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ของไกลคอลในน้ำ

นางสาวปานกมล พฤกษ์สุนันท์

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EFFECT OF MOLECULAR SIZE ON THE ACTIVITY COEFFICIENT OF GLYCOLS IN AQUEOUS SOLUTION

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ปานกมล พฤกษ์สุนันท์ : ผลกระทบของขนาดโมเลกุลที่มีต่อค่าสัมประสิทธิ์แอกติวิตีของไกลคอลในน้ำ (EFFECT OF MOLECULAR SIZE ON THE ACTIVITY COEFFICIENT OF GLYCOLS IN AQUEOUS SOLUTION) อ.ที่ปรึกษา : รศ.ดร.เกริกชัย สุกาญจนัจที, อ.ที่ปรึกษาร่วม : อ.ขนิษฐา มาลยเวช, 140 หน้า, ISBN 974-13-1029-3.

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาผลกระทบของขนาดโมเลกุลที่มีต่อค่าสัมประสิทธิ์แอกติวิตีของไกลคอลในน้ำ ซึ่งไกลคอลที่นำมาศึกษาผลกระทบดังกล่าวได้แก่ เอทีลีนไกลคอล, 1,2-โพรพีลีนไกลคอล และ 1,4-บิวทีลีนไกลคอล โดยในงานวิจัยได้ทำการออกแบบเครื่องมือสร้างสมดุลเฟสไอ-ของเหลว เพื่อเก็บข้อมูลสมดุลเฟสของระบบสององค์ประกอบ 1,4-บิวทีลีนไกลคอล-น้ำ ซึ่งได้ควบคุมอุณหภูมิให้คงที่ที่ 98, 110 และ 122 องศาเซลเซียส เนื่องจากอุณหภูมิทั้งสามค่านี้สามารถครอบคลุมช่วงอุณหภูมิออบติมัมของการกลั่นสารละลายไกลคอลในน้ำได้ แล้วนำข้อมูลสมดุลที่ได้มาหาค่าสัมประสิทธิ์แอกติวิตีของ 1,4-บิวทีลีนไกลคอลในน้ำโดยการฟิตข้อมูลกับโมเดล UNIQUAC และสมการWilson ด้วยโปรแกรมการคำนวณที่เขียนขึ้น และนำมาเปรียบเทียบกับค่าสัมประสิทธิ์แอกติวิตีที่จากการฟิตข้อมูลของเอทีลีนไกลคอล และ 1,2-โพรพีลีนไกลคอล ในน้ำ ที่ผู้อื่นทำวิจัยไว้ ด้วยโปรแกรมข้างต้น เพื่อศึกษาผลกระทบของขนาดโมเลกุลที่มีต่อค่าดังกล่าว

จากงานวิจัยพบว่า โมเดล UNIQUACและ Wilson สามารถใช้ได้ดีกับระบบที่ศึกษา ค่าสัมประสิทธิ์แอกติวิตีของระบบไกลคอลในน้ำแต่ละระบบขึ้นอยู่กับอุณหภูมิและองค์ประกอบของสารในระบบ นอกจากนี้ค่าสัมประสิทธิ์แอกติวิตีของไกลคอลในน้ำยังขึ้นอยู่กับขนาดและรูปร่างโมเลกุลของไกลคอลอีกด้วย โดยเมื่อพิจารณาไกลคอลที่มีโครงสร้างโมเลกุลแบบเส้นตรงแล้วพบว่าไกลคอลที่มีขนาดโมเลกุลใหญ่กว่ามีค่าสัมประสิทธิ์แอกติวิตีต่ำกว่า ส่วนไกลคอลที่มีโครงสร้างโมเลกุลแบบกิ่งมีค่าสัมประสิทธิ์แอกติวิตีสูงกว่าไกลคอลที่มีโครงสร้างแบบเส้นตรง ผลกระทบของขนาดร่วมกับรูปร่างโมเลกุลของไกลคอลในน้ำต่อค่าสัมประสิทธิ์แอกติวิตีนี้อาจอธิบายได้ด้วยแรงกระทำระหว่างโมเลกุลของสารซึ่งสามารถแสดงได้ด้วยค่าจุดเดือดของสาร อย่างไรก็ตามผลกระทบของขนาดโมเลกุลไกลคอลในน้ำจะแสดงแนวโน้มได้ชัดเจนกว่าเมื่อพิจารณาค่าพารามิเตอร์ของโมเดล โดยค่าพารามิเตอร์ของทั้งสองโมเดลคือ UNIQUACและWilsonนั้นขึ้นอยู่กับอุณหภูมิของระบบด้วย

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต

สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา

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KEY WORD : MOLECULAR SIZE / ACTIVITY COEFFICIENT / GLYCOL / WATER / AQUEOUS / VAPOR-LIQUID EQUILIBRIUM / WILSON / UNIQUAC

PARNKAMOL PRUCKSUNAND : EFFECT OF MOLECULAR SIZE ON THE ACTIVITY COEFFICIENCT OF GLYCOLS IN AQUEOUS SOLUTION. THESIS ADVISOR : ASSOC. PROF. KROEKCHAI SUKANJANAJTEE, Ph.D. THESIS CO-ADVISOR : KHANITTA MALAYAWECH. 140 pp. ISBN 974-13-1029-3.

This research was aimed to study effect of molecular size on the activity coefficient of glycols in aqueous solution. The studied glycols were ethylene glycol, 1,2-propylene glycol, and 1,4-butylene glycol. A vapor liquid equilibrium still was designed and used to produce isothermal VLE experimental data for 1,4-butylene glycol-water at temperature of 98, 110, and 122^{o}C, which cover the optimal temperature range for the distillation process of glycols in water. By fitting experimental VLE data of 1,4-butylene glycol in water with UNIQUAC or Wilson model with the aid of computer programming, the activity coefficient was obtained. The estimated activity coefficient of 1,4-butylene glycol in water was compared with that of literature results of ethylene glycol and 1,2-propylene glycol in water to study the effect molecular size.

The results shown that the UNIQUAC and Wilson models are capable of estimating with good accuracy the equilibrium conditions for such mixture. The activity coefficient of each system depends on temperature and composition. The activity coefficient also depends on molecular size and shape of glycols in aqueous solution. The activity coefficient of straight chain glycols trend to decrease when the molecular size is increased and that value of the branch chain glycol is greater than of the straight chain. The effect of molecular size together with molecular structure may be explained by interaction of component, which can be presented by boiling point of component. However, the effect of molecular size of glycols in water can be more significantly presented by the parameters of both UNIQUAC and Wilson models. The parameters were also depended on system temperature.

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
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NOMENCLATURES

a_{mn}	group interaction parameter
Bij	second virial coefficient
BG	1,4-butylene glycol (1,4-butanediol)
b.p.	boiling point temperature, T_b
EG	ethylene glycol (1,2-ethanediol)
f	fugacity
g	free energy
H	enthalpy
MW	molecular weight
N	number of experiment data
n	mole numbers
P	pressure
PG	propylene glycol (1,2-propanediol)
Q	group volume parameter
R	group area parameter
RI	refractive index
S	entropy
T	temperature
T_b	boiling point temperature, b.p.
U	molar internal energy
V	molar volume
x	liquid mole fraction
y	vapor mole fraction
Z	compressibility factor
z	feed mole fraction

Subscripts

app	approximated
c	critical property
cal	calculated value
exp	experimental value

i	i th component
j	j th component
k, m, n	group type
r	residual property
t	total

Superscripts

C	combinatorial contribution
E	excess property
l	liquid phase
v	vapor phase
R	residual contribution
sat	saturated
t	total
∞	infinite dilution

Greek letters

$\hat{\phi}_i$	fugacity coefficient of *i* in solution
γ	activity coefficient
η	viscosity
μ	chemical potential
ω	acentric factor
τ_{ij}	UNIQUAC binary interaction parameter
Λ_{ij}	Wilson parameter

CHAPTER I

INTRODUCTION

In order to design and control the industrial instruments, it is essential to have many basic informations such as density, enthalpy, viscosity, vapor pressure, etc. Particularly in the separation process that appertaining inter-phase transfer, distillation for example, need informations of phase equilibrium data or correlation to predict the properties of chemicals in the reactions at the operating condition. Besides, calculation of phase and chemical equilibrium is of fundamental importance for the design and simulation of chemical processes.

In design of the distillation, separation, extraction and absorption process, a reliable technique for estimate the thermodynamic properties of mixture is required not only to minimize the size and complexity of equipment, but also to minimize the energy requirements are of major importance in industrial applications because of their economic implications. Accurate densities for mixtures also are important for custody transfer applications.

In the past, engineers obtained data in laboratory and established equation representing properties correlation such as equation of state that exhibit pressure-volume-temperature correlation. The obtained equation is empirical equation that can not be used in all/other condition but must be limited by temperature range and/or pressure range, etc. In present, there is less experimental data. It is important to get more for improve equations to be more accurate.

Glycols are byproducts in many processes. For example, in the process of recycling PET by hydrolysis with water, ethylene glycol in water is one of the products. Another example is catalytic hydrocracking of sorbital that leads to an aqueous solution of ethylene glycol, propylene glycol, and butylene glycols, glycerol, alcohols, etc. These products can be separated by distillation.

The vapor-liquid equilibrium data for aqueous solutions of glycols in the interested condition of separation is useful for optimization the distillation process to separate the reaction products and technology. The temperature range for the distillation process is about 98-122 ^{o}C and three temperatures of 98, 110 and 122 ^{o}C cover the optimal temperature range for the process.

The equilibrium data obtained by experiment usually are interpolated and extrapolated with an equation model with the objective of using the model in another range of operating conditions. Many equations have been proposed in this field. Wilson, NRTL (Non-Random Two-Liquid) and UNIQUAC (UNIversal QUAsi Chemical) are widely used in systems with contain polar components.

Knowledge of activity coefficient can be crucial for the accurate design of any separation process. It can be estimated by using vapor-liquid equilibrium data. One-parameter Wilson equation is often used to characterize the experimental results and estimate the activity coefficients of glycols in water. Beside, many previous works were shown that the UNIQUAC model is capable of estimating with very good accuracy the equilibrium conditions for such system.

A survey of the publicly accessible literature, especially of available collection of vapor-liquid equilibrium data, revealed a scarcity of such a data, particularly with regard to aqueous and alcoholic solutions of glycols in the interested temperature for distillation process. The present work represents a continuation of experimental studies on vapor-liquid equilibrium for binary systems containing glycol in water (Lancia, 1996). The binary system of butylene glycol-water was studied in temperature range for the distillation process.

1.1 Objectives of Study

1.1.1 Producing experimentally isothermal vapor-liquid equilibrium data for the butylene glycol-water binary system.

1.1.2 Correlating the equilibrium data with UNIQUAC and Wilson equation model.

1.1.3 Considering effect of molecular size on the activity coefficient of glycols .

1.2 Scope of Study

Experimental work includes determination of isothermal vapor-liquid equilibrium data for the 1,4-butylene glycol-water system in the temperature range of 98-122^{O}C.

Analytical work includes 1) correlating experimental data with the help of UNIQUAC or Wilson equation, with the aid of computer programming, for which temperature dependent interaction parameters were fitted simultaneously to VLE data, 2) finding out the activity coefficient in aqueous solution of 1,4-butylene glycol from the experimental data, and of ethylene glycol and propylene glycol from literature experimental data (Lancia, 1996) by using the program, and 3) studying the effect of molecular size on the activity coefficient of ethylene glycol, propylene glycol, and butylene glycol in aqueous solution.

1.3 Research Procedure

1.3.1 Literature survey.
1.3.2 Literature study.
1.3.3 Chemicals and experimental apparatus preparation.
1.3.4 Laboratory experiment.
1.3.5 Data reduction.
1.3.6 Result analysis and conclusion

1.4 Expected Benefit

1.4.1 Availability of property model, UNIQUAC and Wilson equation, for aqueous solution of glycols is useful in process calculation, such as distillation process optimization.
1.4.2 Knowledge of the effect of molecular size of light glycols on the activity coefficient is useful in furtherance prediction the activity coefficient of higher molecular weight glycols.

CHAPTER II

THEORY

2.1 Phase Equilibrium[*]

A general field of physical chemistry dealing with the various situations which two or more phase (or state of aggregation) can coexist in thermodynamic equilibrium with each other, with the nature of the transitions between phases, and with the effects of temperature and pressure upon this equilibria. Many superficial aspect of the subject are largely quantitative, for example the empirical classification of types of phase diagrams; but the basic problems always are susceptible quantitative thermodynamic treatment, and in many cases, statistical thermodynamic methods can be applied to simple molecular models.

Thermodynamics required that when two phases, α and β, are free to change heat , mechanical work, and matter (chemical species), the temperature T, the pressure P, and the chemical potential (partial molar free energy) μ_i of each particular component i must be equal in both phases at equilibrium. Algebraically, equilibrium exists when $T_\alpha = T_\beta$, $P_\alpha = P_\beta$, $\mu_{i,\alpha} = \mu_{i,\beta}$, and $\mu_{j,\alpha} = \mu_{j,\beta}$.

These conditions of thermal, mechanical, and material equilibrium need not all be present if the equilibrium between phases is subject to inhibiting restrictions. Thus, for a solution of a non volatile solute in equilibrium with the solvent vapor, the condition of equality of solute chemical potentials $\mu_{2,\alpha} = \mu_{2,\beta}$ need not apply, since there can be no solute molecules in the vapor phase. Similarly, in osmotic equilibria, in which solvent molecules can pass through a semipermeable membrane, whereas solute molecules cannot, $\mu_{1,\alpha} = \mu_{1,\beta}$ and $T_{1,\alpha} = T_{2,\beta}$, but the solute chemical potentials μ_2 are unequal, as are the pressures on opposite sides of the membrane.

If a system consists of P phases and C distinguishable components, there are C + 2 thermodynamic variables (C chemical potentials μ_i, plus the temperature and pressure) which are interrelated by an equation for each phase. Since there are P independent equations relating the C + 2 variables, one needs to fix only F = C + 2 –

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[*] Parker (1993)

P variables to define completely the state of the system at equilibrium; the other variables are then beyond control. This relation for the number of degrees of freedom F, or variance, is called the phase rule and was first derived by Willard Gibbs in 1873. It has proved to be a powerful tool in interpreting and classifying types of phase equilibria.

When chemical changes may occur in the system, the number of components C is the number of independent components, this is, the number of components whose amounts can be varied by the experimenter; this is equal to the total number of chemical species present less the number if independent chemical equilibria between them.

An invariant system has no degrees of freedom (F = 0), for which the number of phases P = C + 2. For a one-component system, such an invariant point is a triple point at which three phases coexist at a single temperature and pressure only; for a two-component system, a quadruple point (four phases) would be invariant.

In a univariant system (F = 1), P = C + 1. With a one-component system, one can fix the temperature at which two phases (liquid and gas, for instance) can coexist in equilibrium; then the pressure (here the vapor pressure) is determined and not subject to external control. A univariant system is described by a line in a phase diagram, for example, a plot of vapor pressure versus temperature. The differential equation, Equation (2.1), for such a univariant line in a one-component system was first deduced by B. P. E. Clapeyron in 1834.

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{2.1}$$

In the equation ΔH and ΔV are the enthalpy change (heat absorbed) and volume change, respectively, for the transition from one phase to another.

Binary System

Phase diagrams and binary systems containing two components are easily classified. Typical examples of the important classes (liquid-gas, liquid-liquid, solid-liquid, solid-solid) have been selected for description.

