined by simultaneously matching the liquid density and forcing the vapor and liquid fugacities to be equal at the pure component's vapor pressure. In addition, a modification was made in the mixing rule for *a*. For a binary mixture, this is given by:

$$a_m = z_1^2 a_1 + 2z_1 z_2 (a_1 a_2)^{1/2}(1 - C_{12}) + z_2^2 a_2 \tag{2.2.4.2}$$

C_{12} , which is assumed to be independent of temperature , corrects for the deviation of a_{12} from the geometric mean.

The C_{ij} turns out to be equal to zero for most hydrocarbon/hydrocarbon binaries, especially near ambient temperature. However, nonzero C_{ij}' s may be required when the two components are very different in molecular size, for calculations in the critical region, or for polar components. Thus, the first step in the use of RKJZ is to determine the C_{ij} values for the key binaries.

However, that RKJZ with a constant C_{ij} can adequately correlate the solubility data up to at least 470 K, the maximum temperature of interest in water pollution abatement work. It will, therefore, be possible to use RKJZ, with the C_{ij} determined from the water solubilities, to predict the vapor-liquid equilibrium behavior of water/hydrocarbon systems. However, the water-rich liquid will have to be excluded from such treatment because RKJZ, or any other similar equation of state, cannot predict the solubility or volatility of hydrocarbons in water, as long as a constant C_{ij} is used. To correlate the solubility of hydrocarbons in water, it is necessary to make C_{ij} a very strong function of temperature of an equation of state.

2.2.5 Mixing Rules for Cubic Equations of State

As discussed in the first section of this chapter, the equations of state are generally developed for pure fluids first, then extended to mixtures. The mixture extension requires so-called mixing rules, which are simply means of calculating mixture parameters equivalent to those of pure substances. Except for those of virial coefficients, the mixing rules are more or less arbitrary rules that are to reflect the composition effect on the system properties.

Most of the simple equations of state evolved from the van der Waals' equation use van der Waals' mixing rules with or without modifications. From the viewpoint of mathematical expression, the van der Waals' mixing rules are special forms of the second virial coefficient mixing rule:

$$B = \sum_{i}^{N} \sum_{j}^{N} x_i x_j B_{ij} \qquad (2.2.5.1)$$

If B_{ij} is assumed to be the arithmetic average of B_i and B_j the above equation reduced to

$$B = \sum_{i}^{N} x_i B_i \qquad (2.2.5.2)$$

If B_{ij} is assumed to be the geometric average of B_i and B_j then Equation 2.2.2.1 becomes

$$B = \left(\sum_i^N x_i B_i^{0.5}\right)^2 \qquad (2.2.5.3)$$

The van der Waals' mixing rules for the parameters *b* and *a* are equivalent to Equations 2.2.5.2 and 2.2.5.3, respectively.

At this point, it should be made clear that all the pure fluid parameter symbols presented with subscript "i" which was omitted for simplicity. Thus, for example, Equation 2.2.1.8 should have been written b_i= 0.08664(RT_{ci}/P_{ci}). From this point on, the subscript *i* will be retained to distinguish the pure fluid parameters from its mixture counterparts. Then, the mixing rule for *b* is

$$b = \sum_i^N x_i b_i \qquad (2.2.5.4)$$

where b_i is given by Equation 2.2.1.9 for the Redlich-Kwong and the Soave equations, by Equation 2.2.3.3 for Peng-Robinson equation. The following are the mixing rules for *a* for each of the cubic equations disscussed

Redlich-Kwong:

$$a = \left[\sum_i^N x_i a_i^{0.5}\right]^2 \qquad (2.2.5.5)$$

where a_i is given be Equation 2.2.1.11 together with 2.2.1.10 and 2.2.1.17

Soave:

$$a = \sum_i^N \sum_j^N x_i x_j \left(a_i a_j\right)^{0.5} \left(1 - k_{ij}\right) \qquad (2.2.5.6)$$

where a_i is given be Equation 2.2.1.11 together with 2.2.1.10 and 2.2.2.6

Peng-Robinson:

$$a = \sum_i^N \sum_j^N x_i x_j \left(a_i a_j\right)^{0.5} \left(1 - k_{ij}\right) \qquad (2.2.5.7)$$

where a_i is given be Equation 2.2.1.11 together with 2.2.1.10 and 2.2.3.11

It should be noted that two binary interaction coefficients, k_{ij} ' s, in Equations 2.2.5.6 and 2.2.5.7 are not necessarily the same, and the two equations reduce to the form of Equation 2.2.5.5 if all k_{ij}'s are zero. The values of the binary interaction coefficients are usually obtained from experimental vapor-liquid equilibrium data on binary mixtures by using, for example, a least square curve-fitting method. The binary interaction coefficients may be obtained from other sources of experimental data such as second virial coefficients of binary mixtures.

New mixing rule: [8]

For simplicity, we present the derivation of the new mixing rule here for the van der waals equation of state. The derivation of the new mixing rule and the fugacity coefficient equation for the Peng-Robinson equation is given in the following; a similar derivation can be used for other two-parameter cubic equations of state.

The van der Waals equation of state is given by:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad (2.2.5.8)$$

To apply this equation to mixtures, the equation of state parameters a_m and b_m are made functions of compositions using mixing rules. For example, the traditional van der Waals " one-fluid" mixing model is :

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad b_m = \sum_i \sum_j x_i x_j b_{ij} \qquad (2.2.5.9)$$

Further, the following combining rules are generally assumed:

$$a_{ij} = \sqrt{a_i a_j}\left(1-k_{ij}\right) \qquad b_{ij} = \frac{\left(b_i + b_j\right)}{2} \qquad (2.2.5.10)$$

where k_{ij} is an interaction parameter characteristic of each binary pair. The modification proposed by Panagiotopoulos and Reid (1986) was to make k_{ij} composition-dependent resulting in:

$$a_m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\left(1 - k_{ij} + x_j l_{ij}\right) \qquad (2.2.5.11)$$

While mixing rules should lead to a quadratic dependence of the second virial coefficient on composition, there is no other theoretical restriction on their temperature, density or composition dependence. However, there is an advantage to mixing rules being independent of density since this preserves the cubic nature of equation of state. If we expand the equation as a virial series, the relation between the second virial coefficient *B(T)* and the equation of state parameters is:

$$B(T) = b - \frac{a}{RT} \tag{2.2.5.12}$$

Since, from statistical mechanics, the composition dependence of the second virial coefficient is quadratic:

$$B_m(T) = \sum_i \sum_j x_i x_j B_{ij}(T) \tag{2.2.5.13}$$

we must have that

$$b_m - \frac{a_m}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \tag{2.2.5.14}$$

with $[b - a/(RT)]_{ij}$ being the composition-independent cross second virial coefficient of equation of state. A sufficient, but not necessary, condition for satisfying Eq.2.2.5.14 is the van der Waals one-fluid model of Eq.2.2.5.9. Traditionally this solution has been used at all densities. However, Eq.2.2.5.9 are only one solution to Eq.2.2.5.14; other solutions are possible, which is the subject of this article.

As a digression, for later reference, we note that:

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \frac{F(x)}{RT}} \tag{2.2.5.15}$$

and

$$a_m = b_m F(x) \tag{2.2.5.16}$$

where *F(x)* is an arbitrary function of composition vector *x,* is also a solution of Eq.2.2.5.14.

Many other algebraic solutions are possible, for example,

$$b_m = \sum_i \sum_j x_i x_j b_{ij} + F(x) \qquad a_m = \sum_i \sum_j x_i x_j a_{ij} + RTF(x) \tag{2.2.5.17}$$

though they may be devoid of any physics.

The cross second virial coefficient of Eq.2.2.5.14 can be related to those of the pure components by:

$$\left(b-\frac{a}{RT}\right)_{ij}=\frac{\left(b_i-\frac{a_i}{RT}\right)+\left(b_j-\frac{a_j}{RT}\right)}{2}\left(1-k_{ij}\right) \tag{2.2.5.18}$$

where here k_{ij} is a second virial coefficient binary interaction parameter.

The Helmholtz free energy departure function, which is the difference between the molar Helmholtz free energy of pure species *i* and the ideal gas at the same temperature and pressure, is:

$$A_i(T,P)-A_i^{IG}(T,P)=\left(-\int_{V=\infty}^{V_i}PdV\right)-\left(-\int_{V=\infty}^{V=\frac{RT}{P}}\frac{RT}{V}dV\right) \tag{2.2.5.19}$$

for the van der Waals fluid this becomes:

$$A_i(T,P)-A_i^{IG}(T,P)=-RT\ln\left[\frac{P(V_i-b_i)}{RT}\right]-\frac{a_i}{V_i} \tag{2.2.5.20}$$

Similarly, the mixture Helmholtz free energy departure function, which is the difference between the molar Helmholtz free energy of a mixture, A_m , and that of the same mixture as an ideal gas, A_m^{IGM} , at the same temperature, pressure, and composition is:

$$A_m(T,P,x)-A_m^{IGM}(T,P,x)=-RT\ln\left[\frac{P(V_m-b_m)}{RT}\right]-\frac{a_m}{V_m} \tag{2.2.5.21}$$

Finally, the excess Helmholtz free energy for mixing at constant temperature and pressure, $A^E(T,P,x)$, is:

$$\begin{aligned}
A^E(T,P,x) &= A_m(T,P,x)-A_m^{IM}(T,P,x)\\
&= A_m(T,P,x)-\sum_i x_i A_i(T,P)-RT\sum_i x_i\ln x_i\\
&= A_m^{IGM}(T,P,x)-RT\ln\left[\frac{P(V_m-b_m)}{RT}\right]-\frac{a_m}{V_m}\\
&\quad -\sum_i x_i A_i^{IG}(T,P)+RT\sum_i x_i\ln\left[\frac{P(V_i-b_i)}{RT}\right]+\sum_i\frac{x_i a_i}{V_i}\\
&\quad -RT\sum_i x_i\ln x_i = -\frac{a_m}{V_m}+\sum_i x_i\frac{a_i}{V_i}-RT\ln\left[\frac{P(V_m-b_m)}{RT}\right]\\
&\qquad +RT\sum_i x_i\ln\left[\frac{P(V_i-b_i)}{RT}\right]
\end{aligned} \tag{2.2.5.22}$$

since

$$A_m^{IGM}(T,P,x)-\sum_i x_i A_i^{IG}(T,P)=RT\sum_i x_i \ln x_i \qquad (2.2.5.23)$$

Expressions for the excess Helmholtz free energy of liquid mixtures have usually been derived using lattice models with the assumption that there are no free sites on the lattice. This is approximately equivalent to the assumption that in a liquid solution the molecules are so closely packed that there is no free volume. This limit in an equation of state is:

$$\begin{aligned}\lim_{P\to\infty} V_i &= b_i\\ \lim_{P\to\infty} V_m &= b_m\end{aligned} \qquad (2.2.5.24)$$

Therefore, if we equate the excess Helmholtz free energy at infinite pressure from an equation of state to that of a liquid solution model we have:

$$A_\infty^E(x)=-\frac{a_m}{b_m}+\sum_i x_i \frac{a_i}{b_i} \qquad (2.2.5.25)$$

Equation 2.2.5.25 is analogous to the relation found by Huron and Vidal (1979), but since they used the excess Gibbs free energy at infinite pressure they had to make the additional assumption on the *b* parameter of Eq.2.2.5.10.

Equations 2.2.5.14 and 2.2.5.25 completely define a_m and b_m in terms of $A_\infty^E(x)$ (the high-density term) and k_{ij} (the low-density term). These equations can be solved to obtain

$$b_m=\frac{\sum_i\sum_j x_i x_j\left(b-\frac{a}{RT}\right)_{ij}}{1+\left(\frac{A_\infty^E(x)}{RT}\right)-\sum_i x_i\left(\frac{a_i}{b_i RT}\right)} \qquad (2.2.5.26)$$

and

$$\frac{a_m}{b_m}=\sum_i x_i \frac{a_i}{b_i}-A_\infty^E(x) \qquad (2.2.5.27)$$

Note that Eqs.2.2.5.26 and 2.2.5.27 are in the form of Eqs.2.2.5.15 and 2.2.5.16 with

$$F(x)=\sum_i x_i \frac{a_i}{b_i}-A_\infty^E(x) \qquad (2.2.5.28)$$

Therefore, these mixing rules produce a second virial coefficient which has a quadratic composition dependence, and at low densities these mixing rules predict fugacities similar to a virial equation truncated at the second virial coefficient. At high density, however, the Helmholtz free energy of the solution is that of the chosen liquid activity coefficient model described by $A_{\infty}^{E}(x)$, and could be of either a random or local composition form. Consequently, we have obtained a mixture equation of state model that is correct at both the low-and high-density limits without postulating a density-dependent mixing rule.

It should be noted that the mixing rule suggested by Huron and Vidal(1979) is, in effect, the zeroth-order truncation of a series expansion of Eqs.2.2.5.26 and 2.2.5.27 with respect to *(1/T)* and with k_{ij} set equal to zero. However, since both the excluded volume parameter *b* and the second virial coefficient are of the order *(a/RT)*, the proper composition dependence for the second virial coefficient cannot be preserved unless the expansion is carried beyond the first-order term. In fact, there is no need to expand Eqs. 2.2.5.26 and 2.2.5.27 with respect to temperature.

If, instead of our mixing rule, the van der Waals one-fluid mixing model is used, the form as excess Helmholtz free energy of the liquid has then been dictated to be:

$$A_{\infty}^{E}(x) = \sum x_i \frac{a_i}{b_i} - \frac{\sum\sum x_i x_j a_{ij}}{\sum\sum x_i x_j b_{ij}} \tag{2.2.5.29}$$

Alternatively, if one uses this excess Helmholtz free energy expression in our mixing rule, the van der Waals one-fluid mixing rule is recovered at all densities. However, the mixing rule developed here allows a much more flexible choice of liquid solution model so that, if necessary, local composition effects at high density can be represented accurately. Further, the approach developed here is theoretically correct and can be easily extended to other two-parameter cubic equations of state. For examples, the expressions of mixture parameters and fugacities of components derived for the Peng-Robinson equation of state (Peng and Robinson, 1975) proposed the following modification of the van der Waals equation of state:

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V^2 + 2bV - b^2} \tag{2.2.5.30}$$

If the compressibility factor *PV/(RT)* is expanded in a virial series, the expression for the second virial coefficient is the same as Eq.2.2.5.12. The Helmholtz free energy departure function for the Peng-Robinson equation at a given temperature, pressure and composition is:

$$\frac{\left(A-A^{IGM}\right)}{RT}=-\ln\left[\frac{P(V-b)}{RT}\right]+\frac{a}{2\sqrt{2}bRT}\ln\left[\frac{V+\left(1-\sqrt{2}\right)b}{V+\left(1+\sqrt{2}\right)b}\right] \quad (2.2.5.31)$$

In the limit of pressure going too infinity this becomes:

$$\lim_{P\to\infty}\frac{\left(A-A^{IG}\right)}{RT}=\frac{a}{bRT}C \quad (2.2.5.32)$$

with the constant *C* being:

$$C=\frac{1}{\sqrt{2}}\ln\left(\sqrt{2}-1\right) \quad (2.2.5.33)$$

Therefore, the excess Helmholtz free energy at infinite pressure A_∞^E */(RT)* is:

$$\frac{A_\infty^E}{CRT}=\frac{a_m}{b_mRT}-\sum_i x_i\frac{a_i}{b_iRT} \quad (2.2.5.34)$$

Using the same development as earlier, we obtain the following expressions for equation of state parameters a_m and b_m :

$$b_m=\frac{Q}{(1-D)} \quad (2.2.5.35)$$

and

$$\frac{a_m}{RT}=Q\frac{D}{(1-D)} \quad (2.2.5.36)$$

with *Q* and *D* defined as:

$$Q=\sum_i\sum_j x_ix_j\left(b-\frac{a}{RT}\right)_{ij} \quad (2.2.5.37)$$

and

$$D=\sum_i x_i\frac{a_i}{b_iRT}+\frac{A_\infty^E}{CRT} \quad (2.2.5.38)$$

The thermodynamic properties of a mixture can now be calculated. The fugacity coefficient is computed from:

$$\ln\varphi_i = \int_{\underline{V}}^{\infty}\left[\frac{1}{RT}\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{1}{V}\right]dV - \ln\left(\frac{PV}{RT}\right) \tag{2.2.5.39}$$

For the Peng-Robinson equation of state and an arbitrary set of mixing rules for a_m and b_m we have:

$$\begin{aligned}\ln\varphi_i ={}& -\ln\left[\frac{P(V-b_m)}{RT}\right] + \frac{1}{b_m}\left(\frac{\partial nb_m}{\partial n_i}\right)\left(\frac{PV}{RT}-1\right) \\ &+ \frac{1}{2\sqrt{2}}\left(\frac{a_m}{b_m RT}\right)\left[\frac{1}{a_m}\left(\frac{1}{n}\frac{\partial n^2 a_m}{\partial n_i}\right) - \frac{1}{b_m}\left(\frac{\partial nb_m}{\partial n_i}\right)\right]\ln\left[\frac{V+b_m\left(1-\sqrt{2}\right)}{V+b_m\left(1+\sqrt{2}\right)}\right]\end{aligned} \tag{2.2.5.40}$$

The partial derivatives of a_m and b_m are:

$$\frac{\partial nb_m}{\partial n_i} = \frac{1}{(1-D)}\left(\frac{1}{n}\frac{\partial n^2 Q}{\partial n_i}\right) - \frac{Q}{(1-D)^2}\left(1-\frac{\partial nD}{\partial n_i}\right) \tag{2.2.5.41}$$

and

$$\frac{1}{RT}\left(\frac{1}{n}\frac{\partial n^2 a_m}{\partial n_i}\right) = D\frac{\partial nb_m}{\partial n_i} + b_m\frac{\partial nD}{\partial n_i} \tag{2.2.5.42}$$

with the partial derivatives of Q and D given by:

$$\left(\frac{1}{n}\frac{\partial n^2 Q}{\partial n_i}\right) = 2\sum_j x_j\left(b-\frac{a}{RT}\right)_{ij} \tag{2.2.5.43}$$

and

$$\frac{\partial nD}{\partial n_i} = \frac{a_i}{b_i RT} + \frac{\ln\gamma_{\infty i}}{C} \tag{2.2.5.44}$$

with

$$\ln\gamma_{\infty i} = \frac{1}{RT}\frac{\partial nA_{\infty}^{E}}{\partial n_i} \tag{2.2.5.45}$$

Though any free energy model could have been used, we used the NRTL model was used by Renon and Prausnitz, 1965 here for A_{∞}^{E}/(RT):

$$\frac{A_{\infty}^{E}}{RT}=\sum_{i}x_{i}\left(\frac{\sum_{j}x_{j}\tau_{ji}g_{ij}}{\sum_{k}x_{k}g_{ki}}\right) \tag{2.2.5.46}$$

with

$$g_{ij}=\exp\left(-\alpha_{ij}\tau_{ij}\right) \qquad \left(\alpha_{ij}=\alpha_{ji}\right) \tag{2.2.5.47}$$

In this case, the partial derivatives of A_{∞}^{E}/(RT) with respect to the mole number of each species, which is the logarithm of the species activity coefficient, is given by:

$$\ln\gamma_{\infty i}=\frac{\sum_{j}x_{j}\tau_{ji}g_{ji}}{\sum_{k}x_{k}g_{ki}}+\sum_{j}\frac{x_{j}g_{ij}}{\sum_{k}x_{k}g_{kj}}\left(\tau_{ij}-\frac{\sum_{l}x_{l}\tau_{lj}g_{lj}}{\sum_{k}x_{k}g_{kj}}\right) \tag{2.2.5.48}$$

The mixing rule have been develop by examining experimental vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibrium data for several binary and ternary systems at both low pressures and high pressures, some of which have presented difficulty in other equation of state studies. The systems considers range from almost ideal to highly nonideal mixtures and include some systems that are traditionally described by equations of state, and other for which activity coefficient models are used. It should be noted that since we can always choose Eq.2.2.5.29 for A_{∞}^{E} our mixing rule can never be worse than the one-constant van der Waals one-fluid model and therefore will describe simple hydrocarbon systems quite well. In addition, as we show below, our mixing rule is also applicable to mixtures that previously could not be accurately described by equation of state.

In the following, we will use models for excess Helmholtz free energy, which are normally used for the excess Gibbs free energy. The relation between the two is:

$$G^{E}=A^{E}+PV^{E} \tag{2.2.5.49}$$

Excess Gibbs free energy (activity coefficient) models are used generally as low pressure, and V^{E} is usually small, so that the different between G^{E} and A^{E} is small. Further, if one examines the derivation of G^{E} models, it is evident that it is really a model for A^{E} which has been derived. Also, due to the absence of the $P\underline{V}^{E}$ term, $\underline{A}^{E}$ is much less pressure-dependent than G^{E} . Indeed, to an excellent approximation we have that:

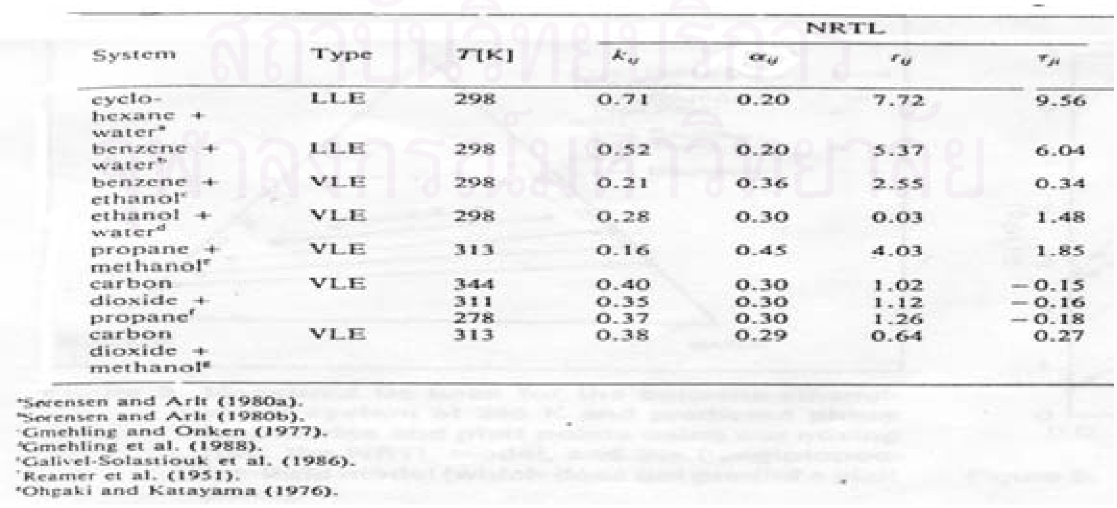
$$G^E(T,x,P=low)=A^E(T,x,P=low)=A^E(T,x,P=\infty) \qquad (2.2.5.50)$$

Therefore, in what follows, we will use the same functional form for A^E at infinite pressure as is now used for G^E at low pressure. It needs to be emphasized that it is the composition dependence of A^E which is important; it s not necessary that for the liquid phase of any specific mixture to be stable over the whole composition range $0<x<1$ to use our mixing rule.