Consider a liquid-vapor equilibrium. In a one-component system, liquid and vapor are in equilibrium at the boiling point. For two–components systems, the two-phase situation is bivariant and more complex. A complete temperature-pressure-composition diagram would be three-dimensional, so most phase diagrams are made for either constant pressure or constant temperature. Figure 2.1 shows the simplest type of binary liquid-vapor temperature-composition diagram, exemplified by the system carbon tetrachloride–stannic chloride, which forms essentially ideal solution. The regions label *G* and *L* are one-phase, gas (vapor) and liquid, respectively; the region labeled *L* + *G* is a two-phase region in which liquid and vapor coexist. If the temperature of a liquid mixture of 40 mole percent $SnCl_4$ (mole fraction = 0.40) is increased at a constant pressure of 1 atm, the change in the system can be traced along the straight line *ab'cd"e* . At low temperatures, only one phase, the liquid, is present, but at 87.5^{o}C (190^{o}F) point *b'*, a vapor phase appears. The composition of this vapor phase is given by point *b"* (mole fraction $SnCl_4$ = 0.18), and the two conjunction phases are connected on the diagram by the tie line *b"b'*. As the temperature is increased further, more vapor is formed; since the vapor is rich in CCl_4 , this component becomes relatively depleted in the liquid phase, and the liquid composition move along the line *b'c'd'*, while the vapor composition moves along the line *b"c"d"*.

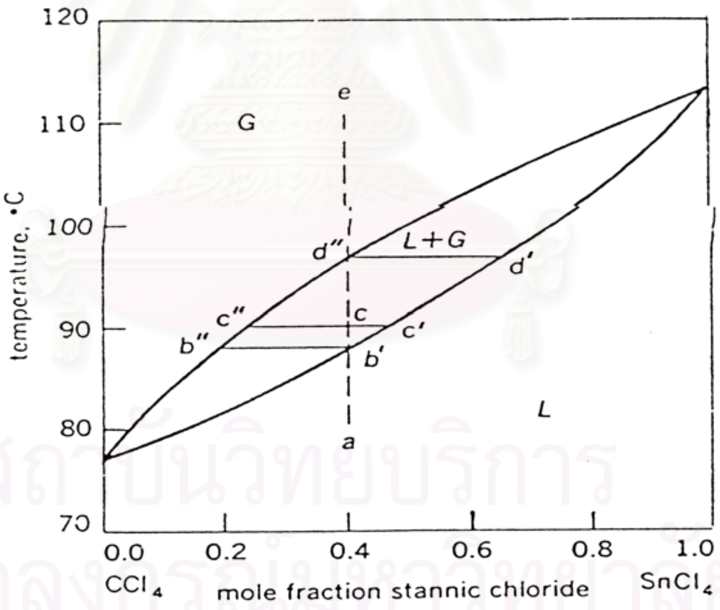


Figure 2.1 Binary liquid-vapor temperature-composition diagram for the system carbon tetrachloride + stannic chloride. *G* = gas (vapor) phase; *L* = liquid phase; *L* + *G* = two coexisting phase. Pressure = 1 atm (10^2 kPa). ^{O}F = (^{O}C x 1.8) + 32.

At 90^{o}C (194^{o}F) the over all composition of the two-phase system is represented by point *c*, but the compositions of vapor and the liquid separately are given by the two ends of the tie line, points *c″* and *c′*, respectively (mole fractions of 0.22 and 0.47, respectively). The relative amounts of the two phases are given by the lever arm principal of physics. The ratio of the moles of vapor to moles of liquid is given by the ratio length *cc′* to the length *c″c*, here 0.07:0.18, or 28%, in the vapor phase. Further increase in temperature produces more and more vapor until, at 97^{o}C (207^{o}F), the liquid phase (point *d′* mole fraction) has become vanishingly small; at higher temperatures, it disappears, and only the vapor phase (point *d″*, mole fraction = 0.40) remains. Further increase in temperature (along the line *d″e*) is uneventful.

In this simple system, there are no maximum or minimum in the liquid and vapor curves; consequently, such liquid mixture can be separate completely into the two pure components by fractional distillation. Systems with maximum boiling points (acetone + chloroform, Figure 2.2) or minimum boiling points (ethanol + benzene, Figure 2.3) cannot be so separated into the pure substances. At the maximum or minimum, the composition of the liquid is identical with that of the vapor with which it is in equilibrium; continued boiling will not alter these compositions, so that these solutions are called constant-boiling mixtures or azeotropes. It should be noted that the solid and liquid lines are smooth curves tangent to each other at such a point; any phase diagram which shows a sharp corner is thermodynamically incorrent.

Maximum boiling mixtures are associated with negative deviations from ideal behavior usually arises from strong attractions between molecules of the different species (sometimes call component formulation). Minimum boiling mixtures are associated with positive deviations from ideal behavior; this usually arises when the attraction between two unlike molecules (*1-2*) is weaker than the average of two like pairs (*1-1* and *2-2*); extreme examples of this arise when one component may be described as associated. The simpler type of phase diagram (Figure 2.1) occurs when the two components mix nearly ideally or when the boiling points are very different.

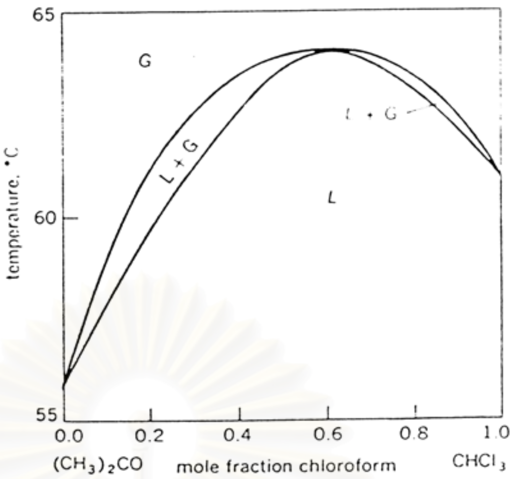


Figure 2.2 Temperature-composition diagram for acetone + chloroform, showing maximum boiling point. Pressure = 1 atm (10^2 kPa). ^{O}F = (^{O}C x 1.8) + 32.

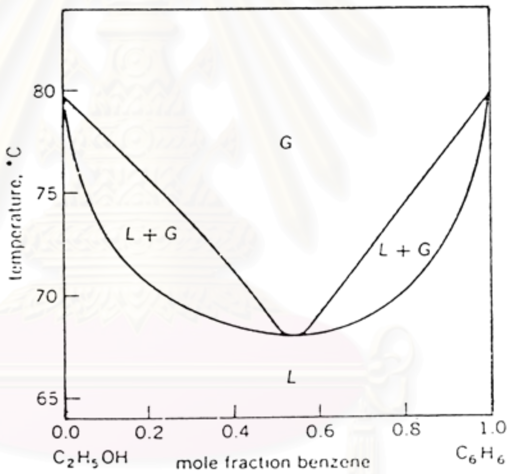


Figure 2.3 Temperature-composition diagram for ethanol + benzene, showing minimum boiling point. ^{O}F = (^{O}C x 1.8) + 32.

Figure 2.3 Temperature-composition diagram for ethanol + benzene, showing minimum boiling point. ^{O}F = (^{O}C x 1.8) + 32.

Multicomponent System

As one proceeds from binary systems to systems with three or more components, the phase diagrams become more complex. Each component add another dimension to the representation of the phase equilibria. Thus for three components, two dimensions are required to represent the phase diagrams for a single temperature and pressure; these are conveniently depicted by a triangular diagram in with each vertex represents a pure component. Figure 2.4 show a diagram of a ternary system in which three liquid phases can coexist. Even when there are three phases, the system is still bivariant. (An example of such a system in water + succinonitrile + diethyl ether.)

A special case of three-component system is that in which there are two immiscible solvents and a third component, soluble in both, distributed between the two phases. The ratio of the concentration of the solute in the two solvents is the distribution coefficient; in dilute solutions, this is independent of the concentration, but the higher concentrations, nonideal behavior of the solute can produce systematic variations of the distribution coefficient which ends on the most concentrated solutions with the ratio of the solubilities in the saturated solutions.

Distribution effects are important in separating similar materials. A small different in distribution coefficient is amplified by multistage equilibria, such as those used in countercurrent extraction and partition chromatography.

The example used to illustrate the various types of phase equilibria are not supposed to suggest that these types are restricted to the particular kind of chemical substances shown. In general, examples of each could have been selected from many kinds of substance such as metals, nonmetallic elements, inorganic salts, and organic nonelectrolytes.

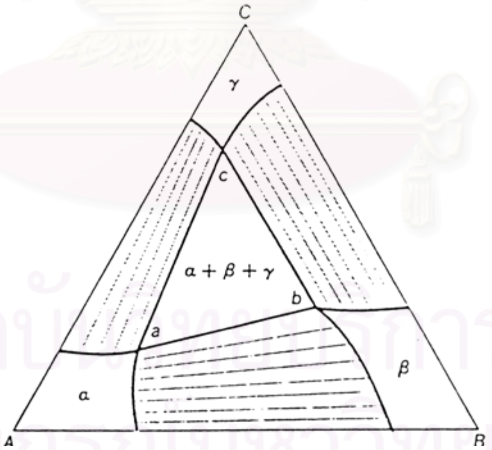


Figure 2.4 Schematic diagram of a three-component system at a fixed temperature and pressure. Points A, B, and C represent the pure liquids. The composition corresponding to a point in the diagram is determined by the positions along a line from each vertex to the opposite side; thus point *b* is 20% *A*, 50% *B*, 30% *C*. Region; α, β, and γ correspond to single phase rich in *A*, *B*, and *C*, respectively; $\alpha + \beta + \gamma$ is a three-phase region; the three saturated solutions have the compositions given by the points a, b, and c. Three two-phase regions, $\alpha + \beta$, $\alpha + \gamma$, and $\beta + \gamma$, are indicated by drawing in the tie lines.

2.2 Chemical Potential and Phase Equilibrium

When equilibrium is attained in a closed *PVT* system consisting of two phases which each may be considered a single-phase open system. The differential changes at the equilibrium state for the two phases with superscripts α and β identifying are

$$d(nU)^{\alpha} = Td(nS)^{\alpha} - Pd(nV)^{\alpha} + \sum \mu_i^{\alpha} dn_i^{\alpha}$$

$$d(nU)^{\beta} = Td(nS)^{\beta} - Pd(nV)^{\beta} + \sum \mu_i^{\beta} dn_i^{\beta}$$

Where *U*, *S* and *V* are molar properties of the phase. n_i is mole numbers of component *i*. And μ_i is called the chemical potential of component *i*.

The equilibrium is in uniformity of temperature (*T*) and pressure (*P*) throughout both phases. The sum of these two equations is

$$dU = TdS^t - PdV^t + \sum \mu_i^{\alpha} dn_i^{\alpha} + \sum \mu_i^{\beta} dn_i^{\beta}$$

From

$$dU^t = TdS^t - PdV^t$$

Thus

$$\sum \mu_i^{\alpha} dn_i^{\alpha} + \sum \mu_i^{\beta} dn_i^{\beta} = 0$$

From mass transfer between the two phases, mass conversion requires that

$$dn_i^{\alpha} = -dn_i^{\beta}$$

Thus

$$\sum (\mu_i^{\alpha} - \mu_i^{\beta}) dn_i^{\alpha} = 0$$

Since the dn_i^{α} are independent and arbitrary, the general equation satisfied for an *N*-component system is

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad (i = 1,2,3,\ldots,N)$$

For more than two phase, application to pairs of phase leads to generalization for π phases:

$$\mu_i^{\alpha} = \mu_i^{\beta} = \ldots = \mu_i^{\pi} \qquad (i = 1,2,3,\ldots,N) \qquad (2.2)$$

This equation is a general criterion for phase equilibrium.

2.3 Vapor-Liquid Equilibrium (VLE)

Similar to pressure, the fugacity of a component *i* in a multicomponent, multiphase system must be the same in all phases at equilibrium. As equation (2.2) we obtain

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} = \ldots = \hat{f}_i^{\pi} \qquad (i = 1,2,3,\ldots,N) \qquad (2.3)$$

which $\hat{f}_i$ is the fugacity of a component *i* in a solution, not a pure-component property and not a partial property.

For the vapor (*v*)-liquid (*l*) equilibrium, equation (2.3) becomes

$$\hat{f}_i^{v} = \hat{f}_i^{l} \qquad (2.4)$$

This equation is common used as the basis for the solution of VLE problems.

From definition of the fugacity coefficient of a component *i* in solution:

$$\hat{\phi}_i = \hat{f}_i / x_i P \qquad (2.5)$$

Where x_i is a mole fraction of a component i in the solution.

And from definition of the activity coefficient of species *i*:

$$\gamma_i = \hat{f}_i / x_i f_i \qquad (2.6)$$

where f_i is the fugacity of pure *i*.

Replaces the fugacities in Equation(2.4) by using Equation (2.5) which let y_i to represent a vapor-phase mole fraction for the vapor phase and using Equation (2.6) for the liquid phase with representing a liquid-phase mole fraction by x_i. Thus we have

$$y_i \hat{\phi}_i P = \gamma_i x_i f_i^{l} \qquad (2.7)$$

For Gas at low pressure,

$$\lim_{P \to 0} \left(\hat{f}_i / x_i P \right) = 1 \qquad \text{and} \qquad \lim_{P \to 0} (f_i / P) = 1$$

Thus $\hat{\phi}_i$ in the left side of Equation (2.7) becomes to unity and f_i^{l} in the right of the equation equal to P_i^{sat} at the equilibrium temperature. So we obtain

$$y_i P = \gamma_i x_i P^{sat} \qquad (2.8)$$

The saturated pressure, P_i^{sat}, is the vapor pressure of pure component *i* at the equilibrium temperature. It is pure component property that we can know.

So in many researches that received y_i, x_i, and *P* from the experimental VLE data, the activity coefficients could be calculated by Equation (2.7) or (2.8) as a function of equilibrium conditions, pressure and temperature.

2.4 Vapor Pressure

Vapor pressure or saturated pressure is the specific property of each component. It is temperature dependent property. By calculation, the vapor pressure P_i^{sat} is usually represented as a function of temperature T by an empirical formula. The derivation of vapor pressure equations may be written as

$$\frac{d \ln P^{sat}}{d\,(1/T)} = \Omega$$

where the quantity of Ω depends on T only. The simplest polynomial expression of sufficient generality for the temperature dependence of Ω is

$$\Omega = B + DT + ET^a$$

where B, D, E, and a are empirical constants.

So the general form of vapor pressure equation is given by substitution and integration as

$$\ln P^{sat} = A - \frac{B}{T} + D \ln T + FT^b \qquad (2.9)$$

where $b = a\text{-}1$, $F = E/b$. This equation in its complete form can reasonably accurate description of the entire vapor pressure.

There are many of widely used vapor-pressure equations for determination of vapor pressure of pure component as the following.

2.4.1 Clausius-Clapeyron Equation

The simplest nontrivial equation for P^{sat} is obtained by let the assignments $D = F = 0$ in Equation (2.9), giving

$$\ln P^{sat} = A - \frac{B}{T}$$

This equation implied that Ω is a constant, independent of T. It never provide absurd values for vapor pressure. It is often used for rough calculation where high accuracy is not required.

2.4.2 Kirchhoff Equation

The result of setting $F = 0$ in Equation (2.9),

$$\ln P^{sat} = A - \frac{B}{T} + D \ln T$$

This implied a linear approximation to the T dependence of Ω. It offers little adventage over the Clausius-Clapeyron equation.

2.4.3 Riedel Equation

One of complete form of the general vapor pressure equation, Equation (2.9), where $b = 6$ ($a = 7$) is proposed, the four-parameter Riedel equation, a favorable expression, is produced.

2.4.4 Antoine Equation

The three-parameter Antonie equation :

$$\ln P^{sat} = A - \frac{B}{T + C}$$

is essentially an empirical modification of Equation (2.9). It implied a nonlinear temperature dependence expression of Ω:

$$\Omega = \frac{BT^2}{\left(T + C\right)^2}$$

This makes the Antoine equation more accurate than three-parameter Kirchhoff equation.

2.4.5 Miller's Equation

Miller's equation use critical pressure and temperature, and boiling point temperature T_b to calculate the vapor pressure.

$$\log P_r^{sat} = -\frac{G}{T_r}\left[1 - T_r^2 + k\left(3 + T_r\right)\left(1 - T_r\right)^3\right]$$

where $$P_r^{sat} = \frac{P^{sat}}{P_c}$$

$$G = 0.210+0.200\text{a}$$

$$\text{a} = \frac{T_{rb}\ln P_c}{1 - T_{rb}}$$

$$k = \frac{(1/2.306G) - (1 + T_{rb})}{(3 + T_{rb})(1 - T_{rb})^2}$$

$$T_{rb} = \frac{T_b}{T_c}$$

2.5 Equations of State (EOS)

Equations of state are widely used to predict thermodynamic behaviors of pure and mixture fluids.. They empirically provide a relation between pressure, density, temperature and (for mixture) composition. The equations of state can be also used to determine equilibrium conditions and other properties. Specially afterwards for the objective of using the equilibrium data in a wide range of operating conditions. Many equations represent the properties of vapor phase but some are for only liquid phase. The most well-known of equation of state models are capable of application in both vapor and liquid phases. But there is no equation appropriate to all solid, liquid and vapor.

In calculation of vapor-liquid equilibrium it is necessary to calculate separately the fugacity of each component in each of the two phases. The fugacity $\hat{f}_i^v$ of component i in the vapor phase is related to its mole fraction y_i in the vapor phase and to the total pressure P by the fucacity coefficient as shown in Equation (2.5) which let y_i to represent the vapor phase mole fraction for the vapor phase in stead of x_i.

The fugacity coefficient is a function of temperature, total pressure, and composition of the vapor phase. It can be found by using the equation of state in the rigorous thermodynamic relation :

$$\ln\hat{\phi}_i = \frac{1}{RT}\int_{V_t}^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V_t,\,n_i \atop j\neq i} - \frac{RT}{V_t}\right]dV_t - \ln Z \tag{2.10}$$

where V_t is total volume having n_1 moles of *1*, n_2 moles of *2*, etc, and Z is the compressibility factor of vapor mixture,

$$Z = \frac{PV}{\left(n_1 + n_2 + \ldots\right)RT}$$

If the vapor mixture have a behavior as ideal gas, at low pressure (less than one atmosphere) as the frequently good example, the integral in Equation (2.10) is zero, Z is unity for all compositions, and $\hat{\phi}_i$ = 1 for each component *i*.

2.5.1 Virial Equation

Among numerous empirical equation of state have been proposed, the virial equation is the only equation of state with firm theoretical basis.

The virial equation of state is a power series in the reciprocal volume

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots \tag{2.11}$$

where V is the molar volume of the gas, B is the second virial coefficient, C is the third virial coefficient, etc.

For a pure vapor, the virial coefficients are function of temperature only. But for a mixture, they are also function of composition within, the rigorous relationships are given below.

$$B_{\text{mixture}} = \sum_i^N \sum_j^N y_i y_j B_{ij} \tag{2.12}$$

$$C_{\text{mixture}} = \sum_i^N \sum_j^N \sum_k^N y_i y_j y_k C_{ijk} \tag{2.13}$$

where each of coefficient B_{ij} and C_{ijk} is function only of temperature. Substitution of Equations (2.11), (2.12), and (2.13) into Equation (2.10) give

$$\ln\widehat{\phi}_i = \frac{2}{V}\sum_{j}^{N} y_i B_{ij} + \frac{2}{2V^2}\sum_{j}^{N}\sum_{k}^{N} y_i y_k C_{ijk} + \ldots - \ln Z$$

For typical industrial operations such as distillation, absorption, or flash separations, the third and higher virial coefficients are neglected, the fugacity coefficient is given by

$$\ln\widehat{\phi}_i = \frac{2}{V}\sum_{j}^{N} y_i B_{ij} - \ln Z$$

The correlation for second virial coefficients B_{ii} for pure gases both of which nonpolar and polar based on a tree-parameter theory of corresponding states is described by Prausnitz (1967).

To estimate the cross-coefficients B_{ij} ($i \neq j$) in mixture, we can calculate from known pure B_{ii} and B_{jj} by using a geometric-mean combination rule as following

$$B_{ij} = \sqrt{B_{ii} B_{jj}} \tag{2.14}$$

In other words, Prausnitz (1967) has used the correlation equations for pure components with suitable rules for the various parameters to present the cross-coefficient B_{ij} of mixture.

In this research, the fugacity coefficient of vapor is calculated from

$$\ln\widehat{\phi}_i = \left[2.0\sum_{j=1}^{N} y_i B_{ij} - B_m\right]\frac{P}{RT} \tag{2.15}$$

with use the Eq. (2.14) to calculate B_{ij}. The second virial coefficients B_{ii} for some pure glycols ware presented in Table A.2.

2.6 Propreties Model

The fugacity $\hat{f}_i^{\,l}$ of component i in the liquid phase is related to its mole fraction x_i in the liquid phase and to the fugacity f_i of pure i by the activity coefficient γ_i as presented in Equation (2.6). To calculate the activity coefficient, there are properties models deserving for mixture containing strongly polar components such the Wilson Equation and UNIQUAC model.

2.6.1 Wilson Equation

Wilson equation is one of activity coefficient equations of multicomponent mixture based on local-composition theory presented the effect of pressure and temperature on some solution properties such as Gibbs free energy of solution, fugacity of a component *i* in a solution, activity coefficient, etc. The equations based on this concept was introduced into solution theory by G. M. Wilson. The Wilson equation is written as

$$g = -\sum_i \left[x_i \ln \left(\sum_j x_j \Lambda_{ij} \right) \right]$$

Wilson equation is usually written as function of activity coefficient as shown below.

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^{n} x_i \Lambda_{ij} \right) - \sum_{k=1}^{n} \left(\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{n} x_j \Lambda_{kj}} \right) \qquad (2.16)$$

Λ_{ij} is the approximate temperature dependence of the parameter for the Wilson equation:

$$\Lambda_{ij} = \frac{V_j^l}{V_i^l} \exp \left(\frac{-A_{ij}}{RT} \right) \qquad (i \neq j)$$

with $\Lambda_{ij} = 1$ for $i = j$

Where V_j^l and V_i^l are the molar volume at temperature T of liquid *j* and *i*, and A_{ij} is a constant independent of composition and temperature which some is collected in the work of Gmehling and Onken, “Vapor-Liquid Equilibrium Data Collection”, a series of volumes (appearing first in 1997). The values of Wilson parameters which may not be negative, usually are in a range of $0 < \Lambda_{ij} < 5$ (Nagahama, Suzuki and Hirata, 1971).

2.6.2 UNIQUAC Model

In the UNIQUAC theory, the deviation from ideal behavior of real solution can be described by a combinatorial contribution, which depends on the differences in the shape and in the dimensions (size) of the molecules, and by a residual contribution, which depends on the energetic interactions between molecules. Consequently, the expression of excess free energy g^E is given by :

$$g^E = g^E_{comb} + g^E_{res}$$

and correspondingly the activity coefficient of the *i* species depends on a combinatorial contribution

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (2.17)$$

where

$$\ln\gamma_i^C = \ln\frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j \qquad (2.18)$$

and

$$\ln\gamma_i^R = q_i\left[1 - \ln\sum_j \theta_i \tau_{ji} - \sum_j \left(\theta_j \tau_{ij} \,/\, \sum_k \theta_k \tau_{kj}\right)\right] \qquad (2.19)$$

which $$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad ; \quad \widehat{z} = 10$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}; \qquad \phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

$$\tau_{ji} = \exp - \left[\frac{u_{ji} - u_{ii}}{RT}\right]$$

$\widehat{z}$ is lattice coordination number, set equal to 10. θ_i is the area fraction and ϕ_i is the segment fraction which is similar to the volume fraction. Pure component parameters r_i and q_i indicate measures of molecular van der Waals volumes and molecular surface areas respectively. The parameters r_i and q_i are calculated as the sum of the group volume and area parameters, R_k and Q_k respectively as described in UNIFAC method. Group parameter R_k and Q_k are obtained from van der Waal group volume and surface areas. Collection of some group parameters R_k and Q_k are given in Table B.1.

The two adjustable binary parameters τ_{ij} and τ_{ji} must be evaluated from experimental phase equilibrium data. In general, ($u_{ji} = u_{ii}$) and ($u_{ij} = u_{jj}$) are linear function of temperature in accordance with $u_{ji} = u_{ij}$ and $\tau_{ii} = \tau_{jj} = 1$. The binary parameters τ_{ij} and τ_{ji} are enough to use for ternary or multicomponent systems, no ternary or higher parameter are required.

The UNIQUAC model gives good representation of both vapor-liquid and liquid-liquid equilibrium for binary and multicomponent mixtures containing a variety of nonelectrolytes such as hydrocabons, ketones, esters, water, amines, alcohols, nitriles, glycols, etc.

2.6.3 UNIFAC Method

The concept of UNIFAC (UNIQUAC functional-group activity coefficients) model following Derr and Deal's (1969) ASOG model let the activity coefficients in mixtures relate to interaction between structure groups. The method is used to reduce experimentally obtained activity coefficient data to obtain parameters characterizing interaction between pairs of structural groups in nonelectrolyte systems and then the collection of parameters is used to predict the activity coefficients for other systems which have no experimental equilibrium data study but contain the functional groups have in the collection. So with use of the interaction parameters, that can be back-calculated from exiting equilibrium data, together with the size parameter, that can be calculated from theory, the prediction of phase equilibrium properties of mixture is available.

Liquid phase activity coefficients can be estimated for non ideal mixture which lack of experiment data by UNIFAC when the assumption of regular solution is not valid because polar components are present.

The UNIFAC method is based on the UNIQUAC method. In the UNIFAC method, the parameters are independent of temperature, available for wide range of type of functional groups. The prediction by the method can be made in a temperature range of 275 to 425 K for pressure up to a few atmospheres.

The combinatorial part in the UNIFAC method is the same as in the UNIQUAC activity coefficients as Equation (2.18). Only pure component properties is used in the equation. Parameters r_i and q_i are calculated by equation below

$$r_i = \sum_k \nu_k^{(i)} R_k \qquad \text{and} \qquad q_i = \sum_k \nu_k^{(i)} Q_k$$

where $\nu_k^{(i)}$ is the number of groups of type k in molecule i, always an integer.

The residual part of the activity coefficients, Equation (2.19) is replaced by the solution-of-groups concept, as below equation is instead of.

$$\ln\gamma_i^R = \sum_k \nu_k^{(i)} [\ln\Gamma_k - \ln\Gamma_k^{(i)}] \tag{2.20}$$

where Γ_k is the group residual activity coefficient, found from an expression similar to Equation (2.19) as below, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i.

$$\ln\Gamma_k = Q_k \left[1 - \ln(\sum_m \theta_m \psi_{mk}) - \sum_m (\theta_m \psi_{km} / \sum_n \theta_n \psi_{nm}) \right] \tag{2.21}$$

where θ_m is the area fracton of group m and the sum the sums over all different group. θ_m is calculated in a manner similar to that of θ_i as by Equation (2.22). The Equation (2.21) also hold for $\ln\Gamma_k^{(i)}$.

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$$

where X_m is the mole fraction of group m in the mixture. The group interaction parameter ψ_{mn} is given by

$$\psi_{mn} = \exp\left[\frac{u_{mn} - u_{nn}}{RT} \right] = \exp - (a_{mn} / T)$$

where u_{mn} is a measure of the energy of interaction between groups m and n. The group interaction parameter a_{mn} obtained from a database using wide range of experiment results. The a_{mn} has unit of kelvins. The $a_{mn} \neq a_{mn}$ but when $m = n$, $a_{mn} = 0$ and $\psi_{mn} = 1$. Some of these are shown in Table B.2.

CHAPTER III

LITERATURE REVIEWS

Many past researches shown that the system containing similar groups of components often correlate with the same equation model. In some glycols-water binary mixtures, the equilibrium data were correlated with the Wilson, NRTL and UNIQUAC equations and the activity coefficient could be evaluated.

Although the UNIQUAC can accurately describe the behavior of mixture containing strongly polar species, as those considered in this work, but Wilson equation is simplifier and is also good for correlating many past research data.

3.1 Related Literature

A survey of the aqueous solution of glycols system, revealed the temperature range for the distillation process is about 98-122 ^{o}C and three temperatures of 98, 110 and 122 ^{o}C cover the optimal temperature range for the process. VLE of ethylene glycol - water, propylene glycol - water, and ethylene glycol - propylene glycol at this three temperatures were determined by Lancia et al. (1996). The data were correlated by UNIQUAC equation with the assumption of low pressure and the Equation (2.8) hold. Experimental results for the mixture water-ethylene glycol and water–propylene glycol is shown in the Table3.1 and Table 3.2, accordingly.

The work of Lancia et al. (1996) inform that the UNIQUAC model has been successfully applied to the mixture ethylene glycol - propylene glycol – water in the temperature range of 98-122 ^{o}C. The ternary mixture and the three binary mixtures which can be obtained from these three species have been considered. In particular, vapor-liquid equilibrium data relative to the binary systems have been used to evaluate the binary interaction parameters. For example, UNIQUAC interaction parameters (τ) for the binary mixtures at the temperatures of experiment are shown in Table 3.3. Afterwards, such parameters have been used to predict the equilibrium conditions for the ternary system, and a satisfactory agreement has been found between model and experimental results.

According to UNIQUAC method, the work of Lancia et al. (1996) used the expression proposed by Kikic et al. (1980), the combinatorial part, differed from the original, was evaluated the expression:

$$\ln\gamma_i^C = \ln\frac{\vartheta_i}{x_i} + 1 - \frac{\vartheta_i}{x_i} \qquad (3.1)$$

where is ϑ_i is the volume fraction for the *i* specied which is defined as :

$$\vartheta_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}}$$

However, the work of Kikic et al. (1980) studied only in saturated aliphatic hydrocarbons, not polar components as considered in Lancia (1996)'s and this work.

Table 3.1 Experimental results for the mixture water (*1*)-ethylene glycol (*2*) by Lancia et al. (1996).

T = 98 °C (371 K)			*T* = 110 °C (383 K)			*T* = 122 °C (395 K)		
P(kPa)	x_1(-)	y_1(-)	*P*(kPa)	x_1(-)	y_1(-)	*P*(kPa)	x_1(-)	y_1(-)
4.25	0.026	0.570	5.33	0.012	0.330	7.31	0.006	0.191
5.32	0.039	0.680	7.46	0.029	0.561	16.48	0.050	0.673
9.57	0.089	0.826	10.93	0.055	0.715	17.28	0.055	0.668
13.69	0.137	0.879	11.86	0.063	0.737	19.93	0.069	0.721
33.62	0.377	0.964	14.53	0.083	0.782	22.73	0.089	0.765
53.16	0.594	0.986	15.46	0.095	0.805	23.12	0.093	0.769
65.92	0.710	0.992	23.33	0.159	0.882	27.11	0.119	0.836
68.44	0.733	0.995	29.06	0.199	0.900	32.69	0.144	0.821
70.83	0.754	0.994	34.92	0.25	0.924	42.53	0.215	0.881
81.07	0.841	0.997	41.32	0.300	0.939	45.18	0.225	0.889
90.77	0.912	0.998	71.44	0.562	0.978	49.17	0.235	0.898
92.76	0.970	0.999	79.71	0.613	0.989	70.43	0.386	0.941
			91.17	0.667	0.988	83.72	0.467	0.959
			118.36	0.826	0.999	106.58	0.586	0.976
						131.83	0.684	0.985
						149.64	0.753	0.992

Table 3.2 Experimental results for the mixture water (*1*)-propylene glycol (*2*) by Lancia et al. (1996).