The parameters in our mixing rule are cross virial coefficient interaction coefficient and the coefficient in the expression used for the excess Helmholtz free energy. Thus, for example, there are three parameters per binary if the Wilson model is used, and four parameters (including $\propto$) if the NRTL model is used.

In the following examples, we have used the Stryjek and Vera(1986) modification of the Peng-Robinson (1975) equation of state. To get the correct pure-component vapor pressures, the equation of state constants for all pure components were computed using the correlation of Stryjek and Vera (1986). For demonstration, the NRTL model was used in our calculations here, though any other A^E (or G^E) model could be used as well. Interaction parameters were obtained by regression of data for binary mixtures at the temperatures of interest; their values and the results of the correlation are given in Table 2.2.5.1. In all cases, the ternary results reported here are predictions using parameters fit to binary data only.

Table 2.2.5.1 : Binary Data Sources, Parameters [8]



System	Type	T[K]	NRTL			
			k_{ij}	α_{ij}	τ_{ij}	τ_{ji}
cyclohexane + water[a]	LLE	298	0.71	0.20	7.72	9.56
benzene + water[b]	LLE	298	0.52	0.20	5.37	6.04
benzene + ethanol[c]	VLE	298	0.21	0.36	2.55	0.34
ethanol + water[d]	VLE	298	0.28	0.30	0.03	1.48
propane + methanol[e]	VLE	313	0.16	0.45	4.03	1.85
carbon dioxide + propane[f]	VLE	344 311 278	0.40 0.35 0.37	0.30 0.30 0.30	1.02 1.12 1.26	−0.15 −0.16 −0.18
carbon dioxide + methanol[g]	VLE	313	0.38	0.29	0.64	0.27

[a] Sørensen and Arlt (1980a).
[b] Sørensen and Arlt (1980b).
[c] Gmehling and Onken (1977).
[d] Gmehling et al. (1988).
[e] Galivel-Solastiouk et al. (1986).
[f] Reamer et al. (1951).
[g] Ohgaki and Katayama (1976).

In contrast, here we have derived a theoretically correct mixing rule for cubic equations of state (though the procedure is applicable to other equations of state as well), which applies to all mixtures, A unique feature of this mixing rule is that, while t is independent of density when combined with an equation of state, it converges to the activity coefficient model prescribed by the user at high density and at low densities to a virial equation of state with a second virial coefficient that is quadratic in composition. We need to emphasize that it is not the mixing rule alone that produces this density dependence, since the mixing rule is density-independent, but rather the combination of the mixing rule and the equation of state.

This mixing rule provides a unified and consistent way of combining equations of state and excess free energy models to encompass mixtures that previously could only be described by one or the other. Further, not only is the model theoretically correct, but as we have shown here, it is reasonably accurate in describing both simple and complex phase behavior of binary and ternary systems for the diverse systems we have considered. Since we have complete freedom in choosing the expression A_{∞}^{E} , our mixing rule can be used to describe a wide variety of mixtures and phase behavior, and most importantly, systems that could not previously be described by equations of state.

2.2.6 Thermodynamic Functions from EOS : *Fugacity Coefficient* [5]

The fugacity coefficient of each component in a solution is required for phase equilibrium calculation. The fugacity coefficient expressions for the Redlich-Kwong, the Wilson, and the Soave equations are derived from Equations 2.2.6.1 and 2.2.1.1 Equation 2.2.6.1 is

$$\ln\phi_i = \frac{1}{RT}\int_{\infty}^{V}\left[\frac{RT}{V_t}-\left(\frac{\partial P}{\partial n_i}\right)_{T,V_t,n_j}\right]dV_t - \ln Z \qquad (2.2.6.1)$$

The derivative in this equation can be obtained from Equation 2.2.1.1 written in terms of total volume, V_t.

$$P = \frac{nRT}{V_t - nb} - \frac{n^2 a}{V_t\left(V_t + nb\right)}$$

Differentiating *P* in this equation with respect to n_i, at constant *T,* V_t and n_j, gives

$$\left(\frac{\partial P}{\partial n_i}\right)_{T,V_t,n_j} = \frac{RT}{V_t - nb} - \left[\frac{nRT}{(V_t - nb)^2} + \frac{n^2 a}{V_t(V_t + nb)}\right]\left(\frac{\partial(nb)}{\partial n_i}\right)_{n_j} + \frac{1}{V_t(V_t + nb)}\frac{\partial}{\partial n_i}\left(n^2 a\right)_{T,n_j} \quad (2.2.6.2)$$

Combining Equations 2.1.2.1.1 and 2.1.2.1.3 and making the integration give

$$\ln\phi_i = -\ln\left(Z - \frac{Pb}{RT}\right) + (Z-1)B_i^{'} - \frac{a}{bRT}\left(A_i^{'} - B_i^{'}\right)\ln\left(1 + \frac{b}{V}\right) \quad (2.2.6.3)$$

Using the notations of *A* and *B* instead of *a* and *b* gives

$$\ln\phi_i = -\ln(Z - B) + (Z-1)B_i^{'} - \frac{A}{B}\left(A_i^{'} - B_i^{'}\right)\ln\left(1 + \frac{B}{Z}\right) \quad (2.2.6.3a)$$

where $A_i^{'} = \frac{1}{an}\left[\frac{\partial(n^2 a)}{\partial n_i}\right]_{T,n_j}$

$$B_i^{'} = \frac{1}{b}\left(\frac{\partial(nb)}{\partial n_i}\right)_{n_j}$$

$B_i^{'}$ is obtained from Equation 2.2.2.4 for all the Redlich-Kwong , the Wilson, and the Soave equations:

$$B_i^{'} = \frac{b_i}{b} \quad (2.2.6.4)$$

on the other hand, $A_i^{'}$ varies from equation to equation as follows:

Redlich-Kwong ---- From Equation 2.2.5.5:

$$A_i^{i} = 2\left(\frac{a_i}{a}\right)^{0.5} \quad (2.2.6.5)$$

Soave ---- From Equation 2.2.5.6

$$A_i^{'} = \frac{1}{a}\left[2a_i^{0.5}\sum_j^N x_j a_j^{0.5}\left(1 - k_{ij}\right)\right] \quad (2.2.6.6)$$

Peng-Robinson ----The fugacity coefficient expression for Peng-Robinson equation may be derived from Equations 2.2.6.1 and 2.2.3.1, by using the same procedure used for deriving Equation 2.2.6.3. The expression is

$$\ln\phi_i = -\ln\left(Z - \frac{Pb}{RT}\right) + (Z-1)B_i^{'} - \frac{a}{2^{1.5}bRT}\left(A_i^{'} - B_i^{'}\right)\ln\left[\frac{V + \left(2^{0.5}+1\right)b}{V - \left(2^{0.5}-1\right)b}\right] \quad (2.2.6.7)$$

$$\ln\phi_i = -\ln(Z - B) + (Z-1)B_i^{'} - \frac{A}{2^{1.5}B}\left(A_i^{'} - B_i^{'}\right)\ln\left[\frac{Z + \left(2^{0.5}+1\right)B}{Z - \left(2^{0.5}-1\right)B}\right] \quad (2.2.6.7a)$$

where $B_i^{'}$ and $A_i^{'}$ are given by Equations 2.2.6.4 and 2.2.6.6, but with the b_i and a_i being given by Equations 2.2.3.3 and 2.2.3.4.

2.2.7 Alternate(computer) method for hydrocarbon-hydrocarbon and hydrocarbon-nonhydrocarbon vapor-liquid equilibrium [7]

Discussion

Vapor-liquid K-values for mixtures of hydrocarbons and nonhydrocarbons are estimated using the Soave modification of the Redlich-Kwong equation of state. In order to compute K-values,the equation of state must be solved to satisfy the following relationships:

$$T^L = T^V$$
$$p^L = p^V$$
$$f_i^L = f_i^V \quad i = 1,2,....n$$

The first two relationships equate t he temperature and pressure in each phase while the next “n” equations equate the fugacities of the individual components in each phase. Thus, there are (n + 2) equations which must be satisfied for an n component mixture.

A simplified flow chart for the equilibrium flash calculation is shown in the procedure diagram. To initiate the calculation, the feed composition and an estimate of the K-values are required.

The calculation steps are as follows:

Step 1: make a flash calculation using a set of assumed K-values and the known feed composition. This gives a set of vapor and liquid compositions.

Step 2: Use the composition to compute the composition dependent parameters in the equation of state, Based on the known temperature and pressure, find the saturated liquid and vapor volumes.

Step 3: Compute the fugacities of all the components in each phase from the equation of state.

Step 4: Check the fugacities. If the fugacities of all components are the same in each phase, stop the calculation.

Step 5: If the fugacities in each phase differ, read just the K-values and go to Step 1.

Similar schemes apply for dew – and bubble-point calculations. For example, gives a more detailed description of the calculations required and a computer program which may be readily adapted to the Soave equation.

The following equations apply to the Soave procedure.

A. Phase Volumes

The equation of state for both the liquid and vapor phases must be solved for the phase volumes based on the phase compositions and temperature and pressure. The compressibility factors in both the liquid and vapor phases are given by equation (2.2.7.1)

$$Z = \left(\frac{V}{(V-b)} - \frac{\alpha a}{RT(V+b)} \right) \qquad (2.2.7.1)$$

The equation of state may be solved iteratively for *Z* or it may be rearranged to a cubic form in V and solved analytically. The latter is recommended as it minimizes the possibility of selecting the incorrect volume root. When the cubic equation is solved, the largest volume is the saturated vapor volume and the smallest volume is the saturated liquid volume. The middle root has no physical significance so far as the calculation is concerned. In the equilibrium calculation, note that no matter which solution technique for the volume is employed, it must be repeated twice since the constants α, *a,* and *b* depend on the composition fo each phase.

B. Fugacity Coefficient

The fugacity of a component in a phase may be calculated once the fugacity coefficient has been evaluated. The relationship between the fugacity and fugacity coefficient is given by equation (2.2.7.2).

$$\overline{f}_i^N = \phi_i^N x_i p \qquad (2.2.7.2)$$

In terms of the Soave equation, the fugacity coeffcient in any liquid or vapor phase may be calculated from equation (2.2.7.3) once the volume of that phase has been determined.

$$In\phi_i^N = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{B}\left[\frac{2\sum x_j \alpha_{ij} a_{ij}}{\alpha a} - \frac{b_i}{b} \right] \ln\left(1 + \frac{B}{Z}\right) \qquad (2.2.7.3)$$

C. Equation Constants for Pure Components

The equation constants for all pure components are calculated from the critical temperature and pressure and the acentric factor.

In terms of the critical constants, ai and bi are given by Equations (2.2.7.4) and (2.2.7.5).

$$a_i = 0.42747 R^2 T_{c_i}^2 / p_{c_i} \tag{2.2.7.4}$$

$$b_i = 0.08664 R T_{c_i} / p_{c_i} \tag{2.2.7.5}$$

For all fluids αi is given by equation (2.2.7.6)

$$\alpha_i = \left[1 + S_{1_i} \left(1 - \sqrt{T_{r_i}}\right) + S_{2_i} \frac{\left(1 - \sqrt{T_{r_i}}\right)}{\sqrt{T_{r_i}}} \right]^2 \tag{2.2.7.6}$$

For components where S_1 and S_2 are not available, S_2 can be set equal to zero; and S_1 may be estimated by

$$S_{1_i} = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2 \tag{2.2.7.7}$$

For each component in the mixture, α_i is determined as follows:

Step 1: Obtain the value of S_1 from Table 2.2.7.1 If a value is not available for a particular compound, estimate a value from equation (2.2.7.7).

Step 2: Obtain a value for S_2 from Table 2.2.7.2 If no value is listed, set the parameter equal to zero.

Step 3: Determine α_i at the specified temperature using equation (2.2.7.6).

D. Equations for Composition Averaged Parameters

The composition averaged parameters αa and *b* are calculated from equations (2.2.7.8) and (2.2.7.9).

$$\alpha a = \sum \sum x_i x_j \alpha_{ij} a_{ij} \tag{2.2.7.8}$$

$$b = \sum x_i b_i \tag{2.2.7.9}$$

The cross mixture parameter $\alpha_{ij} a_{ij}$ is given by equation (2.2.7.9).

$$\alpha_{ij} a_{ij} = \left(1 - k_{ij}\right) \sqrt{\alpha_i \alpha_j a_i a_j} \tag{2.2.7.10}$$

E. Interaction Coefficients

The binary interaction coefficients are used to improve the vapor-liquid predictions. A binary interaction coefficient may be utilized for each binary pair in the multicomponent mixture. For example, for a ternary mixture of CO_2, H_2S_2, and methane, three binary interaction coefficients can be defined. These are as follows: (1) CO_2-H_2S, (2) H_2S-CH_4 and (3) CO_2-CH_4. For the best results, the binary interaction coefficients should be determined from experimental data for conditions commensurate with the subject design. For general calculations the binary interaction coefficients may be assigned as follows:

a. If available, use interaction coefficients from Table 2.2.7.3.

b. Estimate any unavailable interaction coefficients between H_2, H_2S, CO, CO_2, and N_2 with hydrocarbons using equations (2.2.7.1) through (2.2.7.5).

c. Estimate any unavailable interaction coefficients between methane and compounds containing six or more carbon atoms using equation (2.2.7.6).

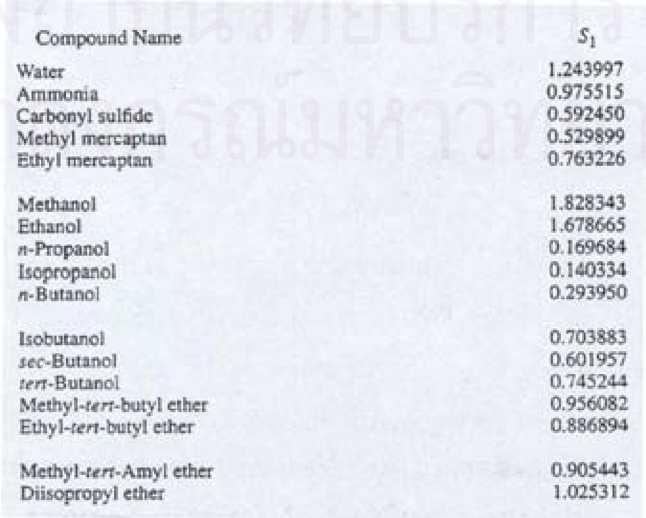
d. For close boiling systems, use values given below.

e. All remaining hydrocarbon-hydrocarbon interaction coefficients are zero:k_{ij}= 0.

Interaction parameters were determined from experimental binary vapor-liquid equilibrium Data for Table 2.2.7.3

Interaction coefficients have a dramatic impact on the accuracy of the predicted relative volatility of the subject pairs. Procedure should be used with caution if data are unavailable to generate interaction parameters for systems of this nature.

TABLE 2.2.7.1: Selected Value of S_1 for equation 2.2.7.6 [7]



Compound Name	S_1
Water	1.243997
Ammonia	0.975515
Carbonyl sulfide	0.592450
Methyl mercaptan	0.529899
Ethyl mercaptan	0.763226
Methanol	1.828343
Ethanol	1.678665
n-Propanol	0.169684
Isopropanol	0.140334
n-Butanol	0.293950
Isobutanol	0.703883
sec-Butanol	0.601957
tert-Butanol	0.745244
Methyl-*tert*-butyl ether	0.956082
Ethyl-*tert*-butyl ether	0.886894
Methyl-*tert*-Amyl ether	0.905443
Diisopropyl ether	1.025312

TABLE 2.2.7.2 : Selected value of S_2 for equation 2.2.7.6 [7]

Compound Name	S_2
NONHYDROCARBONS	
Hydrogen	-0.025891
Water	-0.201789*
Ammonia	-0.087598
Hydrogen sulfide	0.010699
Nitrogen	-0.011016
Carbon monoxide	-0.025280
Carbon dioxide	-0.004474
Argon	-0.011721
PARAFFINS	
Methane	-0.012223
Ethane	-0.012416
Propane	-0.003791
n-Butane	0.003010
Isobutane	0.006209
n-Pentane	-0.000636
Isopentane	-0.005345
Neopentane	0.000695
n-Hexane	-0.007459
2-Methylpentane	-0.003898
3-Methylpentane	-0.009786
2,2-Dimethylbutane	-0.006195
2,3-Dimethylbutane	-0.004579
n-Heptane	-0.003031
2-Methylhexane	-0.002132
3-Methylhexane	-0.002806
2,2-Dimethylpentane	-0.003786
2,3-Dimethylpentane	-0.001338
2,4-Dimethylpentane	0.000811
3,3-Dimethylpentane	-0.004779
3-Ethylpentane	0.000168
n-Octane	-0.000821
2,2-Dimethylhexane	-0.000599
2,3-Dimethylhexane	-0.002424
2,4-Dimethylhexane	-0.001943
2,5-Dimethylhexane	-0.001621
3,3-Dimethylhexane	-0.001728
3,4-Dimethylhexane	-0.001744
2-Methylheptane	-0.002094
3-Methylheptane	-0.004039
4-Methylheptane	-0.002870
2,2,3-Trimethylpentane	-0.001434
2,2,4-Trimethylpentane	-0.004045
2,3,3-Trimethylpentane	-0.003849
2,3,4-Trimethylpentane	-0.004313
2,2,3,3-Tetramethylbutane	0.035734
3-Ethylhexane	-0.002745
2-Methyl-3-ethylpentane	-0.002499
3-Methyl-3-ethylpentane	-0.004598
n-Nonane	0.005435
3,3-Diethylpentane	-0.009265
2,2,3-Trimethylhexane	0.012650
2,2,5-Trimethylhexane	-0.000017
2,2,3,3-Tetramethylpentane	0.002328
2,2,3,4-Tetramethylpentane	-0.002088
2,2,4,4-Tetramethylpentane	-0.001878
2,3,3,4-Tetramethylpentane	-0.005733
PARAFFINS (Continued)	
n-Decane	0.003324
n-Undecane	-0.012698
n-Dodecane	-0.001931
n-Tetradecane	0.010085
n-Pentadecane	-0.033625
n-Hexadecane	-0.002741
n-Octadecane	-0.003612
n-Eicosane	-0.014476
NAPHTHENES	
Cyclopropane	-0.017047
Cyclobutane	-0.014555
Cyclopentane	-0.003383
Methylcyclopentane	-0.001461
Ethylcyclopentane	-0.002891
1,1-Dimethylcyclopentane	-0.013551
cis-1,2-Dimethylcyclopentane	-0.006564
trans-1,2-Dimethylcyclopentane	-0.009015
cis-1,3-Dimethylcyclopentane	-0.001337
trans-1,3-Dimethylcyclopentane	-0.017759
n-Propylcyclopentane	0.012036
Isopropylcyclopentane	-0.008055
1-Methyl-1-ethylcyclopentane	-0.014972
1,1,2-Trimethylcyclopentane	-0.022620
1,1,3-Trimethylcyclopentane	-0.024026
1,*c*-2,*t*-4-Trimethylcyclopentane	-0.026470
n-Decylcyclopentane	0.003368
Cyclohexane	-0.004637
Methylcyclohexane	-0.000172
1,1-Dimethylcyclohexane	0.007389
cis-1,2-Dimethylcyclohexane	0.014432
trans-1,2-Dimethylcyclohexane	0.007290
cis-1,3-Dimethylcyclohexane	0.010622
cis-1,4-Dimethylcyclohexane	0.014903
trans-1,4-Dimethylcyclohexane	0.007723
n-Propylcyclohexane	0.021283
Isopropylcyclohexane	-0.033961
n-Butylcyclohexane	0.028388
sec-Butylcyclohexane	0.025957
tert-Butylcyclohexane	-0.000764
n-Decylcyclohexane	-0.003096
Cycloheptane	-0.004421
Cyclooctane	0.467088
OLEFINS	
Ethylene	-0.002805
Propylene	-0.006163
1-Butene	0.001178
cis-2-Butene	-0.005287
trans-2-Butene	-0.016832
Isobutene	0.000612
1-Pentene	-0.003670
cis-2-Pentene	-0.002330
trans-2-Pentene	-0.001574
2-Methyl-1-butene	-0.003510
2-Methyl-2-butene	-0.011281
3-Methyl-1-butene	-0.004255
1-Hexene	-0.003219
cis-2-Hexene	0.003966

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* Use only for low concentrations of water in hydrocarbons.