T = 98 °C (371 K)			T = 110 °C (383 K)			T = 122 °C (395 K)		
P(kPa)	x_1(-)	y_1(-)	P(kPa)	x_1(-)	y_1(-)	P(kPa)	x_1(-)	y_1(-)
3.32	0.004	0.124	5.86	0.005	0.124	14.88	0.030	0.430
4.39	0.016	0.339	6.66	0.010	0.211	25.25	0.080	0.679
5.71	0.033	0.517	11.20	0.043	0.557	38.01	0.147	0.796
6.38	0.040	0.570	12.66	0.054	0.615	57.94	0.254	0.881
8.51	0.065	0.681	15.73	0.077	0.696	66.98	0.300	0.900
18.74	0.182	0.871	20.53	0.113	0.774	70.70	0.321	0.908
36.68	0.395	0.951	33.59	0.211	0.876	73.09	0.331	0.915
52.89	0.577	0.976	46.65	0.312	0.922	73.62	0.333	0.916
57.14	0.616	0.981	78.64	0.563	0.971	107.64	0.514	0.959
74.42	0.786	0.992	79.97	0.572	0.972	182.46	0.830	0.980
			115.96	0.795	0.992			

Table 3.3 UNIQUAC interaction parameters (τ) for the mixture water-propylene glycol-ethylene glycol at the temperatures of 98 °C, 110 °C and 122 °C, evaluated by Lancia et al. (1996).

		98 °C	110 °C	122 °C
H_2O(*1*)-EG(*2*)	τ_{12}	2.13	2.35	2.59
	τ_{21}	0.279	0.210	0.161
H_2O(*1*)-PG(*2*)	τ_{12}	1.50	1.62	1.75
	τ_{21}	0.533	0.449	0.383
PG(*1*)-EG(*2*)	τ_{12}	1.39	1.51	1.62
	τ_{21}	0.661	0.581	0.515

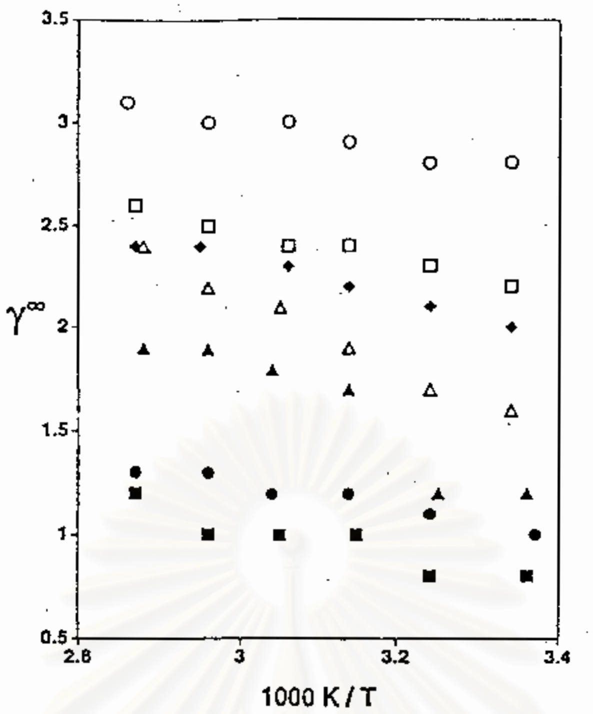
Activity coefficients of glycols at infinite dilution of aqueous solution of ethylene glycol, propylene glycols and butylene glycols were obtained experimentally by Suleiman and Eckert (1994). They used dew point technique in their experimental work. They informed that the new developed dew point technique used in their work is especially suitable to this type of system with very low relative volatility (e.g. < 0.5), where other methods are inapplicable. A one parameter Wilson equation was used to characterize the results and to estimate γ^{∞} for water in the glycols. Partial molar excess enthalpies at infinite dilution were estimated from the temperature derivative of the limiting activity coefficients.

In the work of Suleiman and Eckert (1994), the limiting activity coefficients for 1,2-ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol (1,4-butylene glycol) and 2,3-butanediol in water were measured over a range of temperatures (297-348 K) as shown in Table 3.4. The result shown that the activity coefficients of glycols infinitely diluted in water trend to increase when molecular size is larger and each trend to increase when temperature is higher, not linear, depend on molecular structure also, as illustrated by Figure 3.1. However, they found that there is some disagreement of extrapolated data from other source with dew point data at higher temperature which is where this technique is less accurate, that is within experimental uncertainty. In their work, the disagreement in glycol-water system was shown as an uncertainty of the activity coefficients at infinite dilution as in the Figure 3.2 for ethylene glycol and Figure 3.3 for propylene glycol in water. The dependence of infinite dilution activity coefficients on temperature of other extrapolated data was not in accord with their data.

According to UNIQUAC and UNIFAC models, a combinatorial contribution accounts for size- and shape-effects and a residual contribution accounts for interactions among groups or molecules. Kikic et al. (1980) proposed the development of a new combinatorial part of UNIFAC and UNIQUAC models to improve predictions of the excess Gibbs energy of systems where the residual contribution may be expected to be zero (eg. mixtures of aliphatic hydrocarbons). They offered two modifications of the S-G combinatorial that much better predictions than the original version in the aliphatic hydrocarbon systems. Equation (3.1) is an example of modification. For strongly interacting systems, such as alcohol-paraffin and ketone-paraffin systems with contain strongly interacting groups as examples, the residual part is usually muck larger than the combinatorial part. The modified expression was found to have little effect on the overall correlation of such this type of system; in these cases one may use either the original or the new combinatorial. So this research has used the original one, different from the Lancia et al.(1996) work.

Table 3.4 Activity coefficients of diols (*1*) infinitely diluted in water (*2*), γ_1^∞, obtained by Suleiman and Eckert (1994).

SOLUTE	T/K	γ_1^∞	SOLUTE	T/K	γ_1^∞
1,2-ethanediol	297.5	0.8 ± 0.1	1,3-butanediol	299.1	2.2 ± 0.2
	308.2	0.8 ± 0.1		308.8	2.3 ± 0.2
	317.9	1.0 ± 0.1		318.3	2.4 ± 0.3
	328.2	1.0 ± 0.1		327.3	2.4 ± 0.3
	338.1	1.0 ± 0.1		338.1	2.5 ± 0.3
	348.1	1.2 ± 0.2		348.0	2.6 ± 0.3
1,2-propanediol	296.8	1.0 ± 0.1	1,4-butanediol	299.4	2.8 ± 0.3
	308.3	1.1 ± 0.1		309.1	2.8 ± 0.3
	318.8	1.2 ± 0.1		318.4	2.9 ± 0.3
	328.5	1.2 ± 0.2		326.8	3.0 ± 0.3
	337.9	1.3 ± 0.2		337.6	3.0 ± 0.3
	348.3	1.3 ± 0.2		349.9	3.1 ± 0.4
1,3-propanediol	298.0	1.2 ± 0.2	2,3-butanediol	299.0	1.6 ± 0.2
	307.9	1.2 ± 0.2		308.9	1.7 ± 0.2
	318.7	1.7 ± 0.2		318.5	1.9 ± 0.2
	328.7	1.8 ± 0.2		327.4	2.1 ± 0.2
	338.4	1.9 ± 0.2		337.7	2.2 ± 0.3
	347.5	1.9 ± 0.2		347.4	2.4 ± 0.3
1,2-butanediol	299.2	2.0 ± 0.2			
	308.4	2.1 ± 0.2			
	318.1	2.2 ± 0.2			
	327.3	2.3 ± 0.3			
	338.6	2.4 ± 0.3			
	348.4	2.4 ± 0.3			



(■) 1,2-ethanediol, (●) 1,2-propanediol, (▲) 1,3-propanediol, (♦) 1,2-butanediol, (□) 1,3-butanediol, (○) 1,4-butanediol, (△) 2,3-butanediol.

Figure 3.1 Comparison of γ^∞ values for various diols in water measuerd by dew point method researched by Suleiman and Eckert (1994).

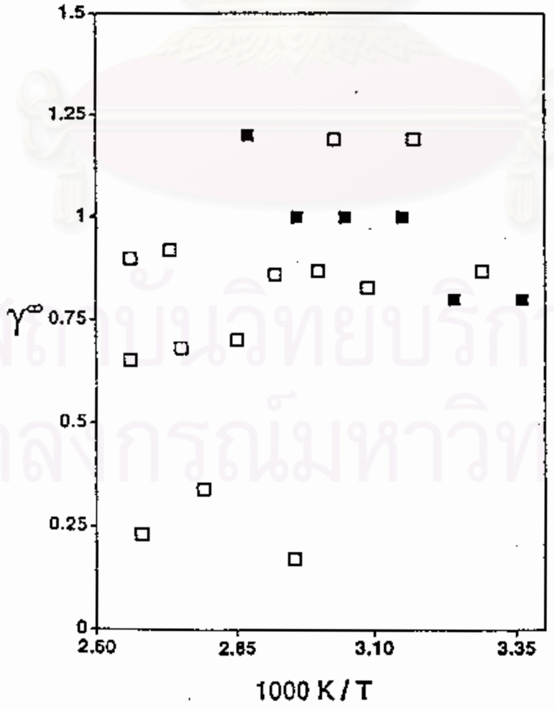


Figure 3.2 Comparision of γ^∞ values for 1,2-ethanediol in water measuerd by dew point method researched by Suleiman and Eckert (1994), (■) , with values obtained by other VLE extrapolated sources, (□) .

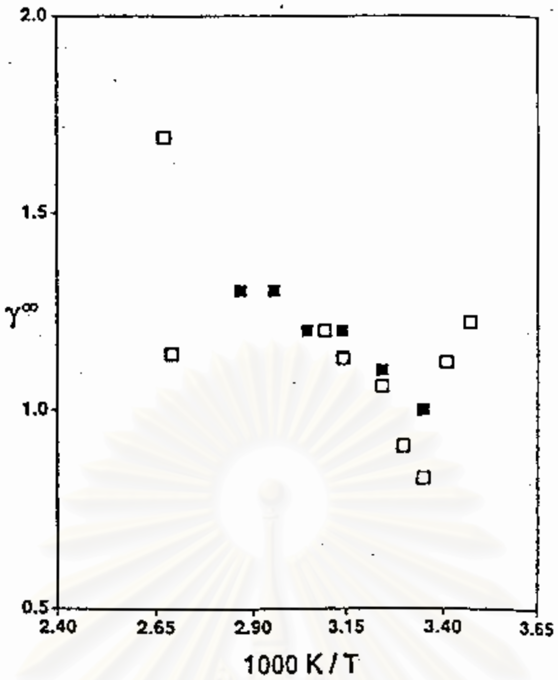


Figure 3.3 Comparision of γ^{∞} values for 1,2-propanediol in water measuerd by dew point method researched by Suleiman and Eckert (1994), (■) , with values obtained by other VLE extrapolated sources, (□) .

3.2 Experiment and Calculation Routes

There are so many researches involving VLE experiment, and so many types of apparatus were used but in the same fundamental. Most experiments aim to receive equilibrium data, particular in the isothermal system, pressure, liquid phase mole fraction and vapor phase mole fraction at equilibrium is need to know. One of the wide-use apparatuses to get all equilibrium data above is the recirculating glass still designed by David Zudkevitch, a sketch of which is found in the papers of McNelis et al. (1989) and Mulins et al. (1989).

However there is a way to complete data by only know the pressure. The work of Rowley and Hoffman (1990), for example, used the total pressure (*PTx*) method, a fast efficient method, to obtain binary vapor-liquid equilibrium data for mixtures of triethylene glycol + n-hexane, triethylene glycol + cyclohexane, and furfural + isoprene. The *PTx* method eliminates difficulties associated with sampling and analysis common in *Pxy* and *Txy* methods. The measured pressures for each charge composition on an isotherm were reduced to equilibrium phase compositions using an equation of state, the Peng-Robinson equation for their work, to calculated vapor phase fugacity coefficients and a properties model, the NRTL model for theirs, for liquid fugacity coefficients. The equilibrium follows Equation (2.4) and the fugacity coefficients of vapor and liquid phase are following Equations (2.5) and (2.6) respectively. The yield of the VLE analysis equation was seemed the form of Equation (2.7), the easy form.

Rowley and Hoffman (1990) regressive calculated the both phase compositions by comparison of measured and calculated pressures, the simplified flow diagram of data reduction procedure is in Figure 3.4.

In this work, used the *PTx* method to obtain the vapor-liquid equilibrium data, only the pressure, and improved the data reduction procedure of Rowley and Hoffman (1990) for the studied system, using Virial (for polar component) EOS to calculated the vapor phase and Wilson or UNIQUAC model to calculated the liquid phase. In addition, liquid phase was sampled to confirm the calculated phase compositions.

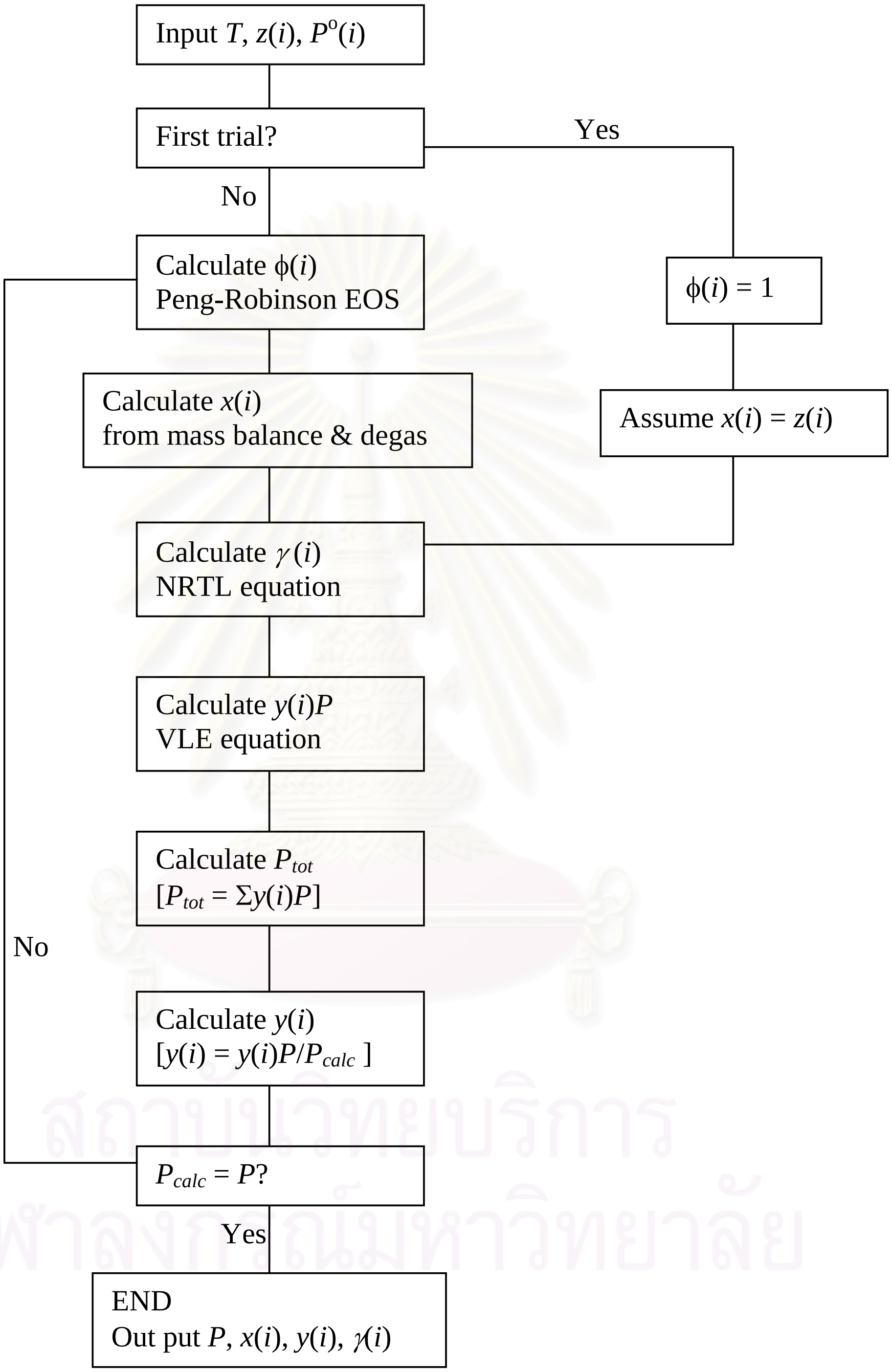


Figure 3.4 Flow chart for VLE data reduction of Rowley and Hoffman (1990)

CHAPTER IV

EXPERIMENT

4.1 Chemicals

All chemicals were used directly as received from the manufacturer without further purification. The properties of source chemicals were displayed in Table 4.1.