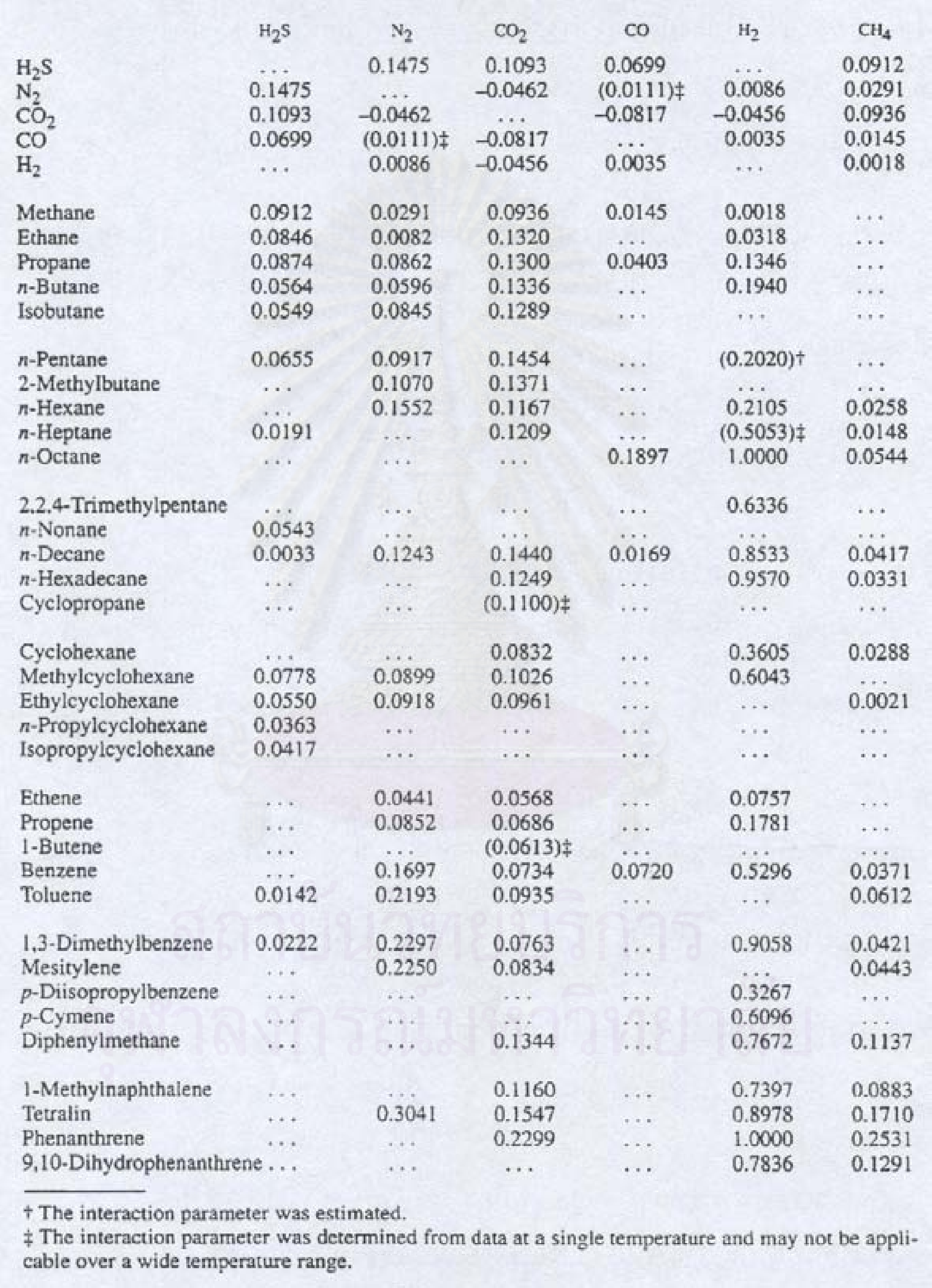
TABLE 2.2.7.2 : Selected value of S_2 for equation 2.2.7.6 (Continued)

Compound Name	S_2
OLEFINS (Continued)	
trans-2-Hexene	0.004891
cis-3-Hexene	–0.005113
trans-3-Hexene	0.000441
2-Methyl-1-pentene	0.005190
2-Methyl-2-pentene	0.011483
3-Methyl-1-pentene	–0.012116
4-Methyl-1-pentene	–0.000858
cis-3-Methyl-2-pentene	0.034720
trans-3-Methyl-2-pentene	–0.024994
cis-4-Methyl-2-pentene	0.001675
trans-4-Methyl-2-pentene	0.000704
2,3-Dimethyl-2-butene	0.016761
2,3-Dimethyl-1-butene	0.004265
3,3-Dimethyl-1-butene	–0.008468
2-Ethyl-1-butene	0.015833
1-Heptene	–0.006221
2-Methyl-1-hexene	0.018598
cis-3-Methyl-3-hexene	0.005120
2,4-Dimethyl-1-pentene	–0.001891
2,4-Dimethyl-2-pentene	0.008488
cis-4,4-Dimethyl-2-pentene	–0.005706
2,3,3-Trimethyl-1-butene	0.000205
3-Methyl-2-ethyl-1-butene	0.006036
1-Octene	–0.002307
2,4,4-Trimethyl-1-pentene	0.004362
1-Nonene	–0.000564
1-Decene	–0.005588
1-Undecene	0.010786
1-Dodecene	0.008653
1-Tridecene	0.005573
1-Tetradecene	0.008227
1-Pentadecene	0.000957
1-Hexadecene	0.010177
1-Octadecene	0.021612
DIOLEFINS AND ACETYLENES	
1,3-Butadiene	–0.009137
1,2-Pentadiene	0.011814
cis-1,3-Pentadiene	0.043579
trans-1,3-Pentadiene	0.052253
1,4-Pentadiene	0.057869
2,3-Pentadiene	0.023742
3-Methyl-1,2-butadiene	0.026266
2-Methyl-1,3-butadiene	0.023298
1,3-Cyclohexadiene	0.010481
1,5-Hexadiene	–0.016851
trans,trans-2,4-Hexadiene	0.000656
Acetylene	0.001831
Propyne	–0.002337
Dimethylacetylene	–0.109294
3-Hexyne	0.022376
AROMATICS	
Benzene	–0.000318
Toluene	–0.005125
Ethylbenzene	–0.004227
m-Xylene	–0.005645
o-Xylene	–0.006569
p-Xylene	–0.010556
AROMATICS (Continued)	
n-Propylbenzene	–0.007551
Isopropylbenzene	–0.008698
1,2,3-Trimethylbenzene	–0.014458
1,2,4-Trimethylbenzene	–0.010675
Mesitylene	–0.014912
m-Ethyltoluene	0.036093
o-Ethyltoluene	0.047885
p-Ethyltoluene	0.036093
1-Methyl-3-ethenyl benzene	–0.036510
n-Butylbenzene	–0.005215
Isobutylbenzene	–0.013419
sec-Butylbenzene	0.018480
tert-Butylbenzene	0.018084
m-Diethylbenzene	0.010750
o-Diethylbenzene	0.011193
p-Diethylbenzene	–0.006384
m-Cymene	0.004533
p-Cymene	0.000849
1,2,3,4-Tetramethylbenzene	–0.005169
1,2,3,5-Tetramethylbenzene	0.019944
1,2,4,5-Tetramethylbenzene	–0.014791
1,4-Diisopropylbenzene	0.022869
n-Decylbenzene	0.011198
Styrene	0.019670
DIAROMATICS AND OTHER HYDROCARBON RINGS	
cis-Decalin	–0.006020
trans-Decalin	0.011339
Tetralin	0.018025
Indene	–0.028120
Naphthalene	–0.005006
1-Methylnaphthalene	0.056699
2-Methylnaphthalene	–0.000472
2,6-Dimethylnaphtalene	–0.014329
Dibenzofuran	0.045513
Bicyclohexyl	–0.020675
Cyclopentene	–0.006625
Biphenyl	0.000398
Diphenylmethane	0.000798
SULFUR COMPOUNDS	
Methyl mercaptan	0.141244
Ethyl mercaptan	0.003516
Carbonyl sulfide	0.026420
OXYGENATED COMPOUNDS	
Methanol	–0.430885
Ethanol	–0.216396
n-Propanol	1.188769
Isopropanol	1.269059
n-Butanol	1.005612
Isobutanol	0.503560
sec-Butanol	0.600508
tert-Butanol	0.484002
Methyl-*tert*-butyl ether	–0.053074
Ethyl-*tert*-butyl ether	0.046280
Methyl-*tert*-amyl ether	0.010549
Diisopropyl ether	–0.033494

Note: For compounds not listed in Table 8D1.3, S_2 should be set to zero.

TABLE 2.2.7.3 : Recommend interaction coefficients for the Soave procedure [7]

I. *Interaction Coefficients Determined from Vapor-Liquid Equilibrium Data*



	H_2S	N_2	CO_2	CO	H_2	CH_4
H_2S	. . .	0.1475	0.1093	0.0699	. . .	0.0912
N_2	0.1475	. . .	–0.0462	(0.0111)‡	0.0086	0.0291
CO_2	0.1093	–0.0462	. . .	–0.0817	–0.0456	0.0936
CO	0.0699	(0.0111)‡	–0.0817	. . .	0.0035	0.0145
H_2	. . .	0.0086	–0.0456	0.0035	. . .	0.0018
Methane	0.0912	0.0291	0.0936	0.0145	0.0018	. . .
Ethane	0.0846	0.0082	0.1320	. . .	0.0318	. . .
Propane	0.0874	0.0862	0.1300	0.0403	0.1346	. . .
n-Butane	0.0564	0.0596	0.1336	. . .	0.1940	. . .
Isobutane	0.0549	0.0845	0.1289	. . .	. . .	. . .
n-Pentane	0.0655	0.0917	0.1454	. . .	(0.2020)†	. . .
2-Methylbutane	. . .	0.1070	0.1371	. . .	. . .	. . .
n-Hexane	. . .	0.1552	0.1167	. . .	0.2105	0.0258
n-Heptane	0.0191	. . .	0.1209	. . .	(0.5053)‡	0.0148
n-Octane	. . .	. . .	. . .	0.1897	1.0000	0.0544
2.2.4-Trimethylpentane	. . .	. . .	. . .	. . .	0.6336	. . .
n-Nonane	0.0543	. . .	. . .	. . .	. . .	. . .
n-Decane	0.0033	0.1243	0.1440	0.0169	0.8533	0.0417
n-Hexadecane	. . .	. . .	0.1249	. . .	0.9570	0.0331
Cyclopropane	. . .	. . .	(0.1100)‡	. . .	. . .	. . .
Cyclohexane	. . .	. . .	0.0832	. . .	0.3605	0.0288
Methylcyclohexane	0.0778	0.0899	0.1026	. . .	0.6043	. . .
Ethylcyclohexane	0.0550	0.0918	0.0961	. . .	. . .	0.0021
n-Propylcyclohexane	0.0363	. . .	. . .	. . .	. . .	. . .
Isopropylcyclohexane	0.0417	. . .	. . .	. . .	. . .	. . .
Ethene	. . .	0.0441	0.0568	. . .	0.0757	. . .
Propene	. . .	0.0852	0.0686	. . .	0.1781	. . .
1-Butene	. . .	. . .	(0.0613)‡	. . .	. . .	. . .
Benzene	. . .	0.1697	0.0734	0.0720	0.5296	0.0371
Toluene	0.0142	0.2193	0.0935	. . .	. . .	0.0612
1,3-Dimethylbenzene	0.0222	0.2297	0.0763	. . .	0.9058	0.0421
Mesitylene	. . .	0.2250	0.0834	. . .	. . .	0.0443
p-Diisopropylbenzene	. . .	. . .	. . .	. . .	0.3267	. . .
p-Cymene	. . .	. . .	. . .	. . .	0.6096	. . .
Diphenylmethane	. . .	. . .	0.1344	. . .	0.7672	0.1137
1-Methylnaphthalene	. . .	. . .	0.1160	. . .	0.7397	0.0883
Tetralin	. . .	0.3041	0.1547	. . .	0.8978	0.1710
Phenanthrene	. . .	. . .	0.2299	. . .	1.0000	0.2531
9,10-Dihydrophenanthrene	. . .	. . .	. . .	. . .	0.7836	0.1291

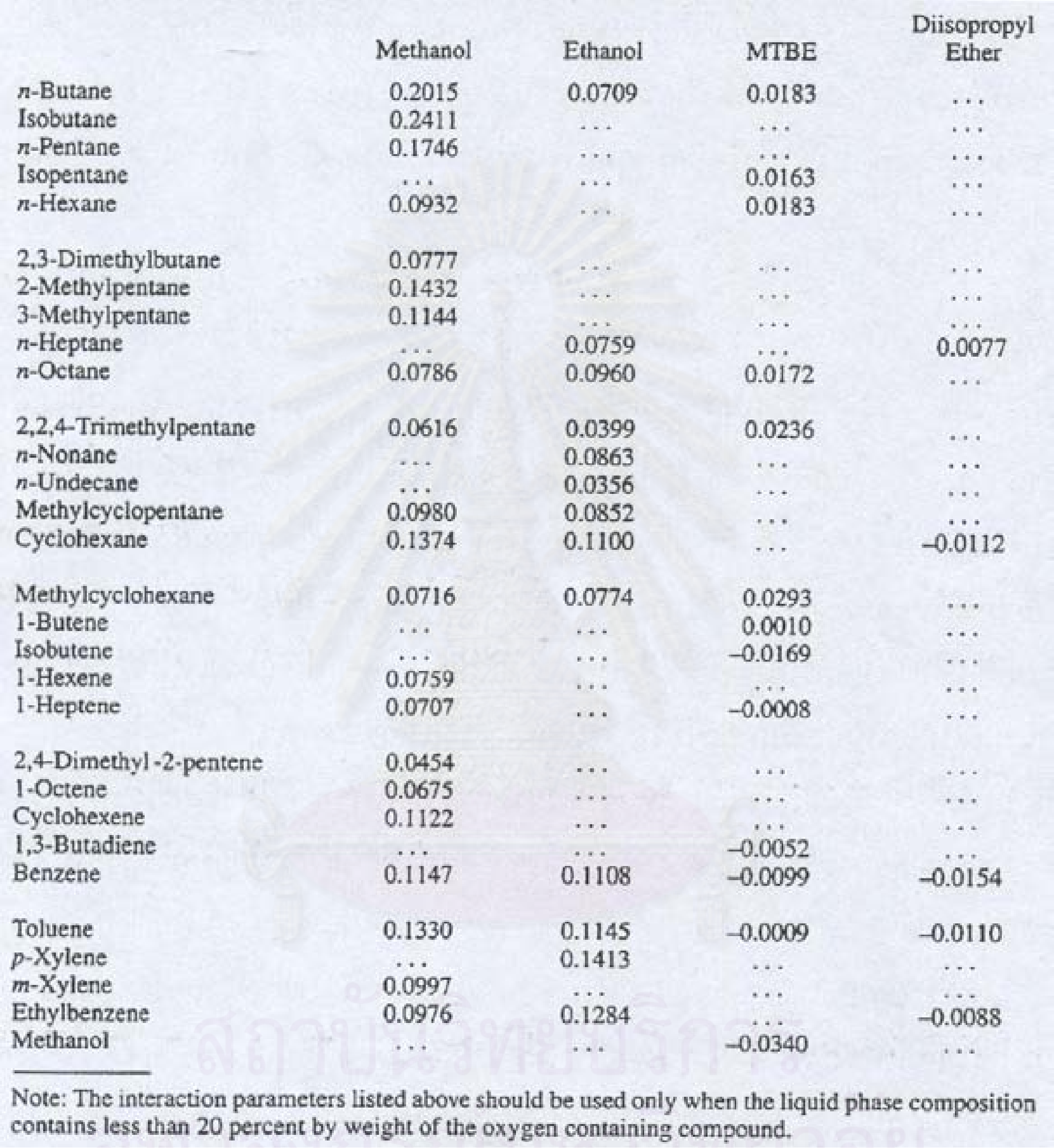
---

† The interaction parameter was estimated.

‡ The interaction parameter was determined from data at a single temperature and may not be applicable over a wide temperature range.

TABLE 2.2.7.3 : Recommened interaction coefficients for the Soave procedure (Continued)

II. *Interaction Coefficients for Systems of Hydrocarbons and Common Oxygenates*



	Methanol	Ethanol	MTBE	Diisopropyl Ether
n-Butane	0.2015	0.0709	0.0183	. . .
Isobutane	0.2411	. . .	. . .	. . .
n-Pentane	0.1746	. . .	. . .	. . .
Isopentane	. . .	. . .	0.0163	. . .
n-Hexane	0.0932	. . .	0.0183	. . .
2,3-Dimethylbutane	0.0777	. . .	. . .	. . .
2-Methylpentane	0.1432	. . .	. . .	. . .
3-Methylpentane	0.1144	. . .	. . .	. . .
n-Heptane	. . .	0.0759	. . .	0.0077
n-Octane	0.0786	0.0960	0.0172	. . .
2,2,4-Trimethylpentane	0.0616	0.0399	0.0236	. . .
n-Nonane	. . .	0.0863	. . .	. . .
n-Undecane	. . .	0.0356	. . .	. . .
Methylcyclopentane	0.0980	0.0852	. . .	. . .
Cyclohexane	0.1374	0.1100	. . .	−0.0112
Methylcyclohexane	0.0716	0.0774	0.0293	. . .
1-Butene	. . .	. . .	0.0010	. . .
Isobutene	. . .	. . .	−0.0169	. . .
1-Hexene	0.0759	. . .	. . .	. . .
1-Heptene	0.0707	. . .	−0.0008	. . .
2,4-Dimethyl-2-pentene	0.0454	. . .	. . .	. . .
1-Octene	0.0675	. . .	. . .	. . .
Cyclohexene	0.1122	. . .	. . .	. . .
1,3-Butadiene	. . .	. . .	−0.0052	. . .
Benzene	0.1147	0.1108	−0.0099	−0.0154
Toluene	0.1330	0.1145	−0.0009	−0.0110
p-Xylene	. . .	0.1413	. . .	. . .
m-Xylene	0.0997	. . .	. . .	. . .
Ethylbenzene	0.0976	0.1284	. . .	−0.0088
Methanol	. . .	. . .	−0.0340	. . .

Note: The interaction parameters listed above should be used only when the liquid phase composition contains less than 20 percent by weight of the oxygen containing compound.

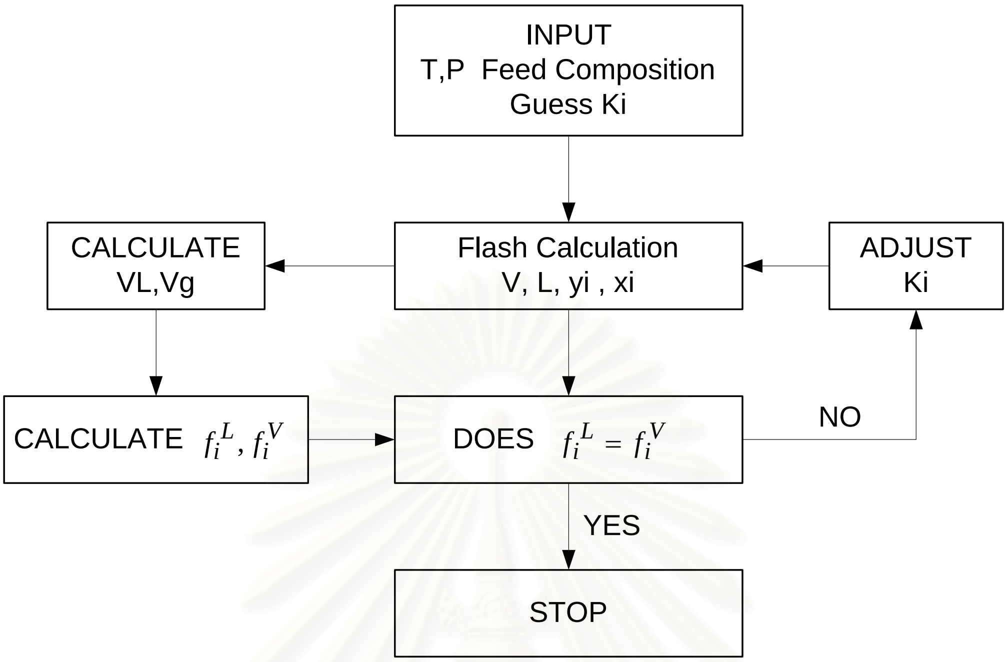


Figure 2.2.7.1 Procedure diagram for K-value calculations [7]

2.3 Hydrocarbons – Water System

2.3.1 Solubility of Hydrocarbons in Water [2]

Much is known about the solubility of hydrocarbons in water especially around 298 K. At higher temperatures, only the solubility of benzene has been extensively investigated. For this reason, our experimental work began with benzene to test the experimental procedure and confirm that accurate solubility measurements could be obtained.

The analysis of the new measurements and selected literature data was carried out with a simple equation:

$$\ln x_{hc} = A + B/T + C\ln T \qquad (2.3.1.1)$$

The values of A,B and C for three hydrocarbons are listed in Table 2.3.1.1. It is not claimed that Equation 2.3.1.1 can provide the best possible fit from 273 K to T_{3c}. However, in view of the considerable uncertainty in the available information, Equation 2.3.1.1 is entirely adequate to represent the temperature dependence of x_{hc}.

After the analysis of the solubility data with Equation 2.3.1.1 ,the meager information on the heat of solution is examined, with particular reference to predicting the minimum in the solubility. Then,the effect of pressure on soluubilities is examined and, finally the solubilities are converted to Henry's constants, which are needed for vapor-liquid equilibrium calculations.

Table 2.3.1.1 : Solubility of Hydrocarbons in Water [2]

$$\ln x_{hc} = A + B/T + C\ln T \text{ ; } T \text{ in } K$$

				Solubility Minimum		Solubility at T3c	
	A	B	C	T, K	x_{hc}	T_{3c}, K	x_{hc}
Benzene	-170.04018	6922.912	24.398795	283.8	3.954x10-4	541.7	2.528x10-2
Cyclohexane	-209.11689	8325.49	29.8231	279.2	1.193x10-5	529.4	1.748x10-3
n-Hexane	-367.98497	16128.646	52.820813	305.4	2.370x10-6	496.7	4.982x10-4

Benzene in Water

Probably more measurements have been made on the solubility of benzene in water than of all other liquid hydrocarbons combined. Many of these references are included in the *API Data Book(Chapter 9,1983)*.

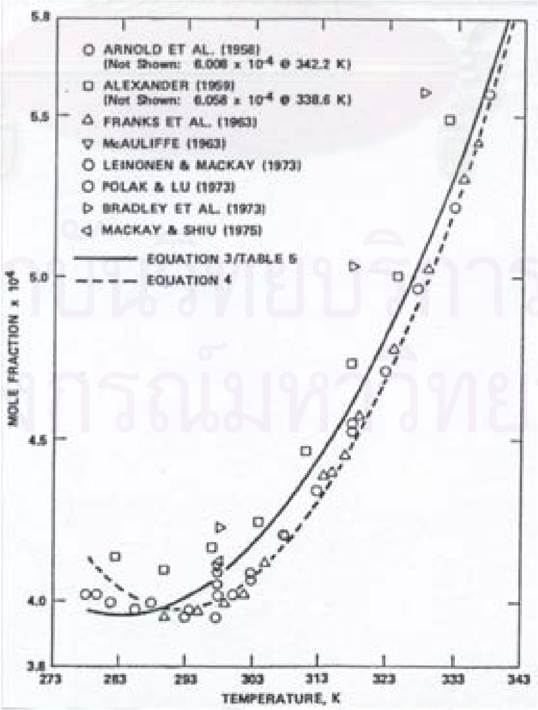


Figure 2.3.1.1 Low-temperature solubility of benzene in water.[2]

Figure 2.3.1.1 presents selected data between the melting point of benzene, 278.68 K, and the atmospheric azeotropic point, 342.40 K. Perhaps the most important reference in this range is Arnold et al.(1958); this reference also includes extensive literature information as well as data for the solubility of solid benzene. Figure 2.3.1.1 includes two lines; one calculated with Equation 2.3.1.1 and one with Equation 2.3.1.2:

$$\ln x_{hc} = -442.92352 + 15{,}357.083/T - 0.061492742T + 70.5431\ln T \quad (2.3.1.2)$$

Because the data of Bradley et al.(1973) and Alexander(1959) were not used in the regression with equation 2.3.1.2, the fit is in closer agreement with the data of Arnold eet al. And Franks et al.(1963). However, the addition of the *T* term in Equation 2.3.1.2 leads to concave-downwards curve above 450 K, which is incorrect. Accordingly, Equation 2.3.1.2 was discarded in favor of simpler Equation 2.3.1.1.

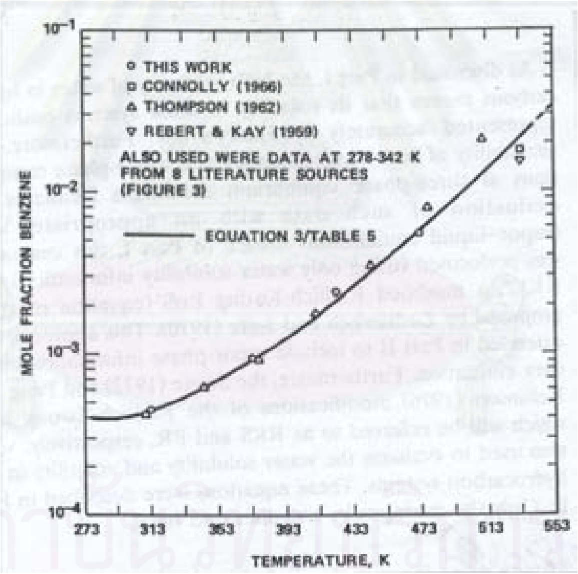


Figure 2.3.1.2 Solubility of benzene in water at three-phase equilibrium pressure.[2]

Figure 2.3.1.2 presents the solubility of benzene in water up to T_{3c} . The only high-temperture data included in the final evaluation, other than the new measurements, where those of Thompson(1962; Thomson and Snyder,1964) and the single values of Connolly (1966) and of Rebert and Kay(1959). As Figure 2.3.1.2 indicates, considerable uncertainty exists at 510-530 K. The fit with Equation 2.3.1.1 with the coefficients in Table 2.3.1.1 is a reasonable compromise, but additional data at 490-530 K would be needed to firmly establish the solubility of benzene as T_{3c} is approached.

2.3.2 Solubility of Water in Hydrocarbons [2]

Water is much more soluble in hydrocarbons than the hydrocarbons in water. Furthermore, the solubility of water increases very rapidly with increasing temperature—there is no minimum in the solubility of water—and reaches a very high value at T_{3c} . However, the available information at high temperature is just as limited as it is for the solubility of hydrocarbons in water. As before, much more is known about water/benzene than any other water/hydrocarbon system.

The analysis of the water solubility data was carried out with an equation that has one more term than Equation 2.3.1.1 :

$$\ln x_w = A + B/T + CT + D\ln T \qquad (2.3.2.1)$$

Table 2.3.2.1 : Solubility of Water in Hydrocarbons [2]

$\ln x_w = A + B/T + CT + D\ln T$; T in K

					Solubility at T_{3c}	
	A	B	C	D	T_{3c}, K	x_w
Benzene[a]	-1.64055	-2029.41	0.00900544	-	541.7	0.601[b]
Cyclohexane	-62.7645	-654.027	-	9.99967	529.4	0.276[c]
n-Hexane	-45.1714	-1635.73	-	7.53503	496.7	0.185[d]

a The use of the A,B and C terms led to a slightly better fit than that with A,B and D.

b Rebert and Kay (1959) report the value 0.6012 at 541.5 K; Umano and Hayano (1957) make no mention of T_{3c}, but report a solubility of 0.5925 at 544.7 K (where there should be no hydrocarbon-rich liquid phase).

c Rebert and Hayworth (1967) report a solubility at their T3c (528.9 K) that is clearly in error: 17.2 wt.% water or xw =0.493. That would make water more soluble in cyclohexane than it is in which is unlikely. It is possible that 17.2 should have been 7.2 wt.% water or xw = 0.266 .This lower value is consistent with a solubility reported by Rebert and Hayworth at 516.4 K: 5.2 wt.% water or xw=0.204.

d Rebert and Hayworth (1967) quote the results of Scheffer (1913), but xw=0.322, while Figure 2 in Scheffer's paper gives xw=0.268.

The values of the four constants for the three systems of interest are listed in Table 2.3.2.1; only three constants were used for each system.

The high solubility of water means that its volatility—from the saturated to the infinitely –dilute solution--- cannot be adequately represented by means of Henry's constant. It is necessary to introduce the effect of composition on volatility. For this reason, the water solubility has also been fitted with a modified Redlich-Kwong Equation of state, which can then be used in vapor-liquid equilibrium calculations.

The effects of temperature and pressure on the solubility of water are related, respectively, to the heat and volume of solution. The heat of solution is shown to be comparable to the energy of a hydrogen bond, while the volume of solution is small but positive (rather than negative, as it is for hydrocarbons in water).

Water in Benzene

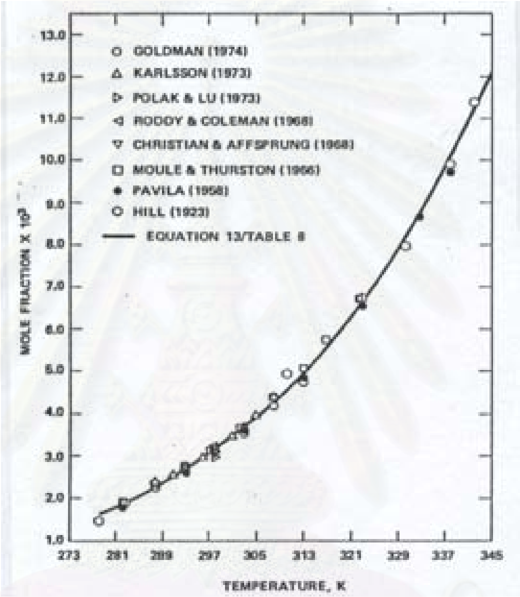


Figure 2.3.2.1 Low-temperature solubility of water in benzene.[2]

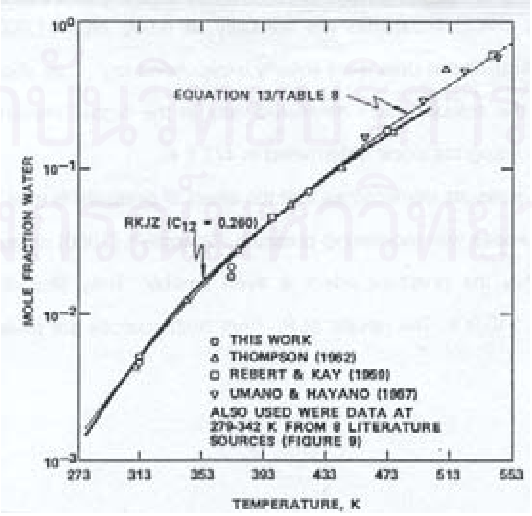


Figure 2.3.2.2 Solubility of water in benzene at three-phase equilibrium pressure.[2]

Figure 2.3.2.1 presents selected data for the low-temperature solubility of water in benzene. Figure 2.3.2.2 presents the solubility of water in benzene up to T_{3c} . The fit of the data with Equation2.3.2.1 is very satisfactory and the predicted x_w at T_{3c} is in good agreement with the data of Rebert and Kay(1959) and of Umano and Hayano (1957). The value of Thompson (1962) at 510.9 K is an extrapolation from a measurement at a higher pressure and will be discussed again later. The new measurements at 373 K are unaccountably too low.

2.3.3 Vapor-Liquid Equilibria of Water in Hydrocarbons [4]

The solubility of water in the hydrocarbons investigated in this work is at least two orders of magnitude higher than the solubility of hydrocarbons in water. However, the solubility of water in the hydrocarbons exhibits a negligible carbon number effect. The solubility of water increases very rapidly with increasing temperature and reaches a very high value at the three-phase critical end point, T_{3c} Unfortunately, there are relatively few literature data available for the solubility or volatility of water at high temperatures.

The water solubility and vapor-phase data obtained in this work suggest that the heat of solution for water in hydrocarbons approaches an infinite value as the temperature approaches T_{3c} That is,

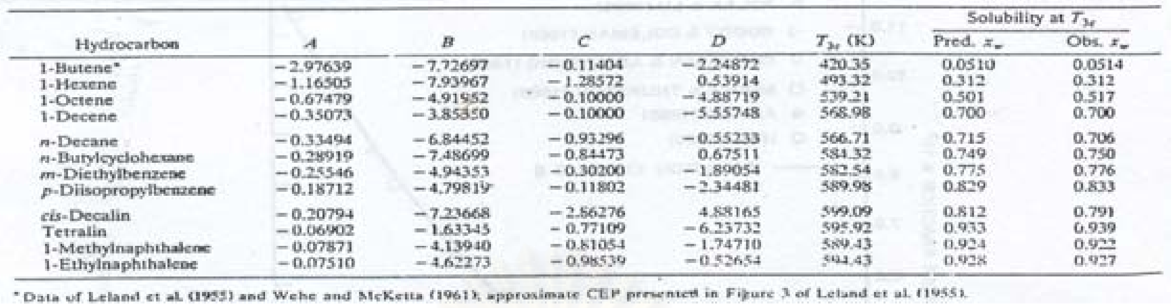
$$\lim_{T \to T_{3C}} \left(\frac{\partial \ln x_w}{\partial T} \right) \cong \lim_{T \to T_{3C}} \left(\frac{\Delta \overline{h}_i}{RT^2} \right) \to +\infty \qquad (2.3.3.1)$$

Accordingly, the analysis of the water solubility data was carried out with an equation that was capable of reproducing this behavior:

$$\ln x_w = A + B(1/T_r - 1) + C(1 - T_r)^{1/3} + D(1 - T_r) \qquad (2.3.3.2)$$

Table 2.3.3.1 : Solubility of Water in Hydrocarbons [4]

$$\ln x_w = A + B(1/T_r - 1) + C(1 - T_r)^{1/3} + D(1 - T_r)\ ;\ T_r = T/T_{3C}$$



Hydrocarbon	A	B	C	D	T_{3c} (K)	Solubility at T_{3c}	
						Pred. x_w	Obs. x_w
1-Butene*	−2.97639	−7.72697	−0.11404	−2.24872	420.35	0.0510	0.0514
1-Hexene	−1.16505	−7.93967	−1.28572	0.53914	493.32	0.312	0.312
1-Octene	−0.67479	−4.91552	−0.10000	−4.88719	539.21	0.501	0.517
1-Decene	−0.35073	−3.85550	−0.10000	−5.55748	568.98	0.700	0.700
n-Decane	−0.33494	−6.84452	−0.93296	−0.55233	566.71	0.715	0.706
n-Butylcyclohexane	−0.28919	−7.48699	−0.84473	0.67511	584.32	0.749	0.750
m-Diethylbenzene	−0.25546	−4.94353	−0.30200	−1.89054	582.54	0.775	0.776
p-Diisopropylbenzene	−0.18712	−4.79819	−0.11802	−2.34481	589.98	0.829	0.833
cis-Decalin	−0.20794	−7.23668	−2.86276	4.88165	599.09	0.812	0.791
Tetralin	−0.06902	−1.63345	−0.77109	−6.23732	595.92	0.933	0.939
1-Methylnaphthalene	−0.07871	−4.13940	−0.81054	−1.74710	589.43	0.924	0.922
1-Ethylnaphthalene	−0.07510	−4.62273	−0.98539	−0.52654	594.43	0.928	0.927

*Data of Leland et al. (1955) and Wehe and McKetta (1961); approximate CEP presented in Figure 3 of Leland et al. (1955).

where $T_r = T/T_{3c}$ Solubility data from 273 K up to and including T_{3c} were incorporated in the final data analysis. Values of the four constants for the hydrocarbon systems investigated are shown in Table 2.3.3.1,along with comparisons between predicted and observed solubilities at T_{3c}

2.3.4 Effect of Pressure; Volume of Solution [2]

The solubility of hydrocarbons in water, like most other liquid-phase peoperties,is a weak function of pressure. In Figure 2.3.4.1, the solubility of benzene has been plotted as a frnction of presure.

Thompson (1962) measured the solubility at 6.996 Mpa (1,000 psig) and 34.575 Mpa (5,000 psig). These data were linearly exrapolated to P_3 , as shown in Figure 2.3.4.1. At 510.9 K, the solubility was measured only at the higher pressure and was extrapolated to P_3 ,by using the slope determined at 477.6 K.

Thompson's results demonstrate that the effect of pressure is mall but positive. That is, solubility increases with increasing pressure. Connolly's (1966) measurements at 533.15 K suggest that the pressure effect is even smaller. They also disagree with Thompson's result at 510.9 K. The results at P_3 from both sources are plotted in Figure 2.3.1.2.

In contrast to Thompson and Connolly, Kudchadker and McKetta (1962) found an extremely large pressure effect. Their 510.9 K isotherm is included in Figure 2.3.4.1.Such a large pressure effect is suspect.

The thermodynamic relationship for the effect of pressure on the solubility is given by (Bradley et al., 1973):

$$\left(\frac{\partial \ln x_i}{\partial P}\right)_T \cong -\frac{\Delta\overline{v_i}}{RT} \qquad (2.3.4.1)$$

where $\Delta\overline{v_i}$ is the volume of solution (or the partial molar excess volume of component $i, \overline{v_i^E}$):

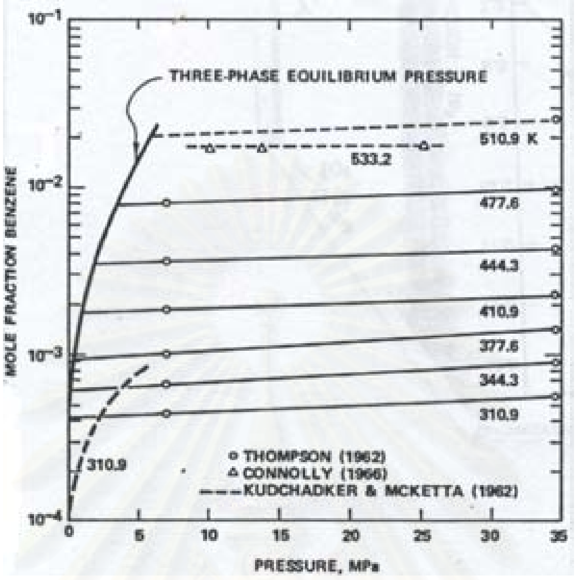


Figure 2.3.4.1. Effect of pressure on solubility of benzene in water.[2]

$$\Delta\overline{v_i} = \overline{v_i}(insolution) - v_i(pure\ hc) \qquad (2.3.4.2)$$

Bradley et al. (1973) have measured the solubility of benzene up to about 120 Mpa between 308 and 333 K.Bradley's results show that increases with pressure, but the effect is a very small one in agreement with Connolly (1966). At 310.9 K, Bradley's measurements lead to a $\left(-\Delta\overline{v}\right)\cong$ 4.5 cm.mol^{-1} ; Thompson's give 21.5 cm. (almost five times higher, but still a small effect), while the measurements of Kudchadker and McKetta lead to the extraordinarily high value of 2,890 cm.mol^{-1}., more than 600 times that obtained from Bradley's results.

The evidence is in favor of only a slight increase of the hydrocarbon solubility with pressure, at least up to pressures of about 100 Mpa. At higher pressures, the measurements of Bradley et al. (1973) on toluene up to 300 Mpa suggest a reverse, but still small, effect: the solubility decreases with increasing pressure.

2.4 Characteristic of Petroleum [5]

Many characteristic properties of pure substances have been measured and compiled over the years. These properties provide vital information for calculating the thermodynamic properties of the pure components as well as of their mixtures.

- 2.4.1 Molecular weight (*MW*)
- 2.4.2 Normal boiling point (*BP*)
- 2.4.3 Specific gravity (*SG*)
- 2.4.4 Critical Properties
    - 2.4.4.1 Critical temperature (T_c)
    - 2.4.4.2 Critical pressure (P_c)
    - 2.4.4.3 Critical compressibility factor (Z_c)
- 2.4.5 Acentric factor (ω)

Also defined in reference to the vapor pressure are the normal boiling point and the acentric factor. The normal boiling point is the temperature at which the vapor pressure is equal to one atmosphere. The specific gravity provides an excellent reference point in the liquid *P-V-T* relationship at low pressure, particularly for hydrocarbon liquids.

2.4.1 Molecular Weight (*MW*)

The molecular weight values in Table 2.4.1 are based on the atomic weights of oxygen = 15.9994, hydrogen = 1.008, and carbon = 12.011, and truncated after four significant digits.

The molecular weight can be exactly calculated for any mixtures consisting of known molecules if the molar or weight compositions are known. However, such a calculation is not possible for mixtures of unknown composition. In this case, the molecular weight is either measured or estimated. The measured values are undoubtedly much less accurate than those computed from atomic weights, and even not readily available for engineering applications. As a result, many estimation techniques have been developed and used for mixtures of unknown compositions, typically for petroleum fractions, which are narrow cuts of petroleum mixtures.

Kesler and Lee proposed the following equation for calculating the molecular weight of petroleum fractions:

$$\begin{aligned} MW = {} & -122726.0 + 948.4SG + (4.652 - 3.3287SG)T_b \\ & + (1 - 0.77084SG - 0.02058SG^2) * (1.3437 - 720.79/T_b)10^7/T_b \\ & + (1 - 0.80882SG + 0.02226SG^2) * (1.828 - 181.98/T_b)10^{12}/T_b^2 \quad (2.4.1.1) \end{aligned}$$

where MW = molecular weight

SG = specific gravity

T_b = normal boiling temperature, °R

More recently, Riazi proposed equation using the same variables . This equation, which has been included in the *API Technical Data Book*, is as follow:

$$MW = 204.38T_b^{0.118}SG^{1.88} * \exp(0.0218T_b)\exp(-3.07SG) \qquad (2.4.1.2)$$

Equations 2.4.1.1 and 2.4.1.2 both based on the normal boiling point and specific gravity, give similar results for pure compounds or petroleum fractions with a normal boiling point less than 800°F. For example, Equations 2.4.1.1 and 2.4.1.2 give *MW*'s of 137.0 and 139.6, respectively, for a petroleum fraction having *SG* = 0.816 and *BP* = 329°F, while the experimentally measured value for fractions is 137. However, for heavier petroleum fractions, the equations give significantly different values of molecular weight , resulting in more than a 10% difference for petroleum fractions of *BP*=1,000°F . It is interesting to note that the calculated *MW* varies linearly with T_b at high T_b in Equation 2.4.1.1 and exponentially in Equation 2.4.1.2. Considering this drastically difference on T_b, the large difference between the two equations in the extrapolated region are not surprising.

Both Equations 2.4.1.1 and 2.4.1.2 follow the general trend of pure compound molecular weight variation with *BP* and *SG.* In other words, for pure compounds the *MW* increases with decreasing *SG* for a given *BP*. This trend , however , often reverses for heavy petroleum fractions, such as those of heavy gas oils. Yet , neither equation reflects this reversal. It is also frequently observed that the experimental molecular weights are significantly different for petroleum samples are different. Form these observations, it is believed that neither equation could be used reliably for petroleum fractions boiling above

1,000°F . It also appears that one or more additional parameters are needed for developing a reliable molecular weight correlation for heavy petroleum fractions.

In any event, the calculated molecular weight significantly affect the separation process calculations for heavy petroleums, simply because the process calculations require the *MW* for converting the amount of each fraction of petroleum, commonly given in either volumetric or weight flow rates, to mole fraction compositions. Note that only molar compositions can be used in the vapor-liquid equilibrium calculations because it is the molecules that move across the phase boundary. Therefore, it is important to use accurate molecular weights for reliable vapor-liquid equilibrium calculations for heavy petroleum fractions.

2.4.2 Normal Boiling Point

The normal point is easy to measure , thus most abundantly available in high accuracy. This is why the normal boiling point , together with the specific gravity, has been dominantly used for correlating other properties, such as the molecular weight and the critical properties. Equations 2.4.1.1 and 2.4.1.2 are examples. The boiling point also provides the basis for measuring the other properties , such as the density and the heat of vaporization. In Table 2.4.1, all the normal boiling points are measured values except for ethyne, for which the normal boiling point is replaced by the sublimation point, as the compound cannot exist as liquid at one atmosphere.

For hydrocarbon mixtures, such as petroleum fractions, the normal boiling point cannot be unequivocally defined, because a petroleum fraction actually boils over a range of temperature. There are five different methods of defining the normal boiling point for petroleum fractions: volume average boiling point (*VABP*), molar average boiling point (*MABP*), weight average boiling point (*WABP*), cubic average boiling point (*CABP*), and mean average boiling point (*MeABP*)

$$VABP = \sum_{i}^{N} x_{vi} T_{bi} \qquad (2.4.2.1)$$

$$MABP = \sum_{i}^{N} x_{i} T_{bi} \qquad (2.4.2.2)$$

$$WABP = \sum_{i}^{N} x_{wi} T_{bi} \qquad (2.4.2.3)$$

$$CABP = \left(\sum_{i}^{N} x_{wi} T_{bi}^{1/3}\right)^{3} \quad (2.4.2.4)$$

$$MeABP = (MABP + CABP)/2 \quad (2.4.2.5)$$

where T_{bi} = normal boiling point of component *i*, in any temperature units except for *CABP* in which the temperature must be in absolute unit.

x_{vi} = volume fraction of component *i*

x_i = mole fraction of component *i*

x_{wi} = weight fraction of component *i*

These five expressions for calculating normal boiling points result in values that do not differ significantly from one another for narrow boiling petroleum fractions.

These five different averages have been widely used when the normal boiling point and the specific gravity were the most common correlating parameters for hydrocarbon properties. But in the past decade, the importance of these methods has been greatly diminished as the corresponding state methods have been extended to property calculations for heavier petroleum mixtures. Now the common practice is to cut the petroleum mixtures sufficiently narrow so that the mid-point can be used as the normal boiling point of the cut in the application of corresponding state methods.

2.4.3 Specific Gravity

The specific gravity of a liquid is defined as the ratio of the density of the liquid to that of water at 60°F and one atmospheric pressure. Because the water density is practically unity (0.999022 g/ml) at this condition, the specific gravity is generally considered as the density of the liquid at 60°F for all practical purpose of engineering calculations.

Because this property is defined at a fixed temperature of 60°F, its values cannot be obtained for certain light hydrocarbons that do not exist as liquid at one atmospheric pressure. For such hydrocarbons, Table 2.4.1 lists the values taken at the saturation pressures with the following exceptions. For methane and ethene the values were obtained by extrapolation, and for ethyne the solid density at the sublimatation point is given. Also , it is not possible to define the specific gravity for high molecular weight hydrocarbons that are solid at 60°F and 1 atmosphere. Table 2.4.1 does not include such hydrocarbons, however.

There is another definition of “gravity” that has been used in the hydrocarbon industry to define the “heaviness” of petroleums. This is called *API* gravity and is precisely related to the specific gravity by the following expression:

$$^{o}API = (141.5/SG) - 131.5 \qquad (2.4.3.1)$$

and

$$SG = 1.0475 - 1{,}511x10^{-4}T_b + 7.127x10^{-8}T_b^2 - \frac{116.4}{T_b} \qquad (2.4.3.2)$$

2.4.4 Critical Properties

The importance of critical properties in corresponding states methods cannot be over emphasized, because the methods are hinged on this point. Over the year, the critical properties have been measured and compiled for many hydrocarbons and other substances. Kudchadker et al. have made a comprehensive review of the experimental values of the critical properties and recommended a most reliable set of the properties for each substance. Most of the critical properties given in Table 2.4.1 are from this source.

For some hydrocarbons that easily undergo thermal decomposition or polymerization at temperatures and pressures near or below the critical point, reliable experimental measurements of the critical properties are practically impossible. For such fluids, plus those substances for which the critical properties have not yet been measured, the properties are commonly estimated from either group contribution methods or empirical equations.

2.4.4.1 Method for the pseudocritical temperature of petroleum fractions [7]

Equation (2.4.4.1) is used to calculate the pseudocritical temperature of petroleum fractions. For this purpose, specific gravity and mean average boiling point must be known or estimated. The equation is as follow:

$$T_{pc} = 10.6443\left[\exp\left(-5.1747x10^{-4}T_b - 0.54444SG + 3.5995x10^{-4}T_bSG\right)\right]T_b^{0.81067}SG^{0.53691} \qquad (2.4.4.1)$$

Where:

Tpc = pseudocritical temperature of petroleum fraction, degrees Rankine.