Table 4.1 Properties of Source Chemicals

Chemical	Ethylene glycol	1,4-Butane diol	Water
Formula	CH_2OHCH_2OH	$C_4H_{10}O_2$	H_2O
Molecular weight	62.070	90.12	18.02
Assay (Purity)	min. 99.5% (GLC)	~99% (GC)	100%
Boiling point (^{o}C)	198.0 (b.r. $\pm$ 1.5)	120-122 (10 mmHg)	100
Melting point (^{o}C)	-	19-21	0
Density (20^{o}C/4^{o}C)	1.109 $\pm$ 0.003	1.014	1.00
Refraction index (20^{o}C/D)	1.4314	1.446	-
Supplier	Carlo Erba	Fluka	(double-distilled water)

4.2 Experimental Apparatuses

4.2.1 Vapor Liquid Equilibrium Still

The equilibrium still used to obtain vapor-liquid equilibrium data is the recirculating glass still new designed by modifying from literature stills, a sketch of which is presented in Figure 4.1. The still is made of Pyrex glass.

4.2.2 Constant Temperature Oil Bath

The automatic temperature controller; FENWAL AR-L series, thermocouple of type Pt100 that have range –199.9 to 850^{o}C of temperature, and a circulated oil bath with heat source from Cole-Parmer stirred-hotplate model 4658 were used to heat the equilibrium still with constant temperature.

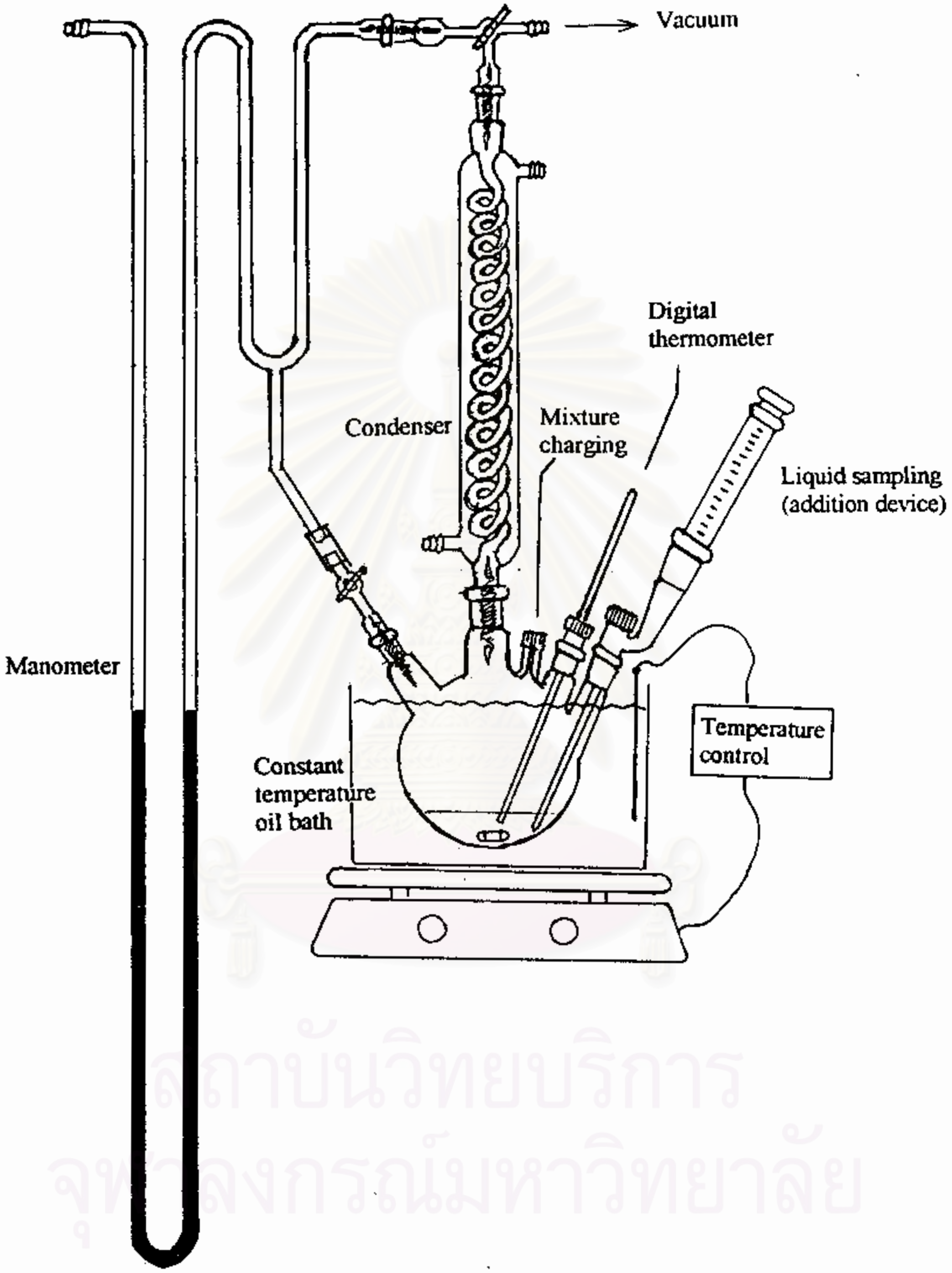


Figure 4.1 Vapor liquid equilibrium still

4.2.3 Vacuum Pump

Edwards vacuum pump model RV3 was connect to the VLE still to avail vacuum for the still before charging mixture.

4.2.4 Digital Thermometer

The microcomputer digital thermometer, JENCO model 7001H, was used to read the system temperature in equilibrium still with an accuracy of 0.1 ^{o}C.

4.2.5 Refractometer

The refractometer, Atoga_1T, have scale range 1.30-1.70 of refractive index with constant temperature cooling water circulation was used to read the refractive index of solutions with an accuracy of 0.0001 in the temperature range of 26.6-26.7^{o}C.

4.3 Experimental Procedure

This work used the *PTx* method (Rowley and Hoffman, 1990) to obtain the vapor-liquid equilibrium data, only the pressure, and improved the data reduction procedure of Rowley and Hoffman (1994) for the studied system, using Virial EOS to calculated the vapor phase and Wilson or UNIQUAC model to calculated the liquid phase. In addition, liquid phase was sampled to confirm the calculated phase compositions.

4.3.1 Calibration of the refractive index of mixture

The refractometer was first accuracy adjusted, using double-distilled water with refractive index read of 1.33 at room temperature.

The refractive index was calibrated with gravimetrically prepared standard mixture for the binary system of 1,4-butylene glycol in water covering the entire composition range of interest consisting of 11 samples including each pure component.

The gravimetrically standard preparation was shown in Table C.1. The calibration results were in Table C.2 and were generated to calibration curve as Figure C.1.

4.3.2 Preparation of Charge Mixtures

1,4-butylene glycol and double-distilled water were gravimetrically prepared in different ratio to obtain various charge mole fractions of 1,4-butylene glycol in water. Expectation of approximate compositions is 0.1, 0.3, 0.5, 0.7 and 0.9 of mole fraction. An accuracy of gravimetrically measurement is 0.0001 g. The preparation is presented in Appendix D.

In addition, to consider for the equivalence of present experiment with literature experimental data researched by Lancia et al. (1996), ethylene glycol was prepared in the same way as of 1,4-butylene glycol for equilibrium experiment.

The gravitrically data of charge mixtures was in Appendix D.

4.3.3 Procedure for Experimental Collecting of Equilibrium data

The equilibrium still was used to obtain the pressure at equilibrium in the systems of ethylene glycol-water and 1,4-butylene glycol-water at 98, 110, and 122^{O}C of temperature by experiment.

The still was cleaned and vacuumed before charging individual mixture of various compositions. The mixture then was heated and stirred with a constant temperature oil bath and a magnetic stirrer placed below the still. Cooled water (about 10^{o}C) was used as cold fluid for the condenser to prevent condensation of vapor in the cooler manometer arm. The oil bath was thermostatted with set point about 10^{o}C above the isotherm system set point to maintain an appreciable boil-up rate and then adjusted until occurred the temperature of desired isotherm in the system as long enough to approach the equilibrium, for greater than 5 hours was the suggestion by Lancia et al. (1996). The system pressure was measure with U-tube mercury manometer. The phase compositions were next calculated from experimental temperature and pressure data with aid of computer programming by correlating with properties models. The interaction parameters of models and the activity coefficients of each system of glycols in water were also determined from experimental data with aid of computer programming.

In addition, to compare with the calculated liquid phase compositions of 1,4-butylene glycol in water, the liquid phase was sampled from such a system.

4.3.4 Finding Out of Experimental Liquid Phase Compositions

The liquid phase was sampled from the still by an addition device and then to find out the compositions, the liquid samples was measured for refractive index and estimated using the calibration curve.

CHAPTER V

DATA REDUCTION

The experimental data was correlated with UNIQUAC (original) and Wilson properties models and to evaluate the interaction parameters of each model, the back calculation method and some mathematical methods were used. This was succeeded by aid of computer programming. The computer programs were written in Qbasic. Flow charts and algorithms of programs were also presented future, in Figure 5.1 and the followings.

5.1 Back Calculation Method

When experimental data on temperature, pressure and liquid phase composition of binary system are available, the parameters in UNIQUAC or Wilson properties model can be determined by back calculation.

The objective function used is

$$\frac{1}{N}\sum_{i=1}^{N}\left|\frac{P_{cal}(i)-P_{\exp}(i)}{P_{\exp}(i)}\right| \tag{5.1}$$

where N is number of experimental data points, P_{exp} is experimental pressure, and P_{cal} is calculated pressure from the model. The mathematical methods required are Newton-Raphson method and the region elimination method.

5.2 Newton-Raphson Method

The Newton-Raphson method is widely used in solution of positive roots of models. The method is employed by which successive approximations to the solution a of an equation $f(a) = 0$ are calculated and solution is found when

$$|a_{n+1}-a_n| < \varepsilon$$

for some suitable small value of ε.

5.3 Region Elimination Method

To evaluate the interaction parameters τ_{ij} and τ_{ji} for UNIQUAC model, or the Wilson parameters Λ_{ij} and Λ_{ji} for Wilson equation, it needs the region elimination method for a two-dimensional search, the method such has capability to eliminate regions of which parameters range out of accurate value for remaining subinterval sufficiently small terminate.

The basic fundamental of the method is the comparison of values of $f(a)$ at two or more points with in range of a with assumption of $f(a)$ is unimodal and has a minimum within the interval.

In each dimension search, the range of parameters was divide into 20 sections and then the objective function of each section was calculated and compared to result decrement of parameter range containing minimum objective function value. New range was divided into 20 sections again and decreased again by the same route until a range of parameters was with in acceptable value.

5.4 Computer Program

The research consists of 3 main programs:

5.4.1 Program for Properties Models' Parameters Evaluating

The interaction parameters of each model were evaluated from *PTx* experimental data following the flow chart in Figure 5.1.

5.4.2 Program for Phase Compositions & Activity Coefficients Estimating by Correlated Models

VLE data such the vapor phase and the activity coefficient could be estimated by correlated models, used the parameters obtained by 5.4.1. The flow chart of the program was illustrated in Figure 5.2.

5.4.3 Program for Liquid Phase Composition & Activity Coefficients Estimating from Experimental Measured Pressures

Measured pressures for each charge composition on an isotherm were reduced to equilibrium phase compositions using the Virial EOS to calculate vapor phase fugacity, the right side of Equations (2.4) and (2.7), and either the

UNIQUAC, Wilson or UNIFAC model to calculate liquid phase fugacity, the left side of those equations And then with the mole balance and mathematical methods, the phase compositions and the activity coefficients of the system was estimated as following as the flow chart in Figure 5.3.

Each main program written in Qbasic were presented in Appendix F. The vapor pressures and calculating parameters used in programs were kept in Appendix A. Flow charts of subprograms were also presented in this chapter.

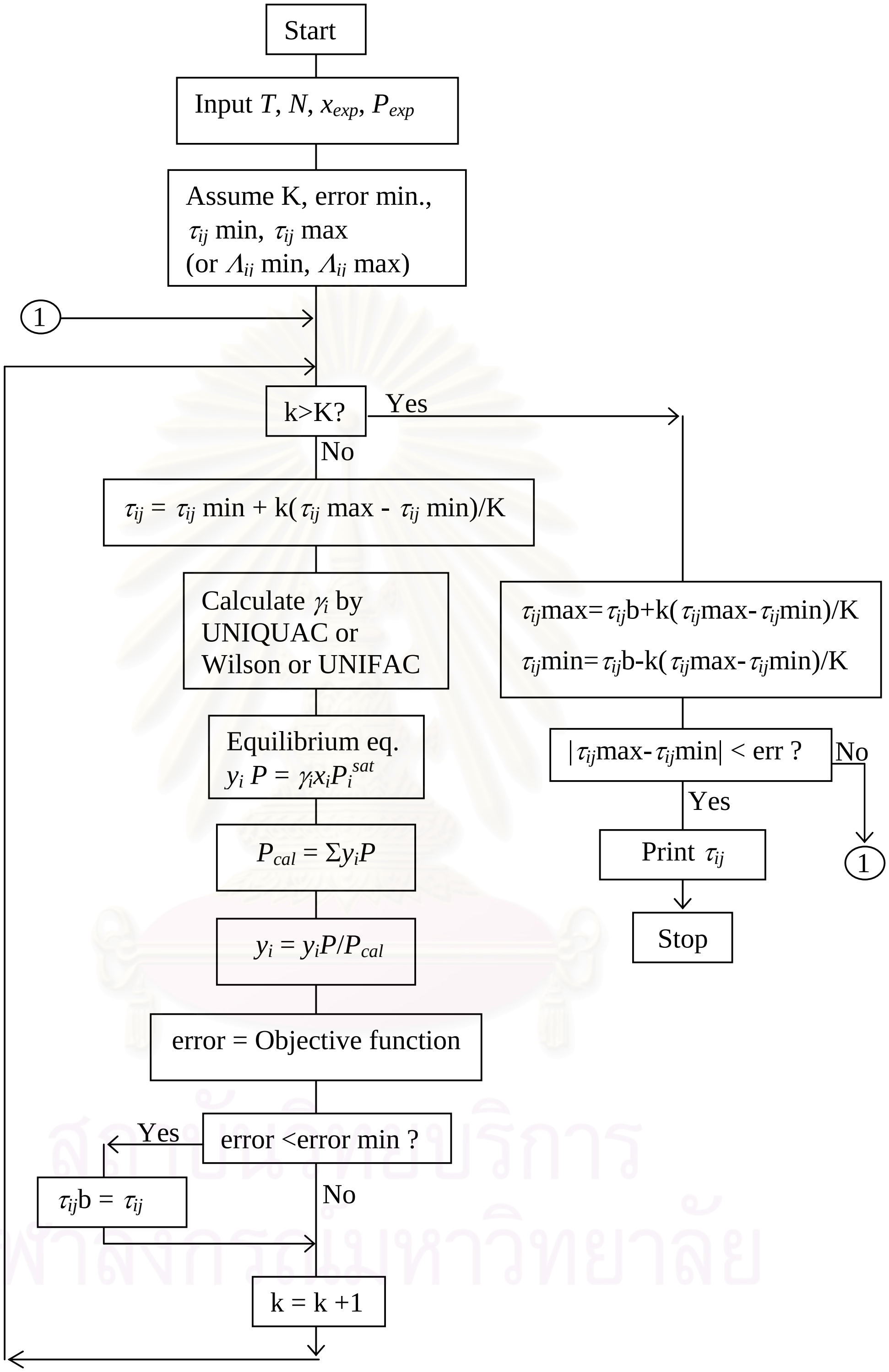


Figure 5.1 Flow chart of main program for Properties Models' Parameters Evaluating.