Tb = mean averge boiling point, degrees Rankine.

Procedure

Step 1 : Obtain the specific gravity of the petroleum fraction.

Step 2 : Obtain the mean average boiling point.

Step 3 : Calculate the pseudocritical temperature using equation (2.4.4.1)

2.4.4.2 Method for the pseudocritical pressure of petroleum fractions [7]

Equation (2.4.4.2) calculates the pseudocritical pressure of petroleum fractions. For this purpose, specific and mean average boiling point must be known or estimated. The equation is as follows:

$$P_{pc} = 6.162x10^{6}\left[\exp\left(-4.725x10^{-3}T_b - 4.8014SG + 3.1939x10^{-3}T_b SG\right)\right]T_b^{-0.4844}SG^{4.0846} \quad (2.4.4.2)$$

Where:

Ppc = pseudocritical pressure ,pounds per square inch absolute.

Tb = mean average boiling point, degrees Rankine.

Procedure

Step 1 : Obtain the specific gravity of the petroleum fraction.

Step 2 : Obtain the mean average boiling point.

Step 3 : Calculate the pseudocritical pressure using equation (2.4.4.2)

2.4.5 Acentric factors [5]

As the defining equation indicates, the acentric factor can be calculated only if the critical temperature, the critical pressure, and the vapor pressure at T_r (reduced temperature) = 0.7 are known. Therefore, its accuracy is dependent on the vapor pressure as well as the critical properties used. Passut and Danner reported a total of 192 acentric factors calculated from experimental vapor pressures and the critical properties contained in *API Technical Data Book.*

Although the acentric factor is as much needed as the critical properties for Pitzer's type of three-parameter are not as readily available as T_c and P_c. Therefore, it is often necessary to estimate the parameter via a correlation. The first acentric factor correlation was presented by Edmister in 1961. This method has been widely used to estimate the acentric factors for pure fluids as well as petroleum fractions.

This correlation uses the following simple vapor pressure equation:

$$log\ P^S = A\ \ + B/T \tag{2.4.5.1}$$

The two constants in this equation may be eliminated by using two sets of P and T , i.e., one atmosphere and T_b , and the criticals, P_c and T_c , to obtain:

$$\log P_r^S = \left(\log P_{br}^S\right)\frac{T_r^{-1}-1}{T_{br}^{-1}-1} \tag{2.4.5.2}$$

where T_r = reduced temperature

T_{br} = reduced temperature at normal boiling point

P_r = reduced vapor at T_r

P_{br} = reduced vapor at T_{br}

Writing this equation at T_r = 0.7 and combining with Equation

$$\omega = -\frac{3}{7}\left(\frac{\log P_{br}^S}{T_{br}^{-1}-1}\right)-1 \tag{2.4.5.3}$$

Lee and kesler derived a more complicated but more accurate expression for heavier fluids from their vapor pressure equation. Since it already satisfies the definition of acentric factor, the acentric factor can be calculated from any known pair of T_r and P_r . As in the case of Equation 2.4.5.3, the T_r and P_r values at the normal boiling point were used:

$$\omega = \frac{\ln P_{br}^S - f^{(0)}\left(T_{br}\right)}{f^{(1)}\left(T_{br}\right)} \tag{2.4.5.4}$$

where $f(0) = 5.92714 - 6.09648/T_r - 1.28862\ lnT_r + 0.16934T_r^6$

$f(1) = 15.2518 - 15.6875/T_r - 13.4721\ lnT_r + 0.4357T_r^6$

From a mathmetical point of view, the acentric factors represented by Equation 2.4.5.3 and 2.4.5.4 become indeterminant for a hypothetical heavy fluid for which the critical temperature and the critical pressure are equal to the normal boiling temperature and one atmosphere, respectively. Although this is a hypothetical case , there is a definite trend that the heavier a fluid is, the nearer to unity is its T_{br} value, while P_c become smaller. As a result, both Equations 2.4.5.3 and 2.4.5.4 become sensitive for heavy fluids. To alleviate the sensitivity, Kesler and Lee proposed an empirical acentric factor equation for the fluids having $T_{br} > 0.8$.

$$\omega = -7.904 + 0.1352K - 0.007465K^2 + 8.359T_{br} + (1.408 - 0.01063K)/T_{br} \qquad (2.4.5.5)$$

where $K = (T_b)^{1/3}/SG$ is Watson characterization factor

2.4.6 ASTM Distillation

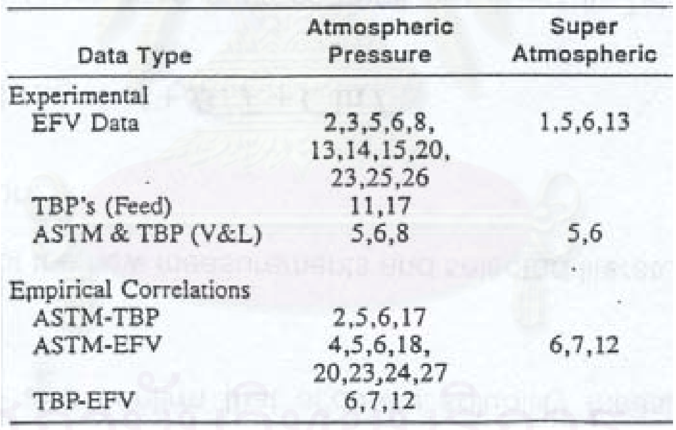
The graphical methods of predicting phase equilibrium for petroleum fractions are based upon empirical correlations of experimental data on samples of the oils. Laboratory evaluation of crude oils includes many measurements-batch distillations to obtain boiling point and specific gravity assays; separation into the various products of gas, gasoline, naphtha, kerosene, diesel, etc.; analyses for sulfur, wax, and asphalts; analyses of viscosities of the middle and heavy oils; etc. All this information is useful in evaluating and pricing the crude oil. It is also useful to the refiner in designing the processing plants for manufacturing the petroleum products for the market.

These assays are boiling point temperatures versus liquid volume percent, or volume fraction, distilled, and specific gravity versus liquid volume percent, or fraction distilled. These distillations are made in batch laboratory stills that are charged with 100 to 1,000 ml, or more, oil, and are of two types. One method, which is designated as an ASTM (American Society for Testing Materials), is a differential distillation, i.e., without reflux so that the “components” of the oil are not collected pure in the order of their boiling points. The other method, which is designated as a TBP (true boiling point), is a refluxed distillation so that the “components” of the oil are distilled and collected nearly pure in order of their individual boiling points.

Included are both experimental data correlations for atmospheric, vacuum, and high-pressure flash curves, and also the same kind of data for the true boiling point assays. Table 2.4.6.1 provides a key to these references, wherein two categories of literature are shown: (1) experimental data and (2) empirical correlations. The references giving data and correlations are divided according to pressure, i.e., atmospheric, super atmospheric and vacuum.

Two types of distillation experimental data were used in developing the correlations presented herein – analytical distillations and equilibrium flash vaporization separations. The first are batch distillation assays run to define the mixture. The second are usually continuous flashes yielding vapor and liquid products that coexist in equilibrium. These data were from published sources and from the Richmond Laboratory of Chevron Research Company.

Table 2.4.6.1 : Key to Literature References on Equilibrium Flash Vaporization (EFV) Distillations and ASTM and TBP Assays [5]



Data Type	Atmospheric Pressure	Super Atmospheric
Experimental		
EFV Data	2,3,5,6,8, 13,14,15,20, 23,25,26	1,5,6,13
TBP's (Feed)	11,17	
ASTM & TBP (V&L)	5,6,8	5,6
Empirical Correlations		
ASTM-TBP	2,5,6,17	
ASTM-EFV	4,5,6,18, 20,23,24,27	6,7,12
TBP-EFV	6,7,12	

Two laboratory experimental methods were used in developing the empirical correlations given in this Examples of these two types of analytical distillation assays are:

Petroleum Fraction Distillation Interconversions [7]

ASTM and true boiling point (TBP) analytical distillations and used to define the volatility characteristics of petroleum fractions and other complex mixtures. Both are batch distillations which differ mainly in the degree of fractionation obtained during the distillation.

ASTM D86 distillations are run in an Engler flask. No packing is employed , and reflux results only from heat losses through the neck of the flask. ASTM distillations are more widely used than TBP distillations because the former are simpler , less expensive , require less simple , and require only approximately one-tenth as much time. ASTM distillations are standardized. TBP distillations vary appreciably in procedure and apparatus.

ASTM Method D86: This method is used for the distillation of motor gasolines, aviation gasolines, aviation turbine fuels, naphthas, kerosenines, gas oils, distillate fuel oils, and similar petroleum products. It is carried out at atmospheric pressure. An exposed thermometer is used, and temperatures are reported without stem corrections. ASTM D86 distillations are plotted in volume percent.

In ASTM D86 distillation there may be a residue left in the distillation equipment as well as a difference between the volume of the original charge and the sum of the distillate and residue. This difference is usually termed “loss” and is generally thought of as volatile components of the charge which have not been recondensed. For preparation of an ASTM distillation for conversion to a TBP distillation, the percent distilled at the reported temperature is the sum of the distillate collected and the loss.

When heated sufficiently hot, petroleum fractions undergo thermal cracking. Although a function of chemical composition, the amount and severity of thermal cracking increase with increasing boiling point, contact time, pressure and temperature. Early editions of this chapter included a correction for cracking for observed ASTM D86 temperatures above 475 F. No correction for cracking is now recommended.

TBP distillations are performed in columns with 15 to 100 theoretical plates at relatively high reflux ratios. The high degree of fractionation in these distillations gives accurate component distributions for mixtures. The lack of use of a standardized apparatus and operational procedure is a disadvantage, but the variations between various laboratories are small because a close approach to perfect separation by boiling point is usually achieved. A TBP curve is also shown in Figure 2.4.6.1 for comparison with an ASTM D86 distillation.

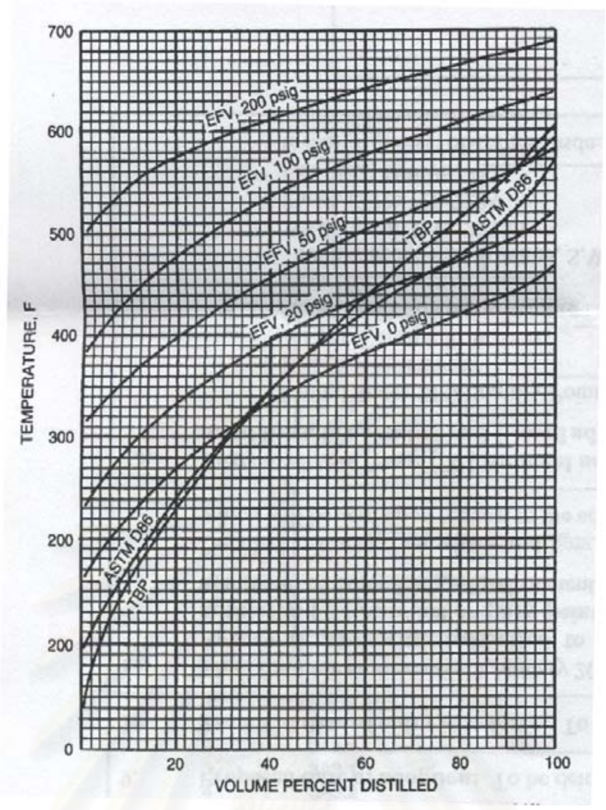


Figure 2.4.6.1 ASTM, True Boiling Point, and Equilibrium Flash Vaporization Distillation Curves for a Naphtha-Kerosine Blend [7]

An equilibrium flash vaporization is an experiment carried out at constant pressure to determine the temperature-volume percent distilled relation. The EFV curve is a plot of temperature against percent by volume of liquid distilled, at a constant pressure. Each point on the EFV curve represents a separate equilibrium experiment. The number of equilibrium experiments needed to define all portions of the EFV curve varies with the shape of the curve. Normally, at least five such experiments are required. Figure 2.4.6.1 also shows the EFV curves of a naphtha-kerosine blend at atmospheric and several superatmospheric pressures compared to ASTM D86 and TBP distillations. The tedious procedures necessary to obtain experimental EFV data have made this type experiment quite rare at this time. Thus, correlations involving EFV have been eliminated from this chapter.

Users are emphatically cautioned against relying heavily on results obtained from these correlations. Because of a lack of standardization and other inherent inadequacies in the methods, the existing ASTM, TBP, and AD data on the same fractions are not sufficiently precise or consistent to develop accurate correlations. Consult the Comments on each Procedure for the accuracy of each method before use.

The correlations of this chapter were developed using data for hydrocarbon stocks and fractions which included many components and exhibited smooth distillation curves. The correlations do not apply to mixtures of few compounds with widely different boiling points.

ASTM Distillations [5]
  D-86 for light petroleum products
  D-158 for gasolines through light gas oils
  D-1160 at 760 mm for middle oils
  D-1160 at 10 mm for heavy oils
TBP Distillations
  Podbielniak Hypercal
  Oldershaw column
  Spinning auger or band

The ASTM distillations are more rapid and cost less to run than the TBP distillations, while the latter are more accurate in defining the characteristics of the oil fractions. When available, the TBP assays are preferred as the basis for calculating properties, but they are often not available. ASTM assays are frequently the only analytical distillations available, so it is necessary to include ASTM's in the correlations and calculations.

TBP distillations usually require larger charge samples. The sample quantity depends upon the sizes of the still flash and the column, which are determined by the number and size of the TBP cuts that are to be collected for making specific gravity measurements. Typical numbers and size of the TBP cuts that are to be collected for making specific gravity measurements. Typical numbers and sizes of these cuts may be ten 10% cuts or twenty 5% cuts. Sample requirements for analytical tests must be considered in selecting sizes of the equilibrium flash vaporization apparatus, as well as those of the batch distillation stills.

Interconversion of ASTM D86-TBP distillations at atmospheric pressure [7]

The following equation is used to convert an ASTM D86 distillation 50% point temperature to a true boiling point distillation 50% point temperature.

$$\text{TBP}(50) = 0.87180(\text{ASTM D86}(50))^{1.0258} \qquad (2.4.6.1)$$

Where :

TBP(50) = true boiling point distillation temperature at 50 volume percent distilled, degree Fahrenheit.

ASTM D86(50)=observed ASTM D86 distillation temperature at 50 volume percent distilled, degrees Fahrenheit.

To determine the difference between adjacent ct points, use the following equation:

$$Y_i = AX_i^B \qquad (2.4.6.2)$$

Where:

Y_i = difference in true boiling point distillation temperature between two cut points, degrees Fahrenheit.

X_i = observed difference in ASTM D86 distillation temperature between two cut points, degrees Fahrenheit.

A,B = constants varying for cut point ranges, described as follows.

i	Cut Point Range	*A*	*B*	MaximumAllowable X_i,(F)
1	100%-90%	0.11798	1.6606	-
2	90%-70%	3.0419	0.75497	100
3	70%-50%	2.5282	0.82002	150
4	50%-30%	3.0305	0.80076	250
5	30%-10%	4.9004	0.71644	250
6	10%-0%	7.4012	0.60244	100

To determine the true boiling point temperature at any percent distilled, add or subtract the proper difference(s) from the predicted 50% true boiling point temperature.

$$\text{TBP}(0) = \text{TBP}(50)-Y_4-Y_5-Y_6$$

$$\text{TBP}(10) = \text{TBP}(50)-Y_4-Y_5$$

$$\text{TBP}(30) = \text{TBP}(50)-Y_4 \qquad (2.4.6.3)$$

TBP(70) = TBP(50)+Y_3

TBP(90) = TBP(50)+Y_3+Y_2

TBP(100) = TBP(50)+Y_3+Y_2+Y_1

Procedure

Step1 : Use equation(2.4.6.1)to calculate the TBP distillation temperature at 50% distilled.

Step2 : Use equation(2.4.6.2)to calculate necessary TBP differences.

Step3 : Use equation(s)(2.4.6.3)to calculate desired TBP distillation temperatures.

2.4.7 Pseudo Components of Petroleum for VLE Calculations [5]

The basis for this modification is the employment of a numerical integration technique, suggested in 1971 by Taylor and Edmister for use in solving petroleum and natural gas processes. The following description of that improvement in graphical integration technique is from that reference.

The material balance of an equilibrium flash vaporization for a component represented by a point on the molar TBP curve for the feed is

$$Fdm_F = Vdm_V + Ldm_L \qquad (2.4.7.1)$$

Since m_F is the total mole fraction distilled up to the temperature T on the TBP curve of the feed, the differential dm_F represents the mole fraction in the feed of the component having a true boiling point of T . Analogous meanings are associated with dm_L and dm_V . The equilibrium relationship for this component is

$$dm_V = Kdm_L \qquad (2.4.7.2)$$

Hence, by combining Equations 2.4.7.1 and 2.4.7.2

$$dm_L = (Fdm_F)/(L + KV) \qquad (2.4.7.3)$$

Integration of Equation 2.4.7.3 over the range of all components in the feed gives

$$\int_0^1 dm_L = 1 = \int_0^1 \left(1/\left(L + KV\right)\right) Fdm_F \qquad (2.4.7.4)$$

In one form of the flash problem, the flash pressure and the quantities of liquid and vapor products must be determined. The solution is obtained by iterative calculations. Flash temperature are assumed unit Equation 2.4.7.4 is satisfied.

Equation 2.4.7.4 was solved by graphical integration in this method the curve being integrated must be divided into an even number of equally sized divisions *n* on the m_F scale, given *n+1* temperature points on the TBP curve.

Thus, the interval width *h* on the m_F abscissa scale is the same for all divisions, while the temperature intervals will be irregular. The total intervals of integration includes all of the “components” in the feed.

For example, 20 divisions along the m_F scale gives a total of 21 pseudo components that are defined by the boiling points and specific gravities at these points. With 10 divisions, the total pseudo components would be 11 . Any even number of divisions may be used, although 10 or 20 are the usual numbers chosen. The quantity m_F takes on fractional values from 0 to unity . This corresponds to components with true boiling point of the mixture.

When this interval of integration is broken into *n* sub-intervals for the application of Simpson’s Rule, the integral is approximated by a summation, as follow:

$$\int_0^1 \frac{dm_f}{L+KV} = \frac{\frac{1}{3}h}{\left(L+KV\right)_{t1}} + \sum_{i=2}^{n} \frac{\left(1/3h\right)\left\{3+\left(-1\right)^i\right\}}{\left(L+KV\right)_{ti}} + \frac{\frac{1}{3}h}{\left(L+KV\right)_{t_{n+1}}} \qquad (2.4.7.5)$$

where h = interval with, fraction of m_F

n = number of divisions (when n=10, h = 0.1; when n = 20, h= 0.05)

t_1 = initial temperature on TBP assay

t_I = TBP assay temperature at point *i*

t_{n+1} = final temperature on TBP assay

The notation $(L+KV)|_{ti}$ indicates that the distribution coefficient *K* is evaluated for that component whose TBP temperature is t_I . For example, K_{ti} is the value of *K* for the component whose TBP is the initial boiling point of the mixture. If 10 sub-intervals are used for approximating the integral, K_{t2} is the value of *K* for the component whose TBP corresponds to a value of 0.1 from m_F on the TBP curve of the feed.

The expression corresponding to Equation 2.4.7.4 for a finite mixture is

$$\sum_{i=1}^{c}\frac{Fx_{F_i}}{L+K_iV} \tag{2.4.7.6}$$

Quantities (1/3*h*) , (1/3*h*)(3+(-1)^{I}), and (1/3*h*) appearing in Equation 2.4.7.5 might be considered the compositions of a pseudo-feed containing *n-1* components. The integral can then be expressed as

$$\int_0^1\frac{dm_F}{L+KV}=\sum_{i=1}^{n+1}\frac{x_{F_i}}{L+K_iV} \tag{2.4.7.7}$$

That is $xF_I = x_{Fn+1} = 1/3h$ and

$X_{Fi} = (1/3h)(3+(-1)^i)$ for $2 \leq i \leq n$ (2.4.7.8)

where x_{Fi} = mole fraction of pseudo-component *i* in feed

In this manner the integral technique can be used in standard programs written for finite component mixtures.

The various points on the TBP curve that characterize the liquid product of a flash process are obtained by integrating Equation 2.4.7.3 from the initial boiling point where m_F=0 to the value of m_F corresponding to the TBP of the point in question. That is

$$m_{L|t}=\int_0^{m_{F|t}}\frac{F}{L+KV}dm_F \tag{2.4.7.9}$$

The subscript *L*|*t* refers to 'liquid' at assay temperature "*t* " and the subscript *F*|*t* refers to "feed" at assay temperature "*t*" The molar TBP curve of the vapor product is found by similar calculation

$$m_{F|t}=\int_0^{m_{F|t}}\frac{KF}{L+KV}dm_F \tag{2.4.7.10}$$

Analogous meaning are associated with the subscripts *V*|*t* and *F*|*t* as those given for *L*|*t* and *F*|*t.*

The procedure using a pseudo-feed composition in the evaluation of the integral in Equation 2.4.7.4 cannot be used for Equations 2.4.7.9 and 2.4.7.10. Simpson’s Rule must be reapplied in the appropriate manner over each of the desired intervals of the integration.

CHAPTER 3

METHODOLOGY

3.1 Experimental Work

3.1.1 Apparatus and technique [9]

Approximately 50 ml of light oil together with 50 ml of distilled water were placed in a 125 ml Hypo-vial, which was closed with a Teflon coated rubber septum and placed in a constant-temperature water bath. In this investigation, the bath was maintained at 25±0.01 °C. Two methods were used to equilibrate water with light oil. Initially, the system under consideration was stirred using a magnetic stirrer for 24 h. The vial was then left in the bath for at least 3 days to ensure the separation of the layers. However, it was subsequently found that when the components were allowed to remain in contact for a sufficiently long period of time (2-4 days) without stirring, the solubility also reached a constant value. For the majority of the experimental determinations, the vials were therefore kept in the thermostat without stirring for at least 7 days before samples were taken for analysis. An excellent agreement was obtained between the results of the two methods.

3.1.2 Determination of the Solubility of Light oil in Water [9]

In this case, the sample of the bottom(water rich) layer must be taken for analysis. For this reason, the vials were placed in the bath with their necks down. To collect the sample, the vial was taken out of the bath, and dried with tissue; then the septum was pierced with the hypodermic needle of a 30 ml syringe. A second needle, connected to compressed air source, was then introduced to push the liquid into syringe. A sample about 15 ml was taken in each analysis, with the exact amount determined by sampling. The sample was placed in a 15 ml Hypo-vial, which was filled beforehand with approximately 2 ml of substance solution containing a known amount of benzene or toluene (whenever benzene interfered with the light oil during the analysis, toluene was used instead). The hypo-vial was then closed with a teflon coated rubber septum.

The vial was closed and hand shaken for 5 min and then after the water and light oil layers had separated, 0.1 to 2 ml(depending on the solubility) of the dodecane layer was injected into a Hewlett-packard model chromatograph equipped with a flame ionization detector and a model 3373B integrator. The samples were analyzed using a 6 ft long, ¼ in. diameter stainless steel column packed with 3% Carbowax 20M on Chromosorb 30/60 mesh.

The temperature of the chromatographic oven was initially maintained at 80 □C. After the peaks of light oil and benzene or toluene had been integrated, the oven temperature was increased to 220 □C and kept there for about 8 min to remove all of the relatively high boiling dodecane. The temperature was then lowered to 80 □C and after stabilization the next sample was analyzed. Each analysis took about 20-30 min. The temperature of the injection port and the detector was kept at 220 □C. Between repeated analyses of unknown samples prepared as described above, the known-composition standard solutions of dodecane with light oil and benzene(toluene) at approximately the same concentrations, and treated the same way as the unknown samples (i.e. shaken with the same amount of water), were analyzed. In this manner, the ratio of response factors of light oil and benzene(toluene) was determined and the amount of light oil could be calculated.

3.1.3 Determination of the Solubility of Water in Light oil [9]

The water-light oil mixture was equilibrated in a similar manner but with the vial opening at the top during the equilibration. After equilibrating for at least 7 days, the vial was lifted partially from the bath. Approximately 15 ml of the light oil layer was taken into a syringe after pressurizing the vial with dry air and injected into a titrimeter vessel (with the exact amount determined by weighting of the syringe), and titrated. A Metrohm model E452 Karl Fischer titrator equipped with a 10 ml buret was used. Commercial stabilized Karl Fischer reagent (Fischer Scientific Co.) was diluted to a titer of about 0.15 mg H_2O /ml. The reagent was frequently standardized with sodium tartrate.

An excess amount of the Karl Fischer reagent was always added to ensure the fast reaction of the small amount of water. The standardized methanol was then added in such an amount so that the titration was always completed by the Karl Fisher reagent.

Precautions were taken to prevent contamination of the samples with glycol. The measurements agreed within experimental error with those obtained for the fresh samples.

All measures of the solubility of light oil in water were repeated at least twice. The determinations of the solubility of water in light oil were repeated at least three times.

Figure 3.1 Karl Fischer (instrument for measure water in light oil)

Figure 3.2 Gas Chromatography (instrument for measure light oil in water)

3.2 Study about cubic equation of state

Study about the using cubic equation of state to predict the saturated water pressure at instantaneous temperature. The saturated water pressure was obtained by equating fugacities of vapor and liquid phases. The calculated saturated pressure from cubic equation of state was compared with saturated pressure from steam table.

3.3 Find proper mixing rule

Find proper mixing rule by comparing between simple mixing rule by *van der Waals* [5] and new mixing rule by *Huron and Vidal* [8] with experimental data of benzene/water system [2], [3], [4]. And the calculated solubility is determined from cubic equation of state at Liquid-Liquid Equilibrium.

3.4 Find proper correlation

Find proper correlation between the parameters in new mixing rule such as k_{ij}(interaction coefficient) , τ_{ij} , τ_{ji} (NRTL model binary interaction parameter) with the property of hydrocarbon such as Boiling Point, Molecular weight and Critical temperature by using mutual solubilities from between hydrocarbon and water to reference[2] , [3] , [4].

3.5 Evaluate excess Gibbs free energy

Evaluate excess Gibbs free energy of hydrocarbon/hydrocarbon mixtures and hydrocarbon/water mixtures from equation.

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\overline{f_i}}{x_i f_i} \qquad (3.5.1)$$

3.6 Formulate the computer program

Figure 3.3 shows flow diagram of program for the calculation of solubility between light oil and water. For the program see Appendix B.

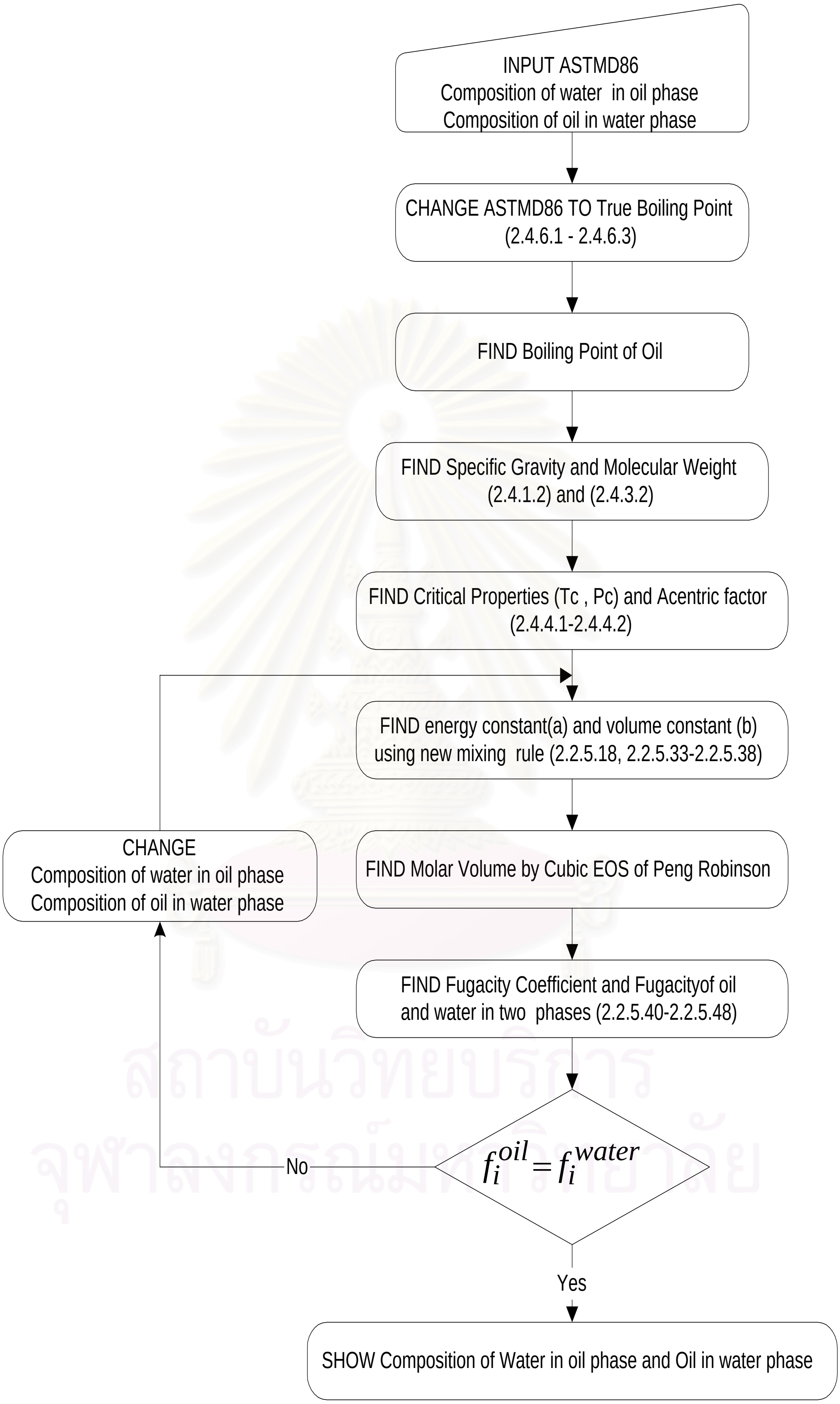


Figure 3.3 Flow diagram for the calculation between light oil and water.

CHAPTER 4
RESULT & DISCUSSION

4.1 RESULT

4.1.1 Experimental Result

Experimental result of water solubility in light oil is presented in Table 4.1.

Table 4.1 The solubility of water in light oil phase use ASTM D4928 method.

SAMPLE NAME	RESULT(%wt)
Gasoline + Water (25°C)	0.023
Diesel + Water (25°C)	0.036

Experimental result of some hydrocarbons of light oil solubility in water is presented in Table 4.2.

Table 4.2 The solubility of light oil in water phase (at 25°C) use GC-MS Coupled with Purge and Trap method.

Test item	Gasoline(ppm)	Diesel(ppm)
Volatile Organic Compounds(VOCs)		
Benzene	10.10	ND
Toluene	148.72	1.31
Ethylbenzene	9.18	0.39
m-xylene	66.41	0.96
p-xylene	127.02	1.33

Remark: - The result obtained by comparing with standard solution of individual compounds (i.e. Benzene, Toluene, Xylene and Ethylbenzene)

- ND = cannot be detected

4.1.2 Show the calculated P^{sat} of water

Show that cubic equation of state can predict P^{sat} of water as in Table 4.3.

Table 4.3 : The saturated water pressure from steam table and the calculated fugacity at the same temperature.

steam table		calculated	
T(R)	P^{sat}(psia)	P^{sat}(psia)	% error
491.69	0.0886	0.0941	0.06
518.67	0.2469	0.2541	0.03
527.67	0.3389	0.3455	0.02
536.67	0.4592	0.4648	0.01
554.67	0.8153	0.8159	0
563.67	1.0696	1.0655	0
572.67	1.3898	1.3790	-0.01
590.67	2.2830	2.2520	-0.01
608.67	3.6272	3.5639	-0.02

4.1.3 Mutual solubility

Table 4.4 shows the results of mutual solubilities of benzene and water by use simple mixing rule and new mixing rule. The new mixing rule can predict mutual solubility accurately.

Table 4.4 : Show the calculated mutual solubility of benzene and water. (at 563.67 R,4.43 psia.)

	experimental data	Simple mixing rule		new mixing rule	
		calculated	%error	calculated	%error
x_h	0.000435	~ 0	100	0.000611	0.400
x_w	0.00501	0.13718	26.38	0.0055	0.098

4.1.4 Correlations of parameters

Table 4.5 shows parameters in new mixing rule, base on system temperature at 25°C and system pressure at 1 atm , such as k_{ij}(interaction coefficient), τ_{ij} , τ_{ji} (NRTL model binary interaction parameter) of hydrocarbons by curve fitting. Figure 4.1 shows curve fitting between the parameters with critical temperature of hydrocarbons. Figure 4.2 shows curve fitting between the parameters with boiling point of hydrocarbons. Figure 4.3 shows curve fitting between the parameters with molecular weight of hydrocarbons.

Table 4.5 : Show property of hydrocarbons and parameters.(at T = 536.67 R, P=14.69 psia) [2] , [3] , [4] , [8]

Hydrocarbon	BP (R)	MW	T_c (R)	x_w	x_{hc}	k_{ij}	τ_{hw}	τ_{wh}
1-Hexene	605.88	84.16	907.20	0.001437	1.2×10^{-5}	0.400	7.76	11.65
n-Hexane	615.42	86.18	913.32	0.00123	4.35×10^{-6}	0.486	7.97	12.55
Benzene	635.76	78.11	1011.96	0.00501	4.435×10^{-4}	0.260	5.40	7.51
n-Octane	717.84	114.20	1023.84	0.001	1.2×10^{-7}	0.467	9.15	18.43
Ethylbenzene	736.92	106.20	1110.96	0.0186	8.6×10^{-5}	0.305	4.75	10.59
n-Decane	805.14	142.30	1113.30	0.00842	1.2×10^{-7}	0.448	7.15	20.18
cis-Decalin	844.20	138.30	1218.96	0.0097	4.1×10^{-7}	0.456	6.80	18.15
Tetralin	865.44	132.20	1296.36	0.0206	9.2×10^{-6}	0.301	5.82	15.44

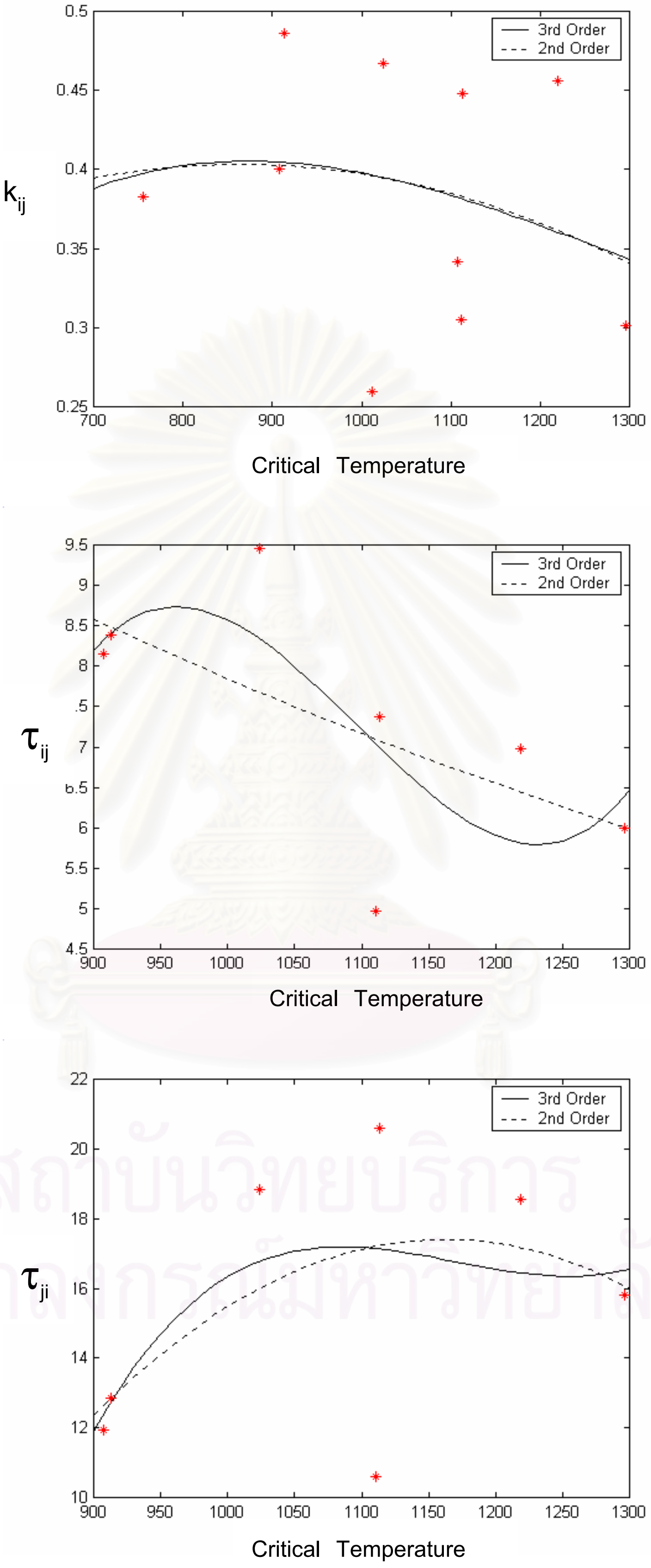


Figure 4.1 Curve fitting between the parameters and Critical temperature.

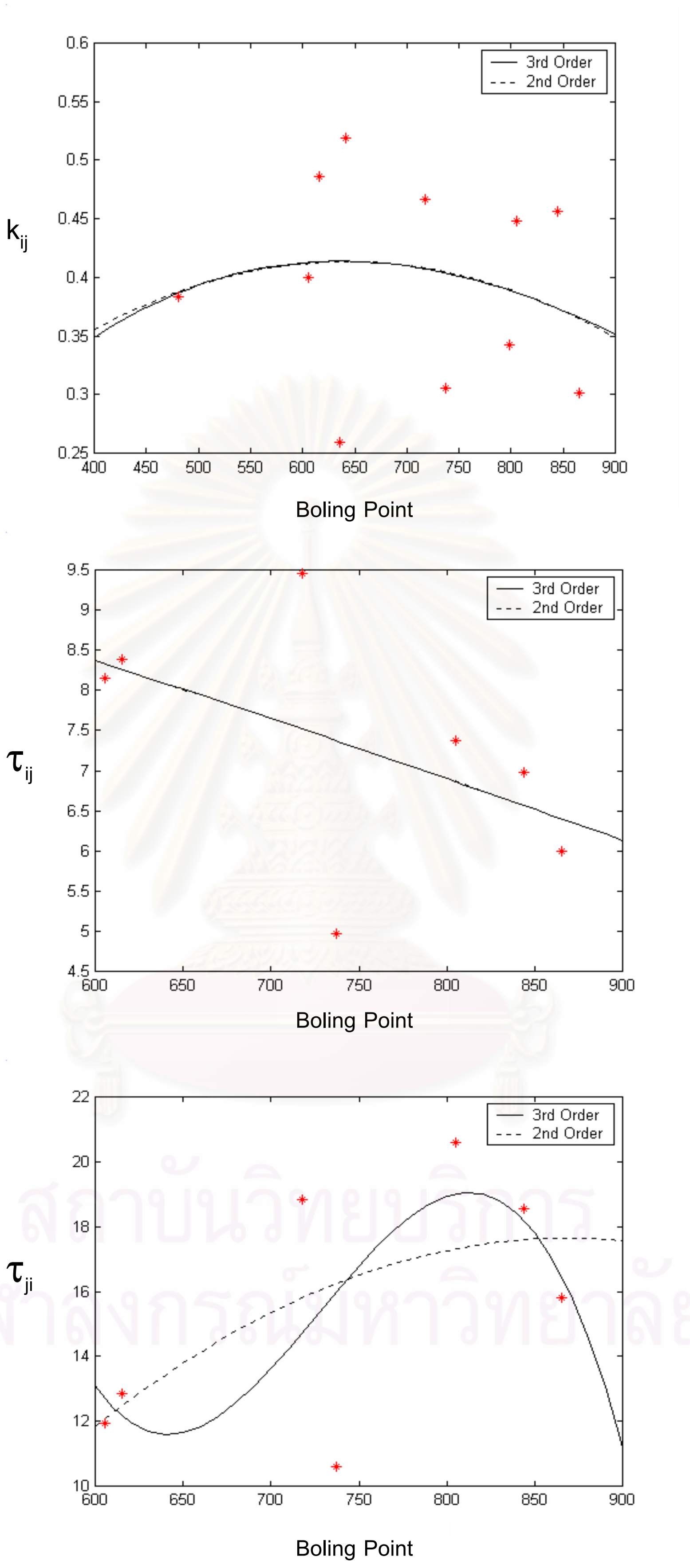


Figure 4.2 Curve fitting between the parameters and Boling Point.

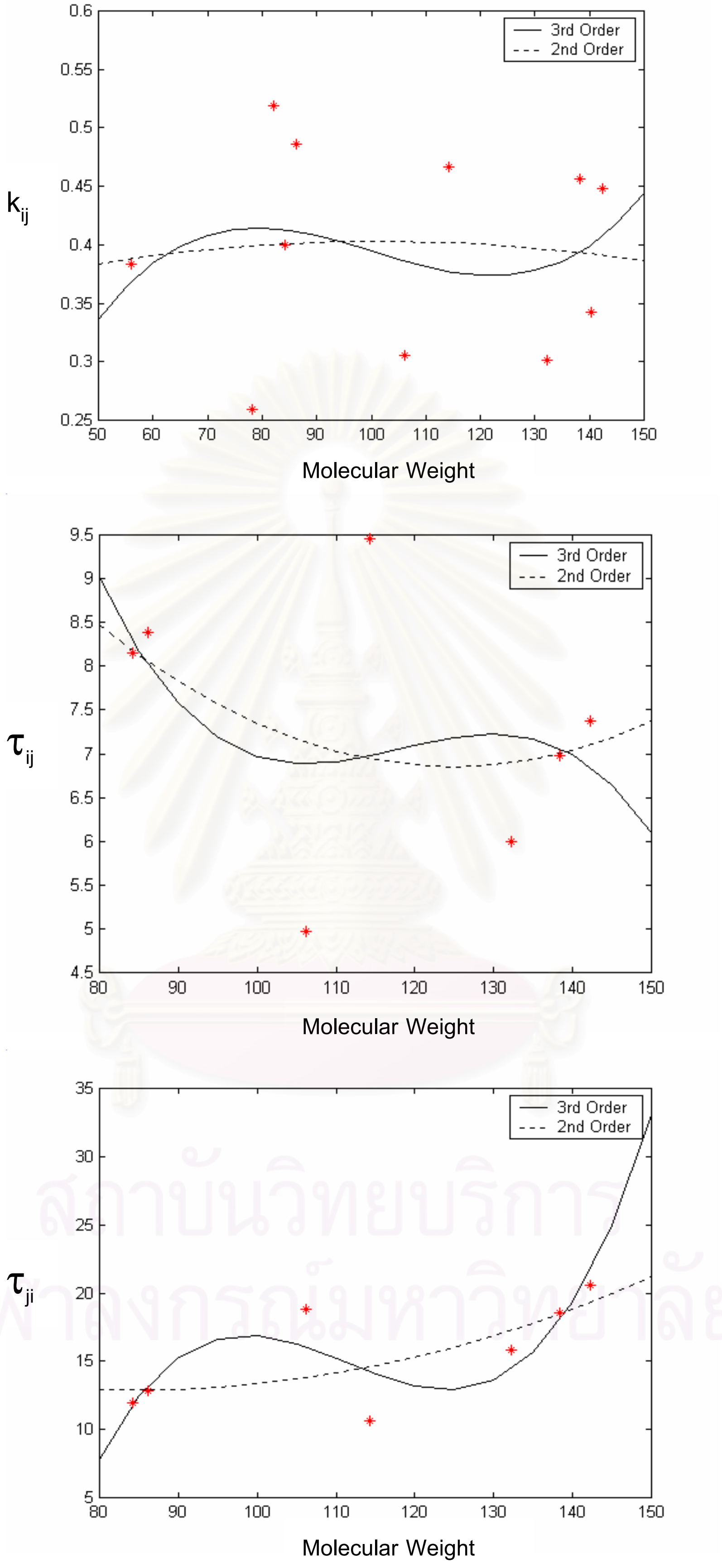


Figure 4.3 Curve fitting between the parameters and Molecular Weight.