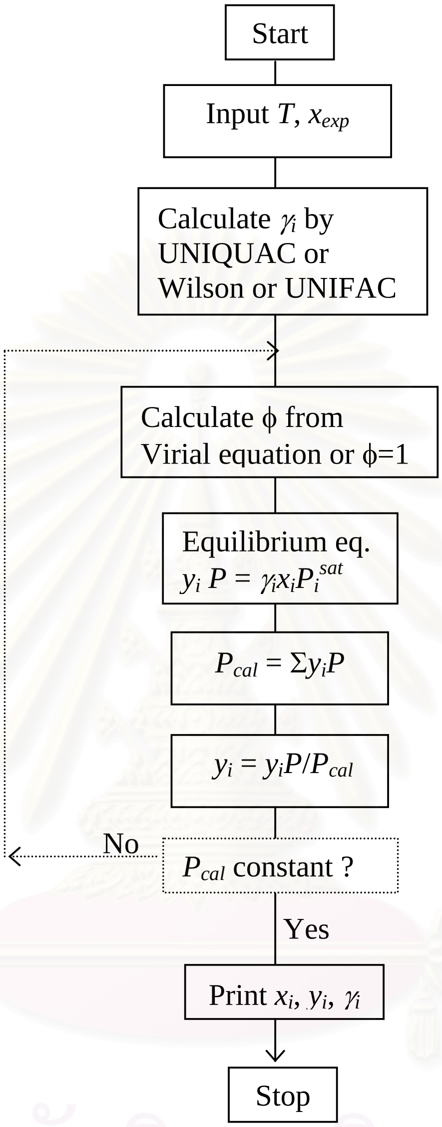


Figure 5.2 Flow chart of main program for phase compositions and activity coefficients estimating by correlated models

Remark : The dash line only for using Virial equation need.

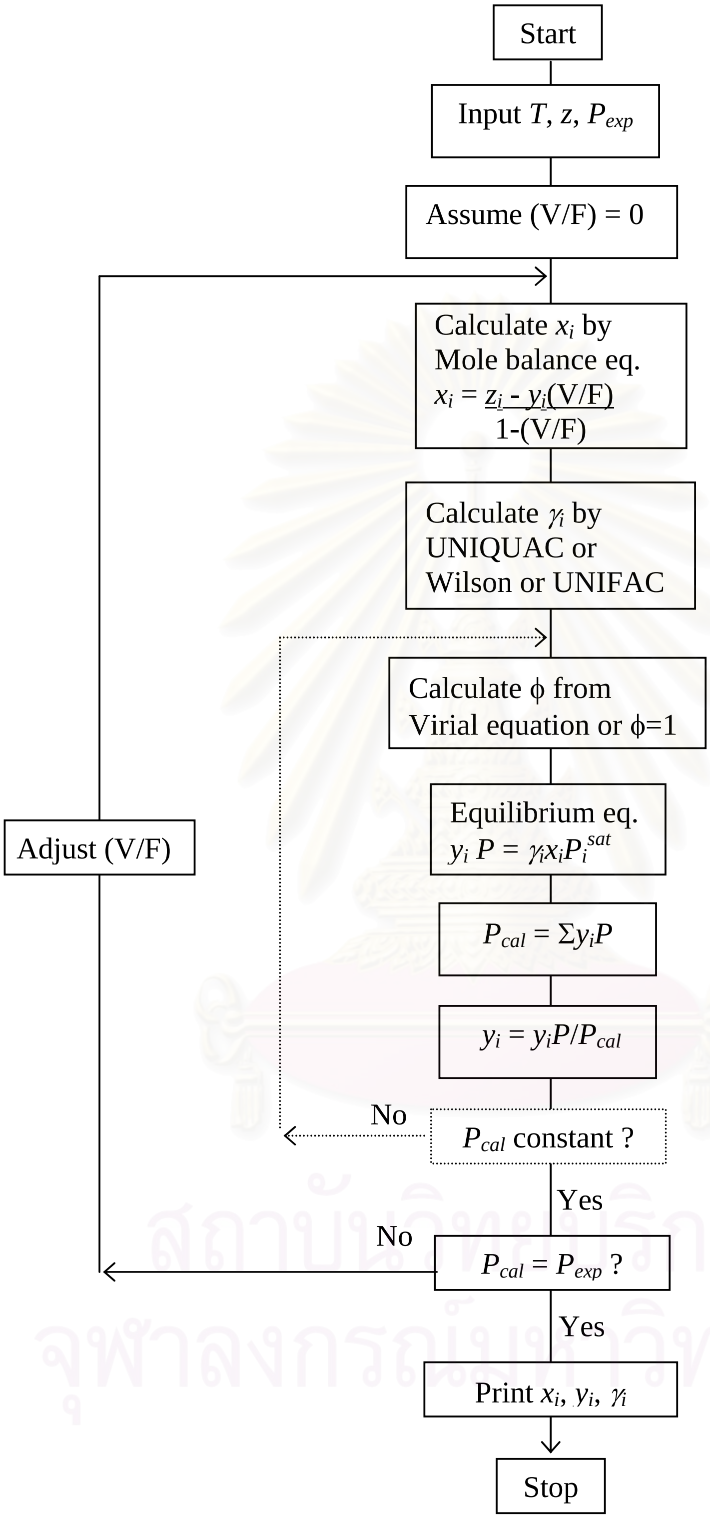


Figure 5.3 Flow chart of main program for liquid phase composition & activity coefficients estimating from experimental measured pressures.

Remark : The dash line only for using Virial equation need.

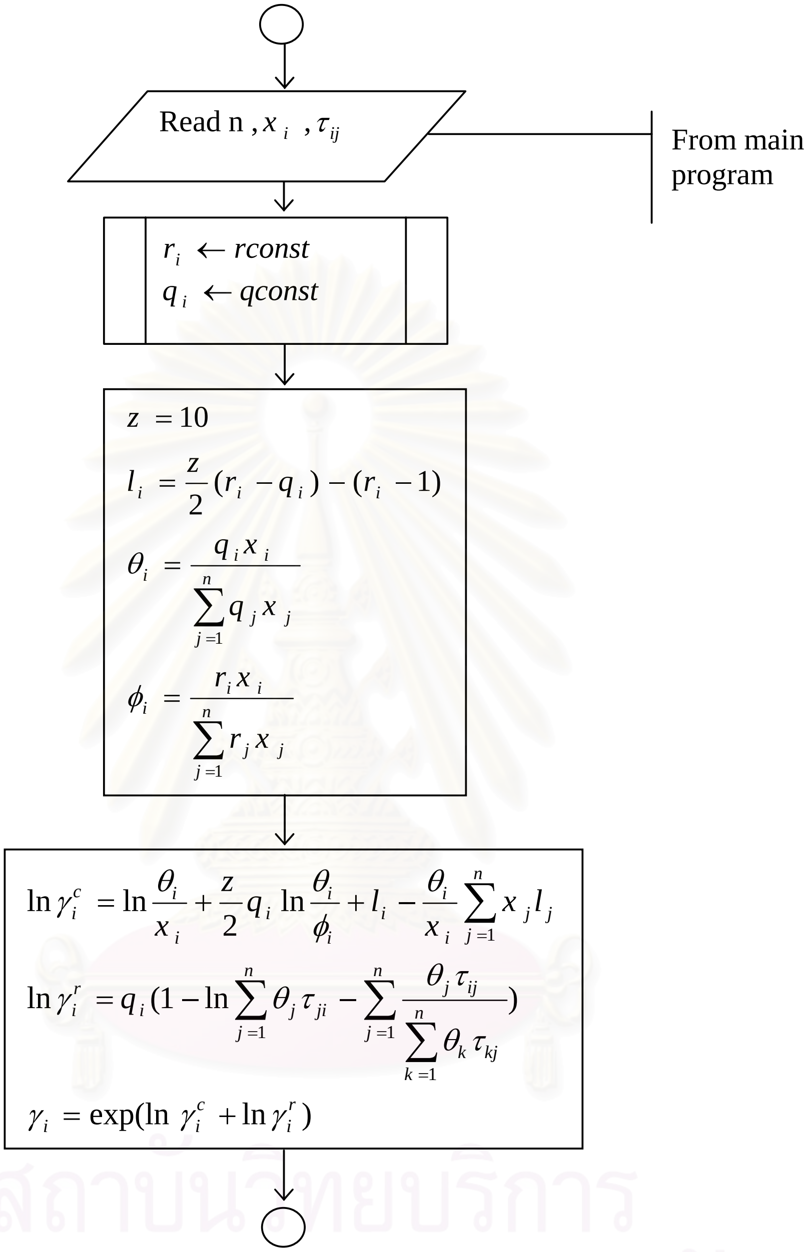


Figure 5.4 Flowchart of subprogram UNIQUAC.

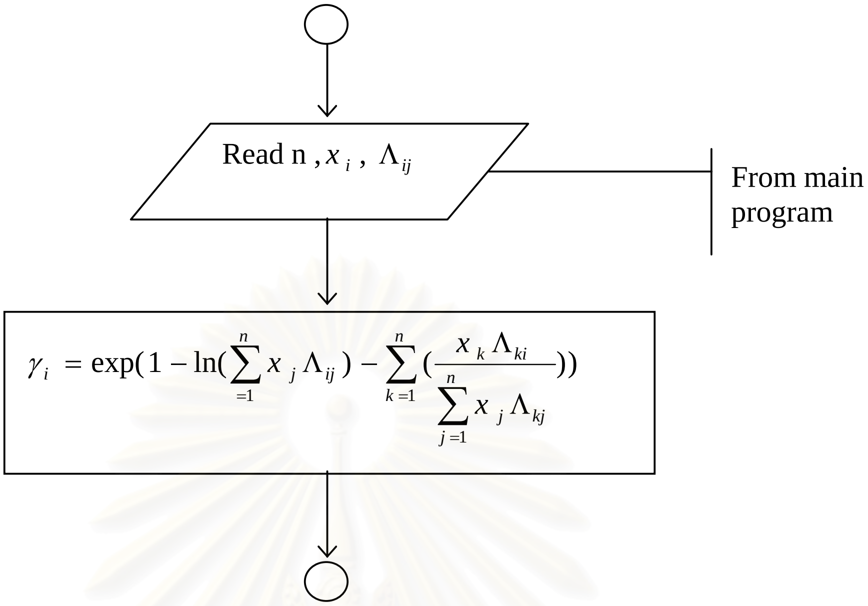


Figure 5.5 Flowchart of subprogram Wilson.

CHAPTER VI

RESULTS AND DISCUSSION

6.1 Experimental VLE Results

The experimental VLE results obtained from the VLE still of the ethylene glycol and 1,4-butylene glycol in water are shown in Tables 6.1 and 6.2, respectively.

Table 6.1 Experimental VLE results of ethylene glycol (*1*)-water (*2*)

$z_{1,app}$	P_{exp} (kPa)		
	98 °C	110 °C	122 °C
0.3	47.5133	79.9634	140.6032
0.5	39.6740	70.5669	69.7180
0.7	23.3720	49.6754	39.4750
0.9	14.0869	21.1037	23.7832

Table 6.2 Experimental VLE results of butylene glycol (*1*)-water (*2*)

$z_{1,app}$	P_{exp} (kPa)		
	98 °C	110 °C	122 °C
0.1	83.1730	108.6610	169.1953
0.3	53.0190	81.8575	111.0171
0.5	41.1994	66.8729	85.3092
0.7	26.8870	62.9266	76.1910
0.9	21.3928	37.8082	48.0590

6.2 Liquid Phase Compositions of Butylene Glycol-Water

The liquid phase samples in 1,4-butylene glycol-water VLE at various experimental conditions were measured via the refractive indexes to determine the mole fractions by using the calibration curve in Figure C.1. The calibrating correlation of refractive index and mixture mole fraction is

$$RI = -0.94238x^6 + 3.31836x^5 - 4.79834x^4 + 3.75944x^3 - 1.80298x^2 + 0.57578x + 1.33042 \quad (6.1)$$

The liquid phase mole fractions of butylene glycol, x_1, is obtained by solving in the Equation (6.1).

Table 6.3 Experimental mole fractions obtained from refractive index calibrating of liquid phase samples in butylene glycol (*1*)-water (*2*) VLE

T	98 ^oC		110 ^oC		122 ^oC	
$z_{1,app}$	RI	x_{exp}	RI	x_{exp}	RI	x_{exp}
0.1	1.3825	0.1327	1.3795	0.1213	1.3792	0.1202
0.3	1.4176	0.3686	1.4200	0.3982	1.4131	0.3206
0.5	1.4294	0.5587	1.4233	0.4447	1.4276	0.5199
0.7	1.4347	0.7162	1.4280	0.5281	1.4320	0.6266
0.9	1.4357	0.7548	1.4339	0.6867	1.4337	0.6806

6.3 UNIQUAC Interaction Parameters

With the aid of computer programming as follow the Figure 5.1 with the UNIQUAC subprogram, the interaction parameters τ_{ij} and τ_{ji} of aqueous solutions of ethylene glycol (EG) and propylene glycol (PG) were obtained from correlating the UNIQUAC model with literature VLE data (*P*,*T*,*x*) of Lancia et al. (1996). For aqueous solution of 1,4-butylene glycol (BG), such parameters were obtained by experimental VLE data containing the liquid phase compositions. The parameters at experimental conditions are presented below.

Table 6.4 UNIQUAC interaction parameters for the binary mixture of glycols (*1*) in water (*2*)

		98^oC	110 ^oC	122 ^oC
EG (1) – H_2O (2)	τ_{12}	1.5006	1.9483	2.3578
	τ_{21}	1.0236	0.7423	0.5008
PG (1) - H_2O (2)	τ_{12}	1.7456	2.2303	2.5996
	τ_{21}	0.6697	0.4471	0.3133
BG (1) – H_2O (2)	τ_{12}	2.3833	2.6999	3.2866
	τ_{21}	0.3863	0.3513	0.2981

The interaction parameters τ_{12} and τ_{21} are the temperature dependent parameters as shown in Figure 6.1A. In each system, the τ_{12} increase when temperature is increased but the τ_{21} decreased when temperature is increased. In small temperature range, both τ_{12} and τ_{21} are linear function of temperature. The interaction parameters also depend on molecular size of each kind of component. The Figure 6.1A also show that in aqueous mixture of glycol, the τ_{12} increase when molecular size of glycol is increased but the τ_{21} decrease when molecular size of glycol is increased. It can be more explained by a plot between the parameter and molecular weight in Figure 6.1B. Trends of the parameter vs molecular weight curve seem to be non-linear even in the small temperature range.