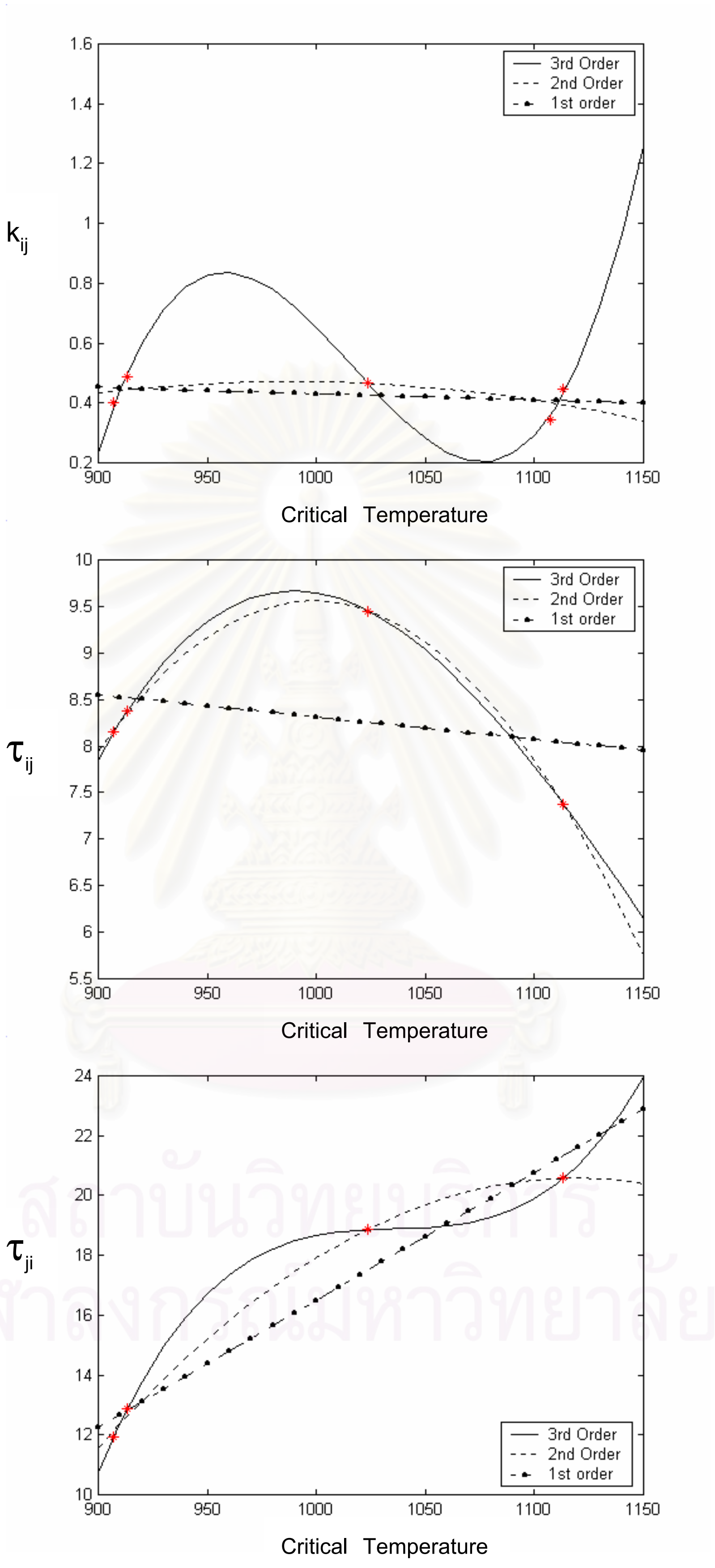


Fig 4.4 Curve fitting between the parameters of Alkane and Critical Temperature.

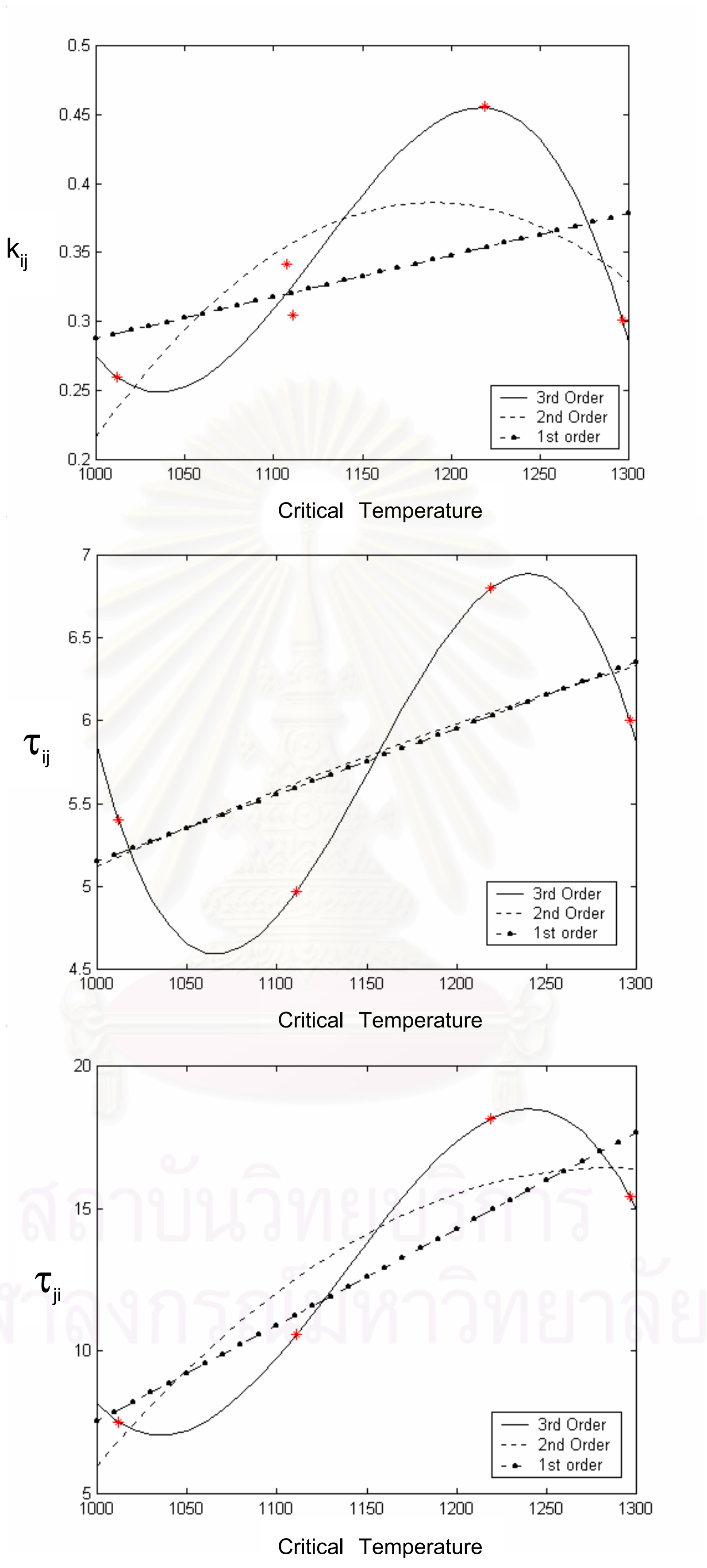


Fig 4.5 Curve fitting between the parameters of Aromatic and Critical Temperature.

Appropriate correlations for parameters in the case of third power polynomial equation is used are as follow:

$$k_{ij} = 1.28x10^{-7}T_c^3 - 3.741x10^{-3}T_c^2 + 3.584x10^{-2}T_c - 10.87$$

$$\tau_{ij} = 2.99x10^{-7}T_c^3 - 9.84x10^{-4}T_c^2 + 1.063T_c - 369.17$$

$$\tau_{ji} = 3.475x10^{-7}T_c^3 - 1.22x10^{-3}T_c^2 + 1.421T_c - 531.92$$

4.1.5 Excess Gibbs free energy

Figure 4.4 shows that excess Gibbs free energy, calculate from equation 3.5.1, of hydrocarbon/hydrocarbon mixture is very small. Therefore these mixtures maybe assumed as ideal solution. That is τ_{ij} and τ_{ji} equal zero.

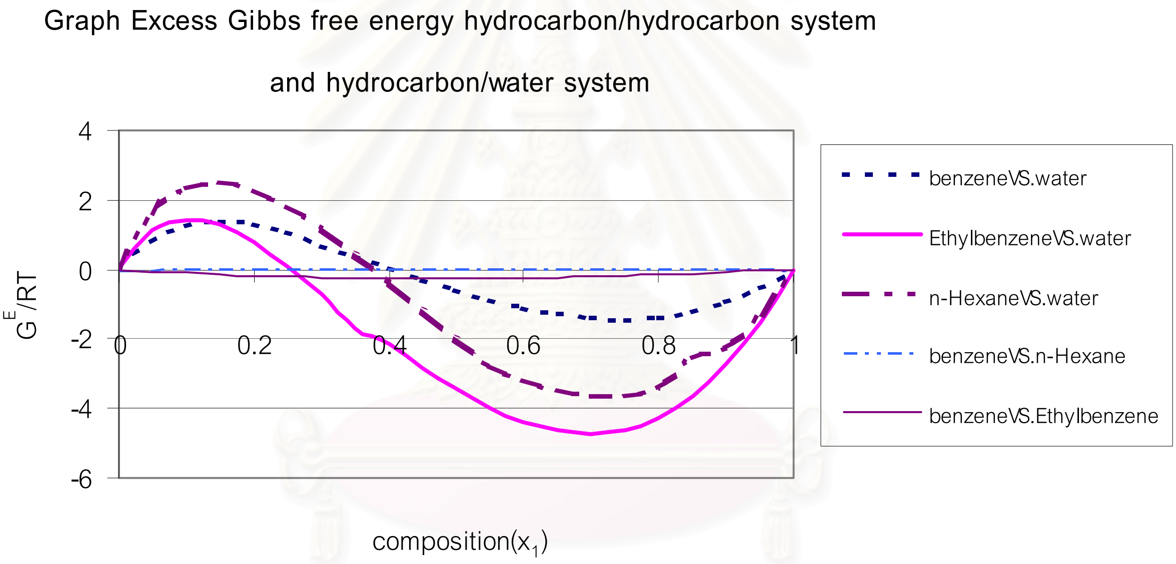


Figure 4.6 $\frac{G^E}{RT}$ for hydrocarbon/hydrocarbon and $\frac{G^E}{RT}$ for hydrocarbon/water system

4.1.6 Calculated Solubility

Table 4.6 shows the result from the calculation program for binary system between light oil, using properties at boiling point 50%Volume of ASTMD86 , and water.

Table 4.6 : The results from the calculation program for light oil compare with the experimental result. (at 637.67 R , 14.7 psia)

		Experimental	calculated	%error
Gasoline+Water	x_{oil}	0.0022	9.78×10^{-7}	*
	x_w	0.0012	0.0016	0.33
Diesel+Water	x_{oil}	0.000437	3.08×10^{-8}	*
	x_w	0.0046	0.0024	0.48

* comparison cannot be done , due to over estimation in the experiment.

4.2 Discussion

4.2.1 In the experimentation with GC Detector, quantity of hydrocarbon can be determined from standard of hydrocarbon. In laboratory of Petroleum Authority of Thailand , only four standard (benzene, toluene, xylene and ethylbenzene) were available. Therefore, curve fitting between percent volume the four hydrocarbons with their boiling point was done, after that, percent volume of light oil was estimated from their boiling point. Since solubility of alkane in water in water is much smaller than that of aromatic in water, the estimated percent volume of light oil in water is too high.

4.2.2 Correlation between parameter and critical temperature is the best because reference data almost cover critical temperature of light oil , gasoline and diesel. From the calculation , the parameters extrapolated by the third order polynomial can predict mutual solubility of light oil and water.

4.2.3 The parameters , τ_{ij} and τ_{ji} , between hydrocarbon and hydrocarbon system can be assumed equal zero because excess Gibbs free energy converge to zero and differentiate from Gibbs free energy between hydrocarbon and water system.

4.2.4 The calculated result can predict mutual solubilities of light oil and water. Although the calculated solubilities of light oil in water phase is much smaller than the experimental result, the calculated result has small order of magnitude as solubility of hydrocarbon in water phase shown in Table 4.5. The experimental result of light oil in water was over estimated as discuss in 4.2.1. Therefore, the cubic equation of state can be determined mutual solubilities of light oil and water.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

5.1.1. Peng Robinson equation can be used to predict phase equilibrium of petroleum fraction and water mixtures.

5.1.2 Mixing rule for cubic equation is important because the simple mixing rule cannot predict solubility in petroleum fraction - water mixtures, while HV-NRTL mixing rule can.

5.1.3 The proper correlation between parameter and critical temperature of hydrocarbon - water system is constructed. The parameters of either light oil , gasoline or diesel oil , and water system can be determined from these correlations.

5.2 Recommendation

5.2.1 Others mixing rule should be tested and compared with the HV-NRTL mixing rule.

5.2.2 Search more reference data to cover wide temperature range for parameters correlations.

REFERENCES

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APPENDICES

APPENDIX A
REFERENCE OF EXPERIMENT

- TYPICAL TEST RESULT of Fuel Oil (Gasoline and Diesel)

  Gasoline

PROPERTY	RESULT	SPECIFICATION	TEST METHOD
API Gravity @60°C	55.9	-	ASTM D 1298
Specific Gravity @ 15.6/15.6 °C	0.7551	-	ASTM D 1298
Octane Number, Research Method	97.1	min 95.0	ASTM D 2699
Octane Number, Motor Method	84.9	min 84.0	ASTM D 2700
Lead Content, g/L	0.003	max 0.013	ASTM D 3348
Oxidation Stability, minutes	>360	min 360	ASTM D 525
Reid Vapour Pressure @37.8°C, kPa(100°F,psi)	60.49	max 62	ASTM D 4953
Existent Gum, mg/100mL	0.001	max 4.0	ASTM D 381
Sulphur Content, %wt	0.013	max 0.10	ASTM D 4294
Copper Strip Corrosion(3h @ 50°C)	No.1	max No.1	ASTM D 130
Distillation :			ASTM D 86
Initial Boiling Point, °C	32.2		
10%vol evaporated, °C	52.2	max 70	
50%vol evaporated, °C	93.9	70-110	
90%vol evaporated, °C	157.7	max 170	
End Point, °C	192.8	max 200	
Residue, %vol	1.1	max 2.0	
Colour	Yellow		Visual
Benzene, %vol	1.7	max 3.5	ASTM D 3606
Aromatic, %vol	34.9	max 50	ASTM D 4420
Oxegenerated Compound (MTBE), %vol	5.85	5.5 – 11.0	ASTM D 4815

THESE RESULTS CONFORM TO “UNLEADED GASOLINE OCTANE 95” SPECIFICATION OF MINISTRY OF COMMERCE, THAILAND

Reference : Petroleum Authority of Thailand

Diesel

PROPERTY	RESULT	SPECIFICATION	TEST METHOD
API Gravity @60°C	37.9	-	ASTM D 1298
Specific Gravity @ 15.6/15.6 $^{\circ}$C	0.8353	0.81 – 0.87	ASTM D 1298
Calculated Cetane Index	55.7	min 47	ASTM D 976
Viscosity, Kinematic, @40°C, cSt	3.323	1.8 – 4.1	ASTM D 445
Pour Point, $^{\circ}$C	-2	max 10	ASTM D 97
Sulphur Content, %wt	0.03	max 0.05	ASTM D 4294
Copper Strip Corrosion (3h@$^{\circ}$C)	No.1	max No.1	ASTM D 130
Carbon Residue, %wt	0.02	max 0.05	ASTM D 4530
Water & Sediment, %vol	Traces	max 0.05	ASTM D 2709
Ash, %wt	0.001	max 0.01	ASTM D 482
Flash Point, (P.M.), $^{\circ}$C		min 52	ASTM D 93
Distillation :			ASTM D86
Initial Boiling Point, $^{\circ}$C	180.4		
10%vol evaporated, $^{\circ}$C	219.4		
50%vol evaporated, $^{\circ}$C	285.3		
90%vol evaporated, $^{\circ}$C	351.8	max 357	
Colour	L 0.5	max 2.0	ASTM D 1500

THESE RESULTS CONFORM TO “HIGH SPEED DIESEL” SPECIFICATION OF MINISTRY OF COMMERCE, THAILAND

Reference : Petroleum Authority of Thailand

Details of Distillation use ASTM86 method (°C).

%Volume	Gasoline	Diesel
IBP	33.8	190.4
5	48.2	217.4
10	52.0	228.4
20	58.4	242.1
30	65.6	255.7
40	74.6	266.9
50	85.9	278.6
60	99.6	291.4
70	116.2	306.7
80	135.4	326.3
90	153.1	353.1
95	163.8	372.9

Remark : IBP = Initial Boiling Point

- Test Method

<u>GC-MS</u>

Column : HP-5MS 5%Phenyl Methyl Siloxane, Capillary 30m x 250μm x 0.25μm
Mode : Constant flow
Pressure : 16.08 psi
Flow : 2.0 ml/min
Inlet Split Gas : He (35:1)
Heater : 250°C

<u>Purge and trap preconcentrator</u>

Line temp : 100°C
Valve temp : 100°C
Purge temp : 40°C
Purge time : 10 min
Sample temp : 40°C

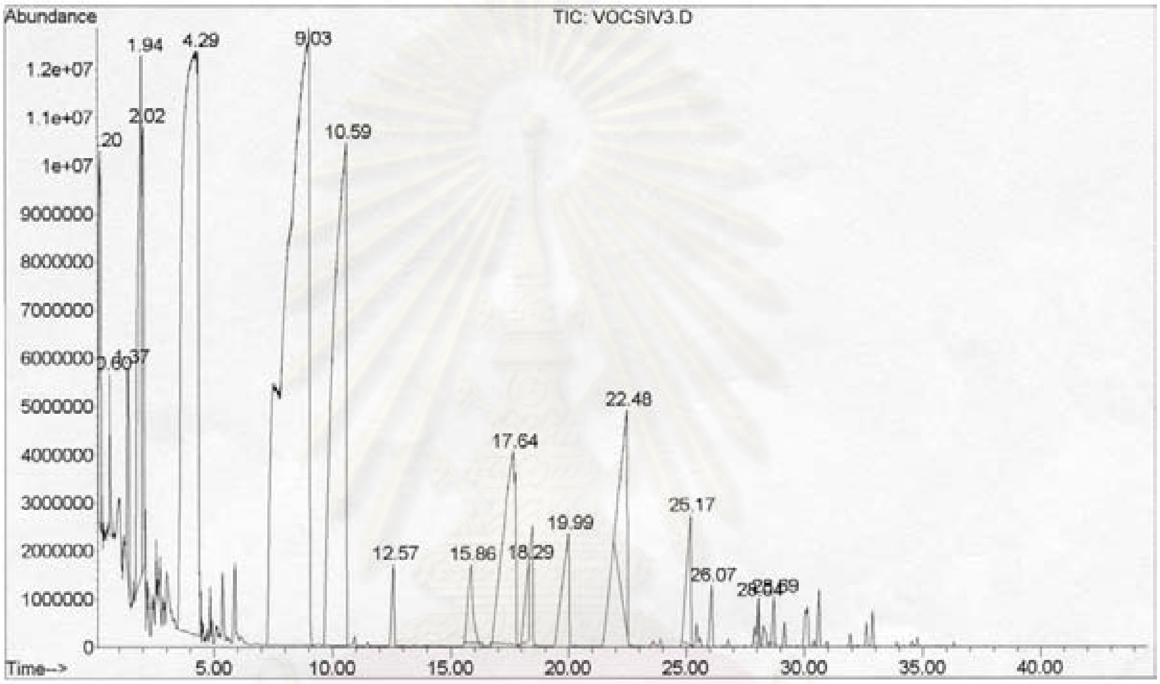
Cryo Focus Temp : -60°C
Cryo Inject Temp : 180°C
Desorp Temp : 220°C
Desorp time : 5 min
Bake time : 20 min

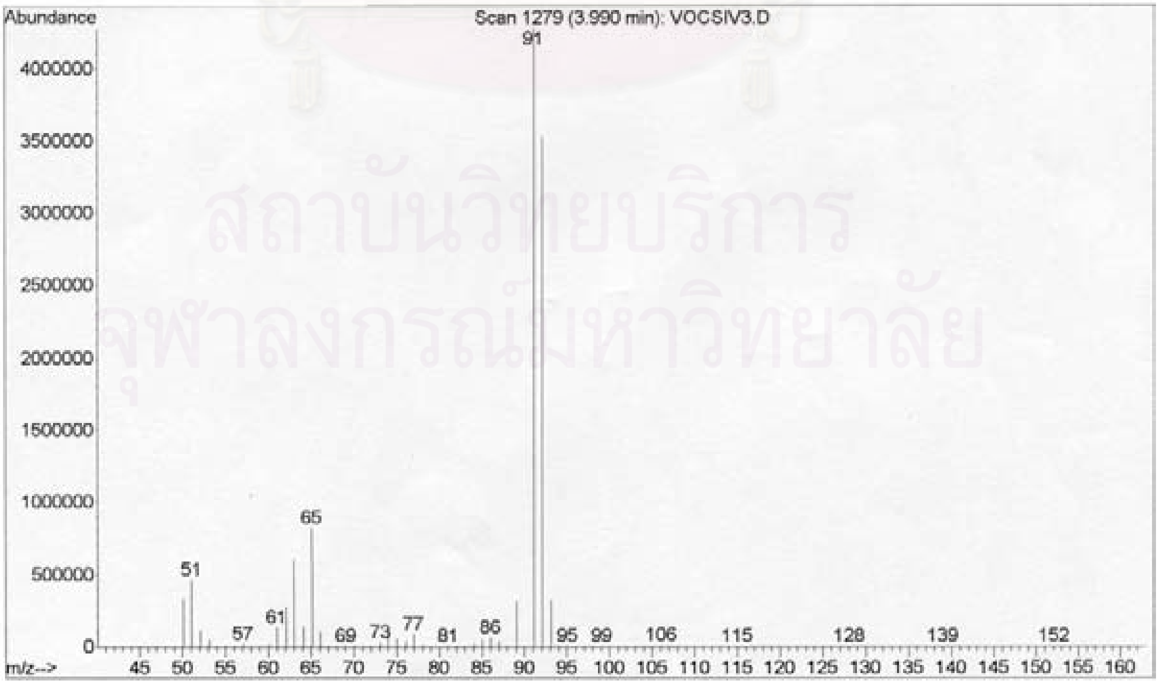
Reference : Petroleum Authority of Thailand

- Graph from GC Detector

Gasoline / Water layer at 25°C

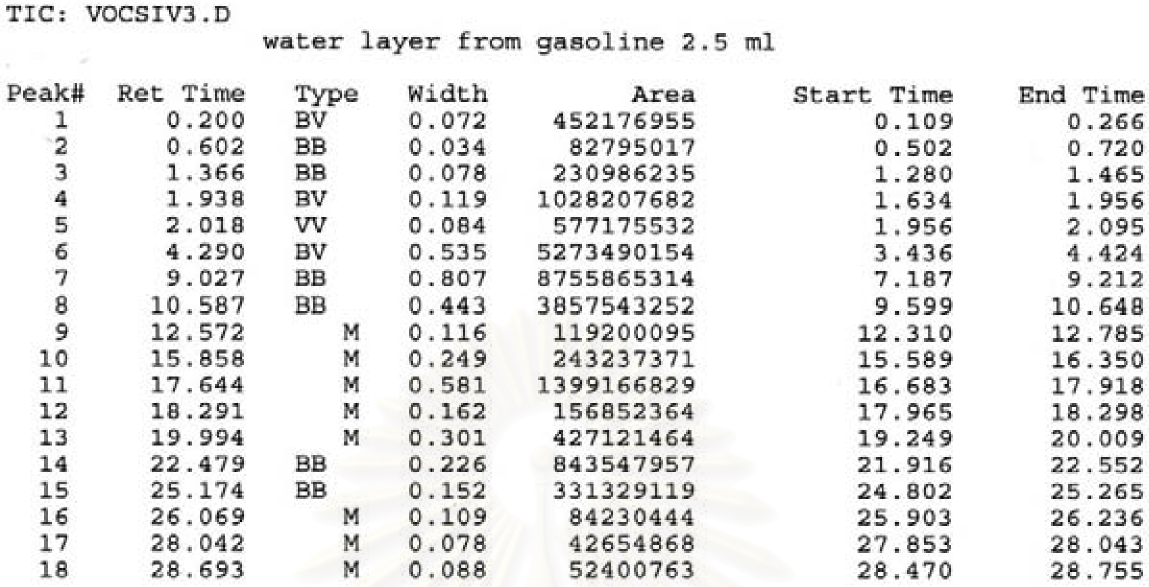
```
File        : C:\HPCHEM\1\DATA\VOCSIV3.D
Operator    : jim
Acquired    : 23 May 2001   4:15 pm using AcqMethod AAPURGE
Instrument :    GC/MS Ins
Sample Name: water layer from gasoline 2.5 ml
Misc Info   : run on 23 May 44 desorp 5 min
Vial Number: 1
```





Reference : Petroleum Authority of Thailand

Show detail about graph.



```
TIC: VOCSIV3.D
                    water layer from gasoline 2.5 ml

Peak#  Ret Time   Type    Width        Area        Start Time    End Time
   1     0.200    BV      0.072     452176955         0.109        0.266
   2     0.602    BB      0.034      82795017         0.502        0.720
   3     1.366    BB      0.078     230986235         1.280        1.465
   4     1.938    BV      0.119    1028207682         1.634        1.956
   5     2.018    VV      0.084     577175532         1.956        2.095
   6     4.290    BV      0.535    5273490154         3.436        4.424
   7     9.027    BB      0.807    8755865314         7.187        9.212
   8    10.587    BB      0.443    3857543252         9.599       10.648
   9    12.572        M   0.116     119200095        12.310       12.785
  10    15.858        M   0.249     243237371        15.589       16.350
  11    17.644        M   0.581    1399166829        16.683       17.918
  12    18.291        M   0.162     156852364        17.965       18.298
  13    19.994        M   0.301     427121464        19.249       20.009
  14    22.479    BB      0.226     843547957        21.916       22.552
  15    25.174    BB      0.152     331329119        24.802       25.265
  16    26.069        M   0.109      84230444        25.903       26.236
  17    28.042        M   0.078      42654868        27.853       28.043
  18    28.693        M   0.088      52400763        28.470       28.755
```

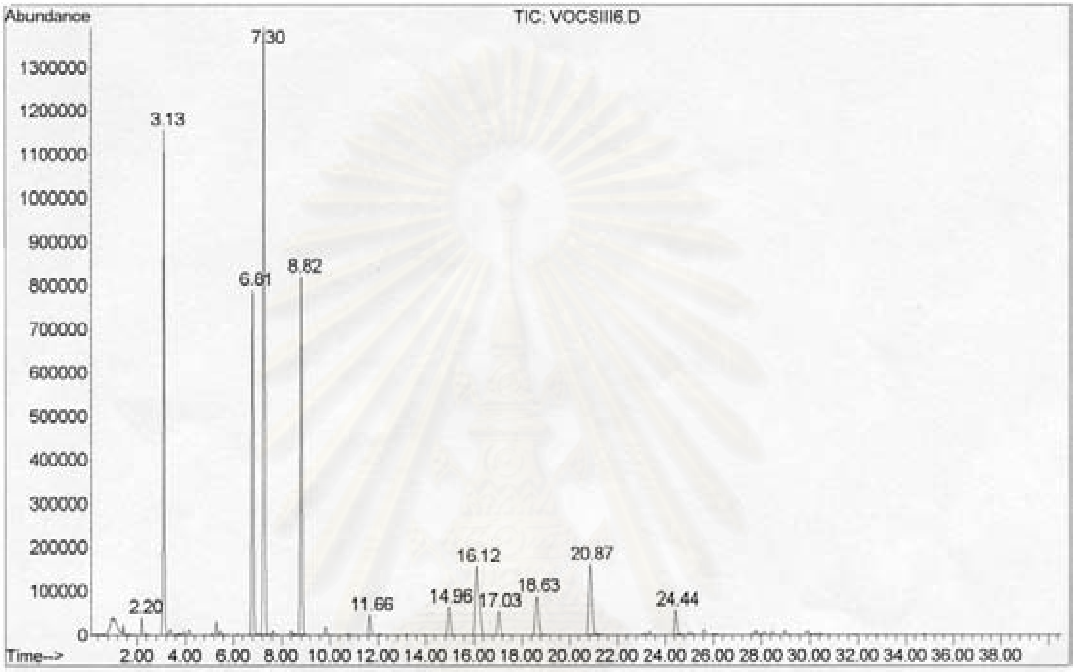
Remark:

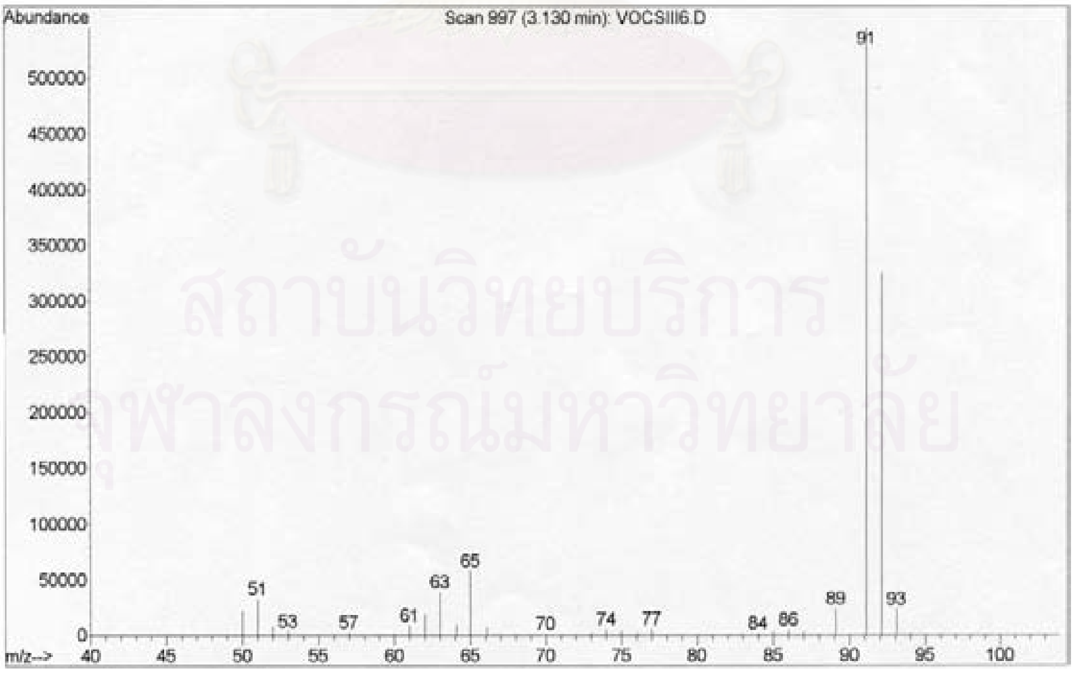
- Peak 5-6 is Toluene
- Peak 7 is para-xylene
- Peak 8 is meta-xylene
- Peak 9 is iso-propylbenzene
- Peak 10 is n-propylbenzene
- Peak 11 is 1,ethyl-2,methylbenzene
- Peak 12,14 is 1,2,4-Trimethylbenzene
- Peak 13 is 1,ethyl-2,methyl benzene
- Peak 15 is C3-benzene
- Peak 16 is 1H-Indene
- Peak 17 is 1,methyl-3,propylbenzene
- Peak 18 is 4,ethyl-1,2,dimethyl benzene

Reference : Petroleum Authority of Thailand

Diesel / Water layer at 25°C

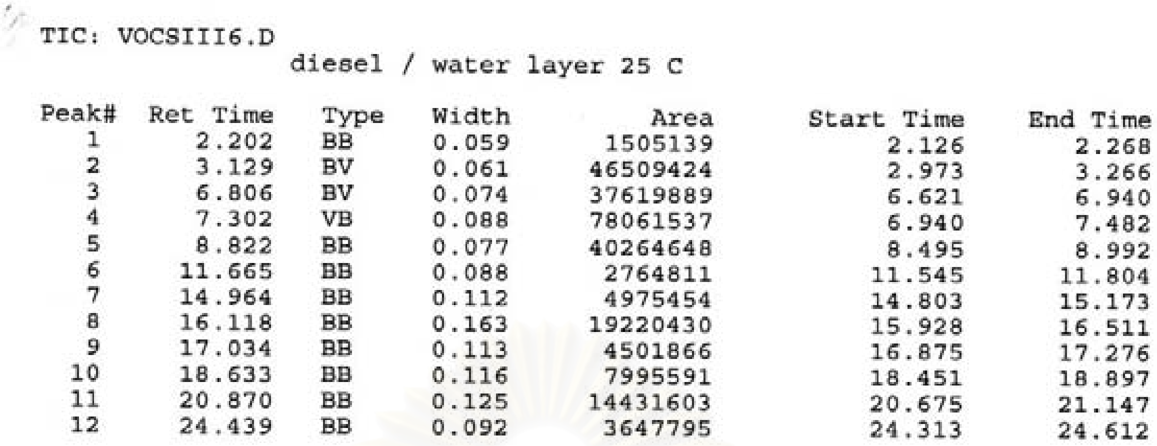
```
File       : C:\HPCHEM\1\DATA\VOCSIII6.D
Operator   : poom
Acquired   : 22 May 2001   3:58 pm using AcqMethod AAPURGE
Instrument :    GC/MS Ins
Sample Name: diesel / water layer 25 C
Misc Info  : 22 May
Vial Number: 1
```





Reference : Petroleum Authority of Thailand

Show detail about graph.



```
TIC: VOCSIII6.D
                  diesel / water layer 25 C

Peak#   Ret Time    Type    Width         Area         Start Time     End Time
  1       2.202     BB      0.059      1505139            2.126         2.268
  2       3.129     BV      0.061     46509424            2.973         3.266
  3       6.806     BV      0.074     37619889            6.621         6.940
  4       7.302     VB      0.088     78061537            6.940         7.482
  5       8.822     BB      0.077     40264648            8.495         8.992
  6      11.665     BB      0.088      2764811           11.545        11.804
  7      14.964     BB      0.112      4975454           14.803        15.173
  8      16.118     BB      0.163     19220430           15.928        16.511
  9      17.034     BB      0.113      4501866           16.875        17.276
 10      18.633     BB      0.116      7995591           18.451        18.897
 11      20.870     BB      0.125     14431603           20.675        21.147
 12      24.439     BB      0.092      3647795           24.313        24.612
```

Remark:

- Peak 2 is Toluene
- Peak 3 is ethylbenzene
- Peak 4 is meta-xylene
- Peak 5 is para-xylene
- Peak 6 is iso-propylbenzene
- Peak 7 is n-propylbenzene
- Peak 8 is 1,ethyl-2,methylbenzene
- Peak 9,12 is 1,3,5-Trimethylbenzene
- Peak 10 is 1,ethyl-4,methyl benzene
- Peak 11 is C3-benzene

Reference : Petroleum Authority of Thailand

APPENDIX B
PROGRAM FOR CALCULATION

- MAIN PROGRAM

```
%%%---PROGRAMM FOR BINARY MODE(oil&water)---%%%

clear

N=1;
%--------------constant of programm---------------%

T = 536.67 ;            % unit R
P = 14.6959 ;           % unit psia
R = 10.731 ;            % unit psia.cu.ft/lb-mole.R

Tcw = 1165.14 ;         % unit R
Pcw = 3203.6 ;          % unit psia
S1w = 1.243997;
S2w = -0.201789;

C = (1/(2^0.5))*log((2^0.5)-1);

%---input ASTM86 of oil(unit degree centigrade)---%

T50C  =  input('T(50)=');

%--------change unit of Temp.(from C to F)--------%

T50 = (T50C*9/5)+32;

%-----change ASTM86 to TBP(True boiling point)----%

Tb50 = 0.8718*T50^1.0258;
Tb = Tb50+459.67;                 % unit R
```

```
%-find Specific gravity and Molecular weight of oil-%

API  =  input('API=');

SG  =  141.5/(API+131.5);
MW  =  20.486*(exp((1.165*Tb*(10^-4))-(7.78712*SG)+(1.1582*Tb*SG*(10^-3))))*(Tb^1.26007)*(SG^4.98308);

%-find mole fraction of oil by input percent weight-%

xw  =  input('%wt water=');
xw  =  (xw/18)/((xw/18)+((100-xw)/MW));
x     =  ((100-xw)/MW)/((xw/18)+((100-xw)/MW));
x(N+1) = xw;

%-----------find Tc,Pc,W(acentric factor)-----------%

Tc = 10.64443*(exp((-5.1747*(10^(-4))*Tb)-(0.54444*SG)+(3.5995*(10^(-4))*Tb*SG)))*(Tb^0.81067)*(SG^0.53691);
Pc = (10^6)*6.162*(exp((-4.725*(10^(-3))*Tb)-(4.8014*SG)+(3.1939*(10^(-3))*Tb*SG)))*(Tb^(-0.4844))*(SG^4.0846);

D   = (Tb^(1/3))/SG;           % D is Watson factor
Tbr = Tb/Tc;
W   = -7.904+(0.1352*D)-(0.00765*(D^2))+(8.359*Tbr)+((1.408-(0.01063*D))/Tbr);

%---constant from test in binary&toa_bi programm---%

Thesis_bi0;

K = [0  K
    K  0];

al = [0   0.2
     0.2 0  ];

Toa = [0       Toa1_2
      Toa2_1  0    ];
```

```
%---------find gij--------%

for i=1:N+1
  for j=1:N+1
     g(i,j)=exp(-al(i,j)*Toa(i,j));
  end
end

%----------find a(i),b(i),alpha constant------------%

for i=1:N
  aac(i) = 0.457235*((R*Tc(i))^2)/Pc(i);
  bb(i)  = 0.077796*R*Tc(i)/Pc(i);
  m(i)   = 0.48508+(1.55171*W(i))-(0.15613*(W(i)^2));

  Tr(i)  = T/Tc(i);
  al_p(i)= (1+(m(i)*(1-(Tr(i)^0.5))))^2;   %al=alpha%

  aa(i)  = aac(i)*al_p(i);
end

aaciw = 0.42748*((R*Tcw)^2)/Pcw;
bbiw = 0.08664*R*Tcw/Pcw;

Trw  = T/Tcw;
al_pw= (1+(S1w*(1-(Trw^0.5)))+(S2w*(1-(Trw^0.5))/(Trw^0.5)))^2;

aaiw  = aaciw*al_pw;

aa(N+1) = aaiw;
bb(N+1) = bbiw;
```

```
%-------------new mixing rules-------------%

thesis_bi1;

for i=1:N+1
   f_L1(i) = f(i);
end
x_x = x;



%%%%%-----------in phase water---------%%%%%

for i=1:N
   y(i) = input('y=');
   x(i) = y(i);
end
y(N+1) = 1-sum(y);
x(N+1) = y(N+1);

thesis_bi1;

for i=1:N+1
   f_L2(i) = f(i);
end



%%%%%-----------find x component and y component which equilibrium -------%%%%%

iteration1 = 0.001;
iteration2 = 0.001;
diff_b = f_L1(1) - f_L2(1);
diff_w = f_L1(2) - f_L2(2);
old_diff_b = diff_b;
old_diff_w = diff_w;
count=0;
```

```
while (abs(diff_b) > 0.00001) | (abs(diff_w) > 0.00001)
  if (abs(diff_b) > 0.00001)
    if ((diff_b > 0) & (old_diff_b >= 0)) | ((diff_b < 0) & (old_diff_b < 0))
      if abs(diff_b) > abs(old_diff_b)
        iteration1 = -iteration1;
      end
    elseif ((diff_b > 0) & (old_diff_b < 0)) | ((diff_b < 0) & (old_diff_b > 0))
      iteration1 = -iteration1/2;
    end
    y_old = y(1);
    y(1) = y_old + iteration1;
    while (y(1) < 0) | (y(1) > 1)
      iteration1 = iteration1/10;
      y(1) = y_old + iteration1;
    end
    y(2) = 1-y(1);
  end
  if (abs(diff_w) > 0.00001)
    if ((diff_w > 0) & (old_diff_w >= 0)) | ((diff_w < 0) & (old_diff_w < 0))
      if abs(diff_w) > abs(old_diff_w)
        iteration2 = -iteration2;
      end
    elseif ((diff_w > 0) & (old_diff_w < 0)) | ((diff_w < 0) & (old_diff_w > 0))
      iteration2 = -iteration2/2;
    end
    x_old = x_x(2);
    x_x(2) = x_old + iteration2;
    while (x_x(2) < 0) | (x_x(2) > 1)
      iteration2 = iteration2/10;
      x_x(2) = x_old + iteration2;
    end
    x_x(1) = 1-x_x(2);
  end
  x = x_x;
  thesis_bi1;     %%%% find fugacity in oil phase %%%%
```

```
  f_L1 = f
  x = y;
  thesis_bi1;        %%%% find fugacity in water phase %%%%
  f_L2 = f
  old_diff_b = diff_b;
  old_diff_w = diff_w;
  diff_b = f_L1(1) - f_L2(1);
  diff_w = f_L1(2) - f_L2(2);
  count = count+1;
end
f_L1
f_L2
x_x
y
count
```

- SUBPROGRAM

- Thesis_bi0

%------------find parameters k_{ij} ,T_{ij} ,T_{ji} of element-------------%

```
T_c   = [755.28 907.2 913.32 1011.96 1023.84 1107.36 1110.96 1113.3 1218.96];
kij      = [0.383 0.4 0.486 0.2595 0.467 0.342 0.305 0.448 0.456];
Q_Q = polyfit(T_c,kij,3);

T__c    = [907.2 913.32 1023.84 1110.96 1113.3 1218.96 1296.36];
T_A12  = [8.15 8.38 9.45 4.97 7.37 6.98 6];
M_M    = polyfit(T__c,T_A12,3);

T_c_    = [907.2 913.32 1023.84 1110.96 1113.3 1218.96 1296.36];
T_A21  = [11.935 12.86 18.85 10.59 20.58 18.55 15.8];
N_N     = polyfit(T_c_,T_A21,3);

K = (Q_Q(1)*Tc.^3)+(Q_Q(2)*Tc.^2)+(Q_Q(3)*Tc.^1)+Q_Q(4);
Toa1_2 = (M_M(1)*Tc.^3)+(M_M(2)*Tc.^2)+(M_M(3)*Tc.^1)+M_M(4);
Toa2_1 = (N_N(1)*Tc.^3)+(N_N(2)*Tc.^2)+(N_N(3)*Tc.^1)+N_N(4);
```

- Thesis_bi1

```
%%%%%--------------New mixing rules---------------%%%%

%-------find Q------%

Q = 0;
for i=1:N+1
  for j=1:N+1
     sum0 = x(i)*x(j)*(((bb(i)-(aa(i)/(R*T)))+(bb(j)-(aa(j)/(R*T))))*(1-K(i,j))/2);
     Q    = sum0 + Q;
  end
end
```

```
%----find A^E/CRT----%

sum3 = 0;
for i=1:N+1
  sum1 = 0;
  for j=1:N+1
     sum0 = x(j)*Toa(j,i)*g(j,i);
     sum1 = sum0+ sum1;
  end
  sum2 = 0;
  for k=1:N+1
     sum0 = x(k)*g(k,i);
     sum2 = sum0+ sum2;
  end
  sum0 = x(i)* sum1/sum2;
  sum3 = sum0+ sum3;
end
A = sum3/C;

%------find D-------%

D = 0;

for i=1:N+1
  sum0 = x(i)*aa(i)/(bb(i)*R*T);
  D    = D + sum0 ;
end
D = D + A;

%----find bm, am----%

bm = Q/(1-D);
am = R*T*Q*D/(1-D);
```

```
%----find activity coefficient----%

for i=1:N+1
  sum1 = 0;
  sum2 = 0;

  for j=1:N+1
    sum0 = x(j)*Toa(j,i)*g(j,i);
    sum1 = sum0+ sum1;
  end
  for k=1:N+1
    sum0 = x(k)*g(k,i);
    sum2 = sum0+ sum2;
  end
  sum5 = 0;
  for j=1:N+1
    sum3 = 0;
    sum4 = 0;
    for l=1:N+1
      sum0 = x(l)*Toa(l,j)*g(l,j);
      sum3 = sum0+ sum3;
    end
    for k=1:N+1
      sum0 = x(k)*g(k,j);
      sum4 = sum0+ sum4;
    end
    sum0 = x(j)*g(i,j)*(Toa(i,j)-(sum3/sum4))/sum4;
    sum5 = sum0+ sum5;
  end

  Act_coef(i) = (sum1/sum2) + sum5;
end

%------find Fi-------%
```

```
for i=1:N+1
  sum1 = 0;
  for j=1:N+1
    sum0 = x(j)*(((bb(i)-(aa(i)/(R*T)))+(bb(j)-(aa(j)/(R*T))))*(1-K(i,j))/2);
    sum1 = sum0+ sum1;
  end
  F(i) = 2*sum1;
end

%------find Ii-------%

for i=1:N+1
  I(i) = (aa(i)/(bb(i)*R*T))+(Act_coef(i)/C);
end

%-------find Ei------%

for i=1:N+1
  E(i) = (F(i)/(1-D)) - (Q*(1-I(i))/((1-D)^2));
end

%-------find Gi------%

for i=1:N+1
  G(i) = (R*T*D*E(i)) + (R*T*bm*I(i));
end

%-------find V-------%
thesis_bi2;




%----find fugacity coefficient----%
```

```
for i=1:N+1
  phi(i)= exp((-log(P*(V-bm)/(R*T))) + (E(i)*((P*V/(R*T))-1)/bm) + (D*((G(i)/am)-(E(i)/bm))*log((V+(bm*(1-(2^0.5))))
          /(V+(bm*(1+(2^0.5)))))/(2*(2^0.5))));
  f(i) = phi(i)*x(i)*P;
end
```

- ☐ thesis_bi2

```
%--------------find V----------------%

VLL = roots([1,-((R*T/P)-bm),(am/P)-(2*bm*R*T/P)-(3*bm^2),-bm*((am/P)-bm-(bm^2))]);

imm = imag(VLL);

start = 1;
for i=1:3
  if start==1&imm(i)==0 & VLL(i)>0
    VL = VLL(i);
    start = 0;
  end
  if start==0
    if VL>VLL(i) & imm(i)==0 & VLL(i)>0
      VL = VLL(i);
    end
  end
end
if start==1
  fprintf('V doesn''''t exist\n')
else
  V = VL;
end
```

BIOGRAPHY

Miss Sasithorn Romlee was born on April 25, 1976 in Bangkok. She graduated from the Department of Chemical Engineering, Faculty of Engineering, King Mongkut institute of Technology' North Bangkok, in 1997. Since then, she worked for Petroleum Authority of Thailand as a supply analyze in Supply Chain Operation Department. In 1998, she continued her studies for her Master Degree in Chemical Engineering, Chulalongkorn University.