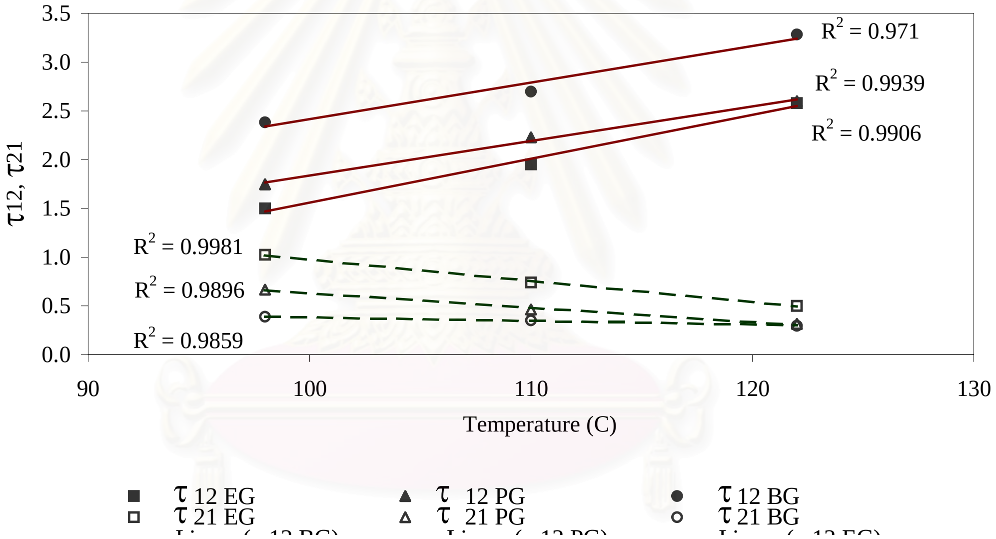


Figure 6.1A UNIQUAC interaction parameter as temperature dependent parameters

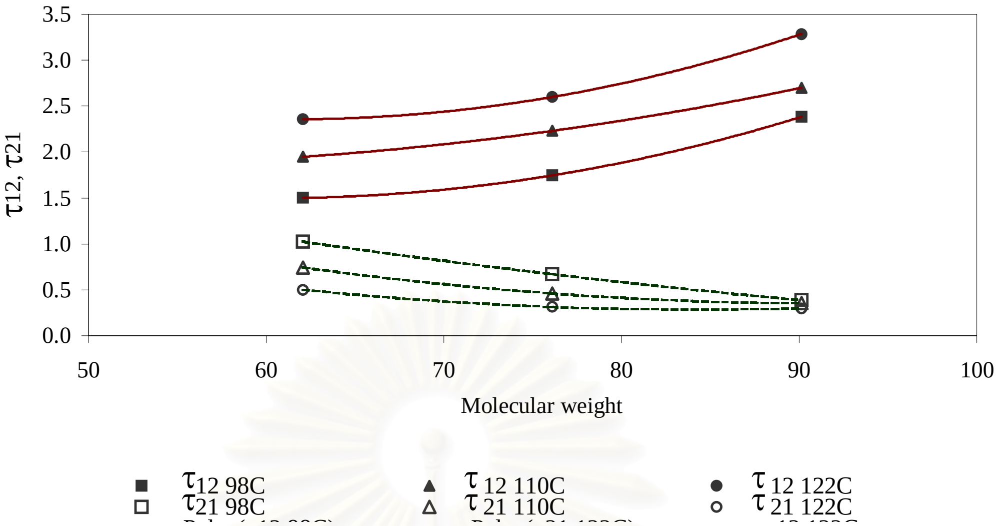


Figure 6.1B UNIQUAC interaction parameter dependent on molecular weight of glycols.

6.4 Wilson Parameters

Same as the τ_{ij} and τ_{ji}, the Wilson parameters Λ_{ij} and Λ_{ji} were also determined by help of computer program as follow the Figure 5.1 when used Wilson subprogram. The results are in Table 6.5. And the temperature dependent behaviours of Wilson parameters are also shown by Figure 6.2A. The figure shows that in each system, the Λ_{12} decrease when temperature is increased but the Λ_{21} increase when temperature is increased. In small temperature range, both Λ_{12} and Λ_{21} are linear function of temperature. The Wilson parameters in aqueous mixture of glycol also depend on molecular size of glycol as show in the Figure 6.2A that the Λ_{12} decrease when molecular size of glycol is increased but the Λ_{21} increase when molecular size of glycol is increased. It can be more explained by a plot between the parameter and molecular weight in Figure 6.2B. Trends of the parameter Λ_{21} vs molecular weight curve seem to be non-linear even in the small temperature range.

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Table 6.5 Wilson parameters for the binary mixture of glycols (*1*) in water (*2*)

		98°C	110 °C	122 °C
EG (1) - H_2O (2)	Λ_{12}	0.8911	0.7761	0.6683
	Λ_{21}	1.3929	1.5833	1.7810
PG (1) - H_2O (2)	Λ_{12}	0.6796	0.5727	0.4525
	Λ_{21}	1.5682	1.6730	1.8647
BG (1) - H_2O (2)	Λ_{12}	0.5273	0.4049	0.3558
	Λ_{21}	1.9054	2.4100	3.2202

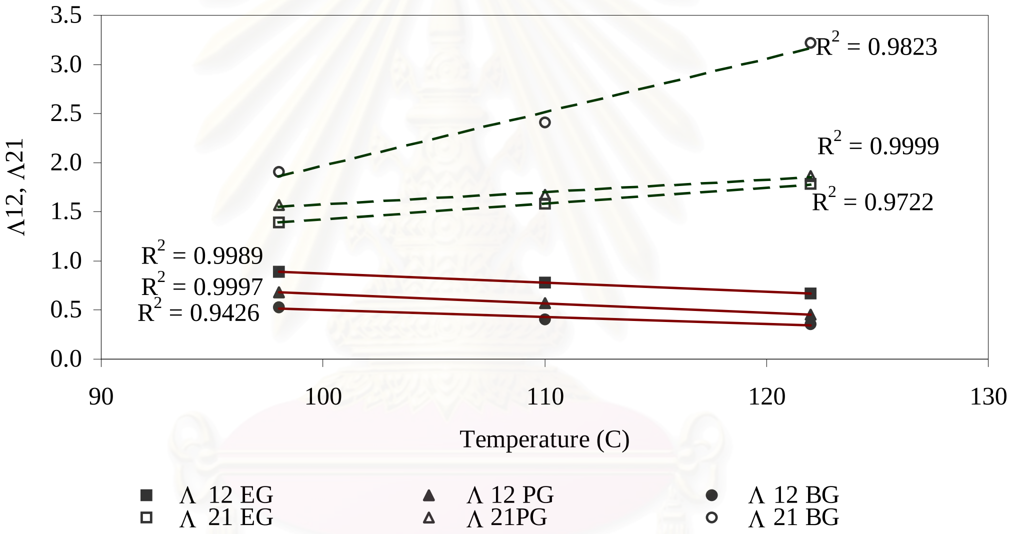

Figure 6.2A Wilson parameter as temperature dependent parameters.

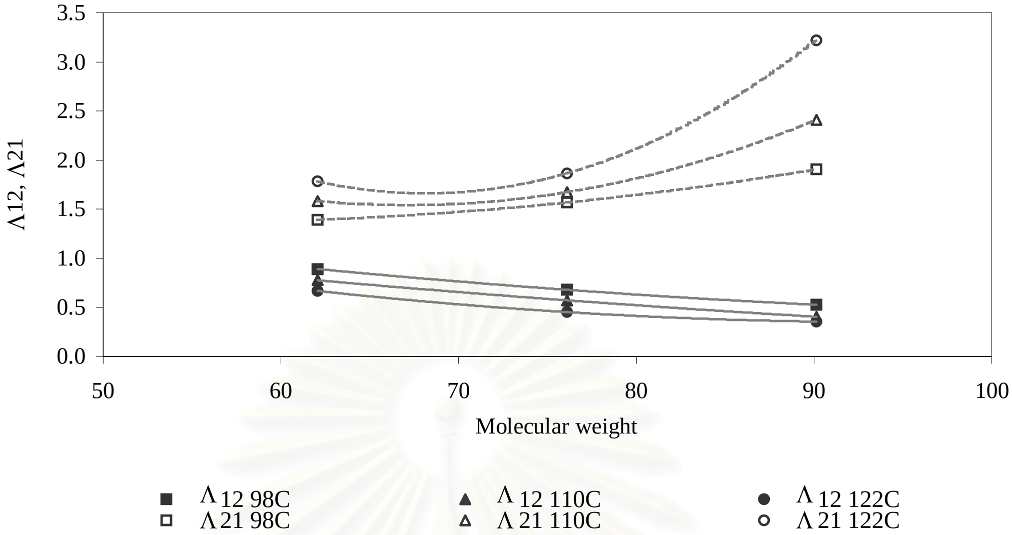

Figure 6.2B Wilson parameter dependence on molecular weight of glycols.

6.5 Comparison Between Experimental and Literature VLE Data of Ethylene Glycol-Water

Charge compositions and measured pressures from the VLE still of ethylene glycol-water system were used to calculate the liquid compositions and other properties by either UNIQUAC or Wilson model as in Tables F.1 to F.6. These were compared with the literature VLE data of the same system researched by Lancia et al (1996) to confirm that the experiment gave accurate data, related with the literature. The comparisons are shown in Figures 6.3 to 6.5 for 98^o to 122^oC of experimental temperatures. Figures show that the experimental results agree with those of the literature.

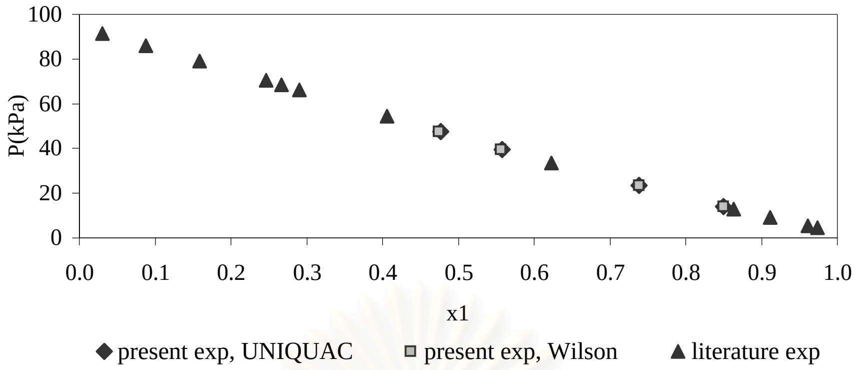

Figure 6.3 Comparison of experiment and literature VLE data of ethylene glycol (*1*)-water (*2*) at 98°C

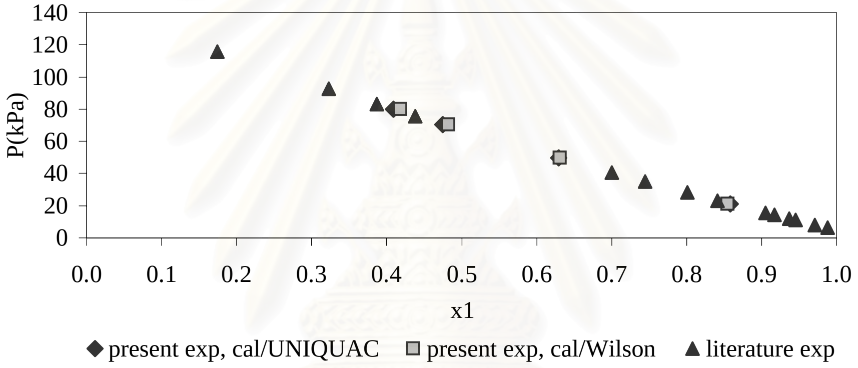

Figure 6.4 Comparison of experiment and literature VLE data of ethylene glycol (*1*)-water (*2*) at 110°C

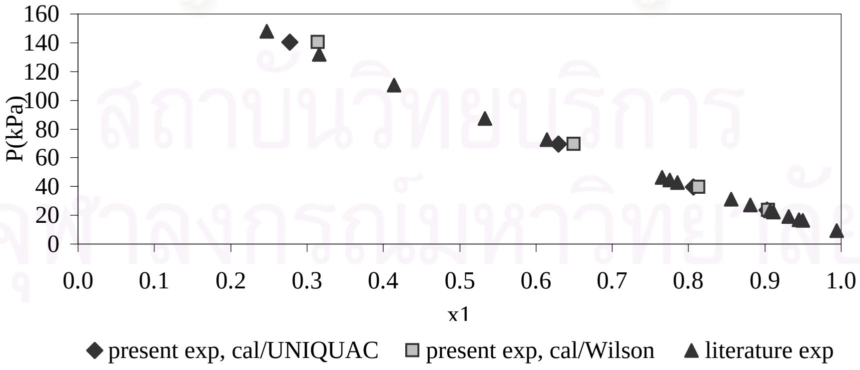

Figure 6.5 Comparison of experiment and literature VLE data of ethylene glycol (*1*)-water (*2*) at 122°C

6.6 Estimation by Virial EOS

The Virial Equation, Equation (2.15) was used to calculated the fugacity of vapor phase for regressive calculation of the both phase compositions as follow the flow chart in Figure 5.2. The second virial coefficients of mixture were calculated from that of pure components, shown in Table A.3, by Equation (2.14). The liquid phase fugacity coefficients that is written in term of the activity coefficients were calculated by properties models, UNIQUAC and Wilson which has correlated with VLE data. The results of using the Virial equation and the UNIQUAC model for the vapor phase of ethylene glycol –water system are following. These are next compared with using the Equation (2.8), with the assumption of ϕ (fc) ≈ 1 at low pressure. With similar comparison, the results of propylene glycol and butylene glycol in water estimated by the Virial equation were similar to that of ethylene glycol.

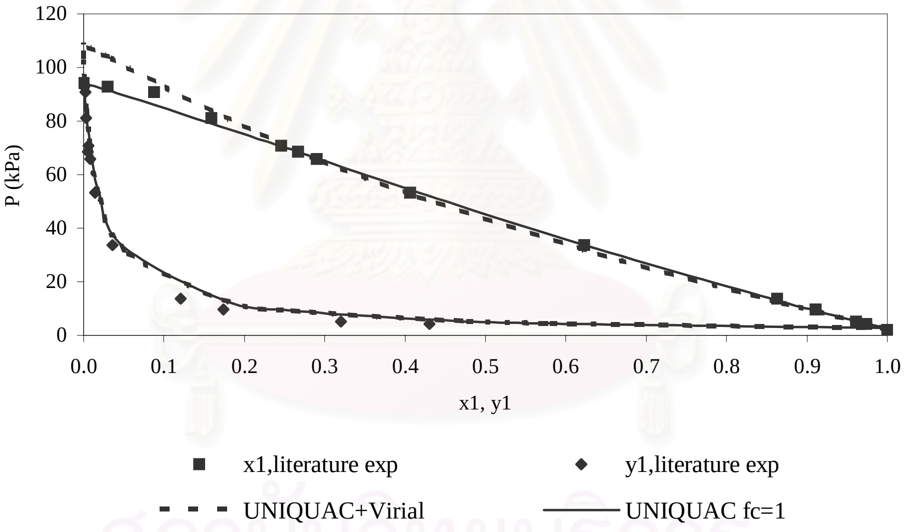

Figure 6.6 VLE data of ethylene glycol (*1*)-water (*2*) at 98^{o}C by experiment and estimation, effect of using the Virial equation.

Figures showed that the Virial Equation provided data not accurate in dilute solution region of glycol in water, about less than 3.5 of mole fraction, and it over estimate vapor pressure of water at all three temperatures. Beside, for the case of the Wilson equation using replacing the UNIQUAC model, the results of Virial estimation are the same.

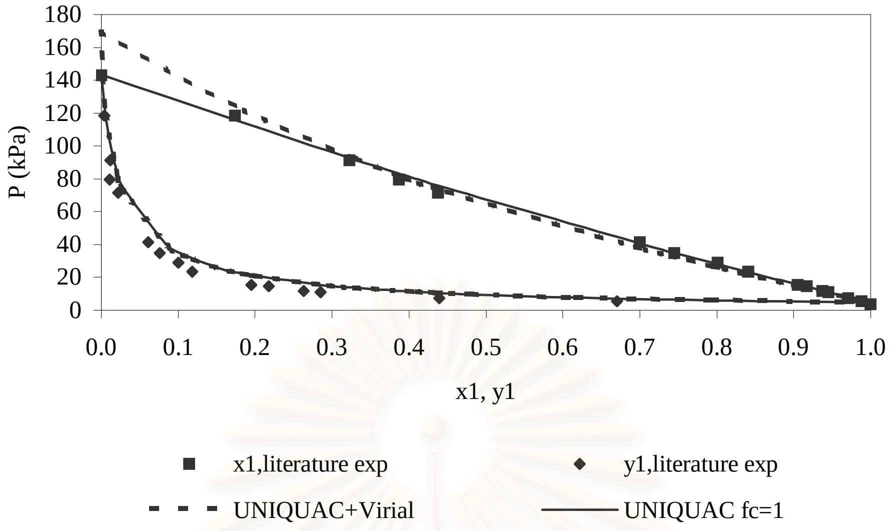

Figure 6.7 VLE data of ethylene glycol (*1*)-water (*2*) at 110^{o}C by experiment and estimation, effect of using the Virial equation.

The pressure under 1 atm. up to 1.5 atm. (about 0-150 kPa) was acceptable to be “low pressure”, and the assumption of the vapor phase fugacity coefficient (fc) $\phi \approx 1$ at low pressure was hold. Because of more accuracy along the compositions of using this assumption in vapor phase calculations as in the figures above, this work is desired to continue on this assumption in estimation of compositions and activity coefficients.

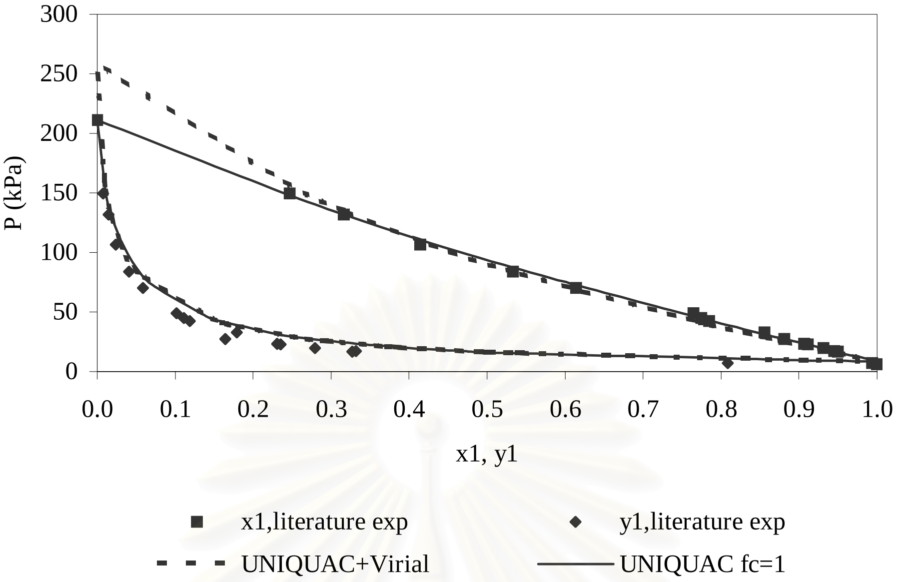

Figure 6.8 VLE data of ethylene glycol (*1*)-water (*2*) at 122°C by experiment and estimation, effect of using the Virial equation.

6.7 Comparison of Experimental and Calculated Liquid Phase Composition of 1,4-Butylene Glycol-Water System

The calculated 2-phase compositions from the measured pressures in 1,4-butylene glycol-water equilibrium using $\phi \approx 1$ for vapor phase calculation and UNIQUAC or Wilson model for liquid phase calculation were shown in Tables F.10 to F.15. By comparison of the x_{cal} in above tables and the x_{exp} in Table 6.3, it is found that for the three temperature considered, the x_{cal} vs the x_{exp} give a “parity plot” as show in Figures 6.9 to 6.14. So the calculated liquid compositions, x_{cal}, and calculation with the aid of presented computer programming could be reliable. Because the liquid compositions calaulated by using each model have slightly difference, this research use the experimental measured liquid copositions, x_{exp}, in result analysis.

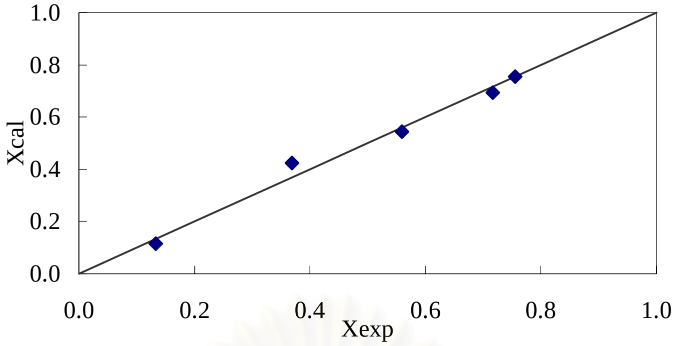

Figure 6.9 Comparison between UNIQUAC calculated and experimental determined liquid phase molar fractions for1,4-butylene glycol (*1*)-water (*2*) mixture at 98°C

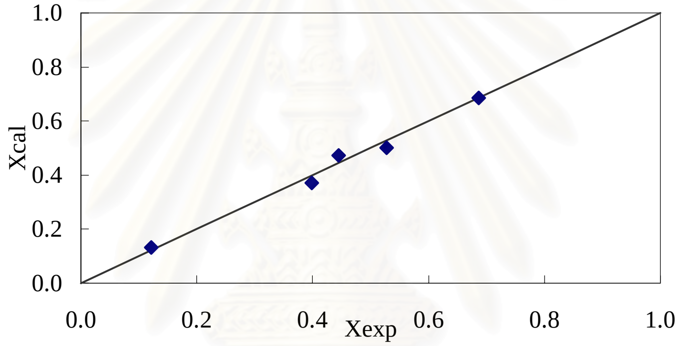

Figure 6.10 Comparison between UNIQUAC calculated and experimental determined liquid phase molar fractions for1,4-butylene glycol (*1*)-water (*2*) mixture at 110°C

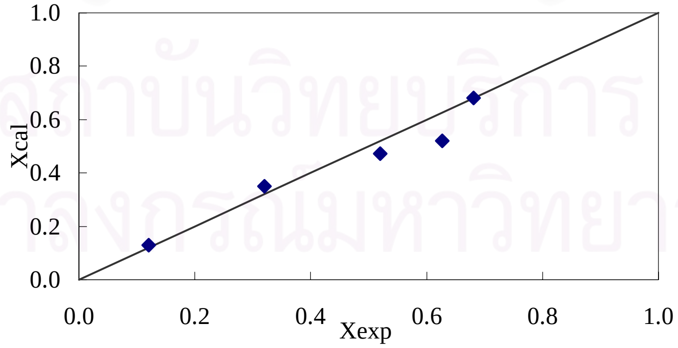

Figure 6.11 Comparison between UNIQUAC calculated and experimental determined liquid phase molar fractions for1,4-butylene glycol (*1*)-water (*2*) mixture at 122°C

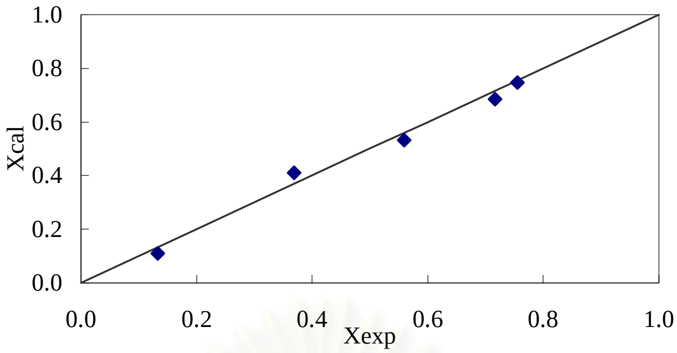

Figure 6.12 Comparison between Wilson calculated and experimental determined liquid phase molar fractions for1,4-butylene glycol (*1*)-water (*2*) mixture at 98°C

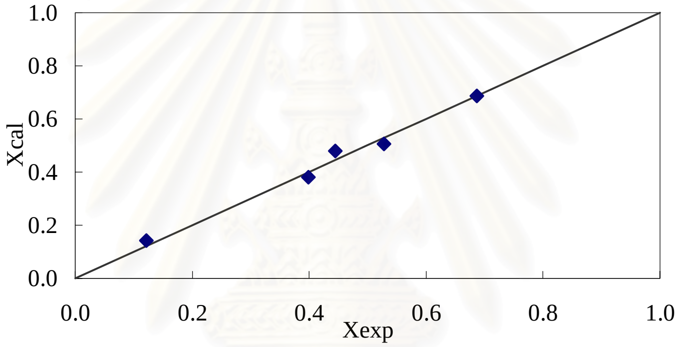

Figure 6.13 Comparison between Wilson calculated and experimental determined liquid phase molar fractions for1,4-butylene glycol (*1*)-water (*2*) mixture at 110°C

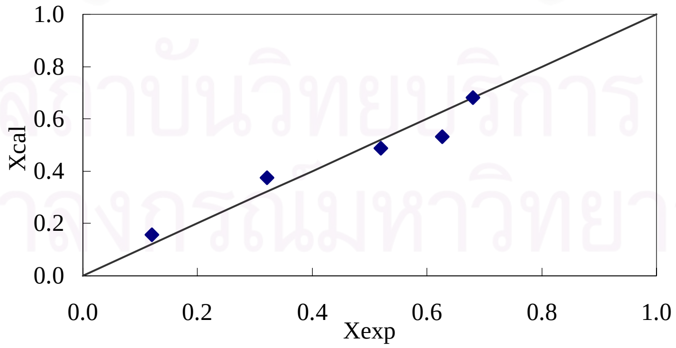

Figure 6.14 Comparison between Wilson calculated and experimental determined liquid phase molar fractions for1,4-butylene glycol (*1*)-water (*2*) mixture at 122°C

6.8 Comparison of UNIFAC, UNIQUAC and Wilson Models Estimations

The results of computer programming calculation of the three studied glycol in water systems at all three temperatures were presented in Appendix F using entire three models; UNIFAC, UNIQUAC, and Wilson for liquid phase calculations. The results at one temperature are compared the three models estimations together in the Figures 6.15 to 6.17 for ethylene glycol, Figures 6.18 to 6.20 for propylene glycol, and Figures 6.21 to 6.23 for 1,4-butylene glycol in aqueous systems.

The UNIFAC method over estimated the VLE of glycols in water systems whereas the UNIQUAC and Wilson models with the correlated parameters in Tables 6.4 and 6.5, respectively, give good estimate for such the systems.

6.9 Deviations of Models Estimations

The deviations of UNIQUAC and Wilson models estimations from the experimental data are shown in Tables 6.6 and 6.7 respectively. Deviations are presented in %AAD (%average absolute deviation) defined as follows.

$$\%\text{AAD} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{P_{cal} - P_{\exp}}{P_{\exp}}\right|$$

Table 6.6 % Average absolute deviations of UNIQUAC model estimations

Temperature	98^{o}C	110 ^{o}C	122 ^{o}C
EG-H_2O	2.6579	3.5989	3.7960
PG-H_2O	3.9657	3.3326	1.9890
BG-H_2O	4.5983	3.7499	8.7003

Table 6.7 % Average absolute deviations of Wilson model estimations

Temperature	98^{o}C	110 ^{o}C	122 ^{o}C
EG-H_2O	2.7066	3.7787	5.7527
PG-H_2O	4.2170	4.2312	1.9614
BG-H_2O	4.8018	3.9269	10.2832

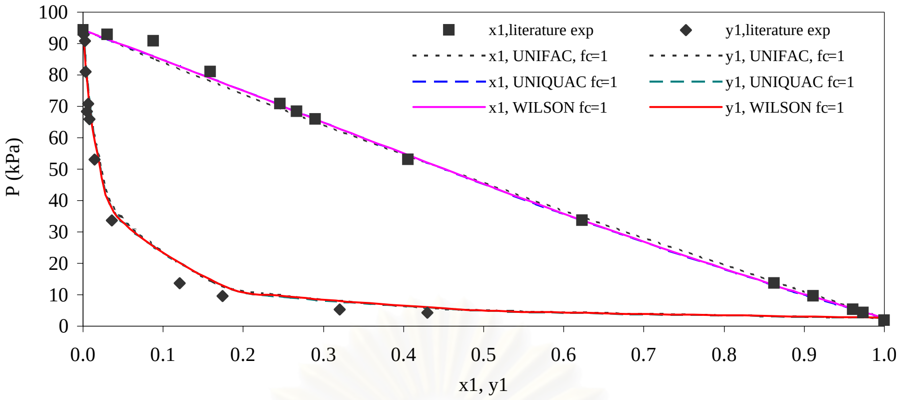

Figure 6.15 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of ethylene glycol(*1*)-water(*2*) system at 98°C

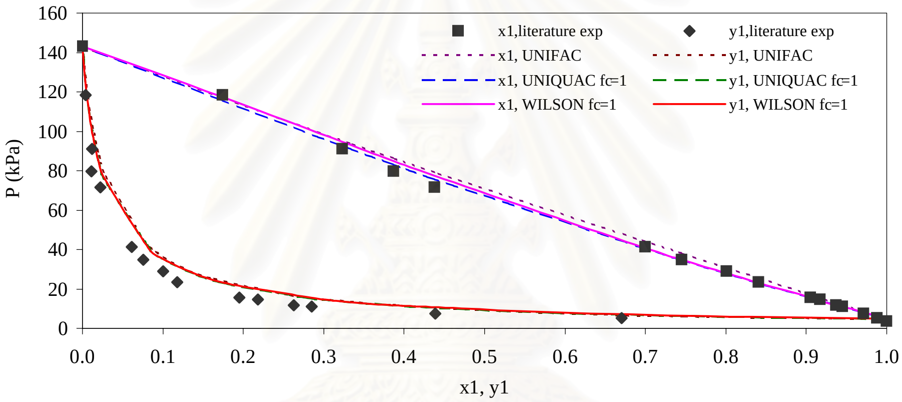

Figure 6.16 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of ethylene glycol(*1*)-water(*2*) system at 110°C

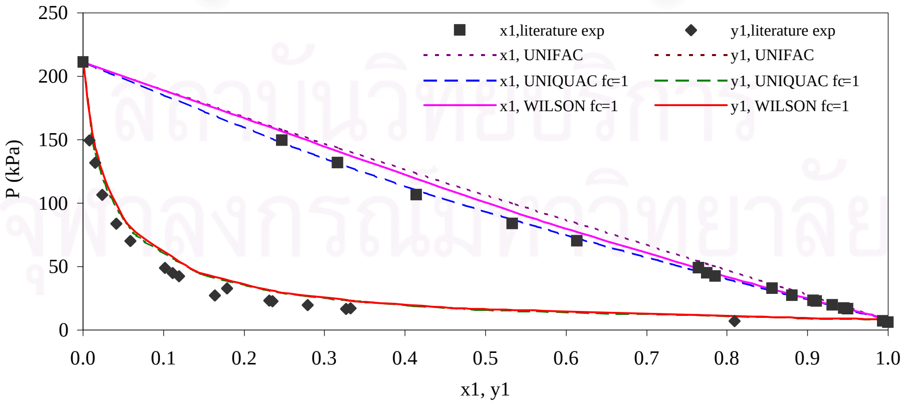

Figure 6.17 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of ethylene glycol(*1*)-water(*2*) system at 122°C

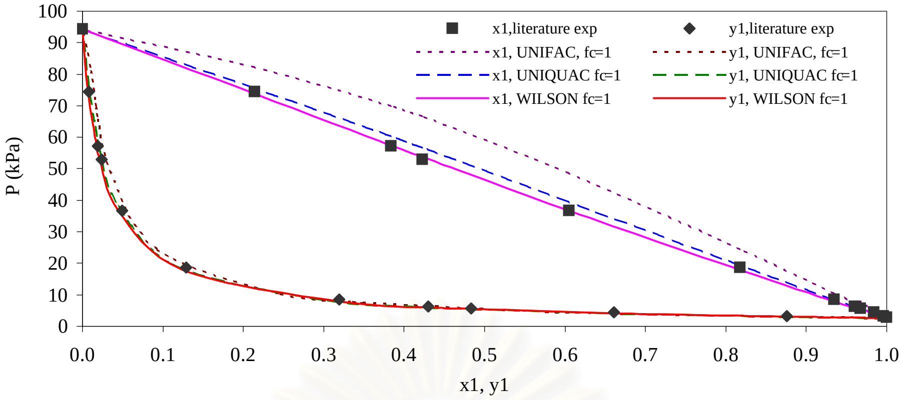

Figure 6.18 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of propylene glycol(*1*)-water(*2*) system at 98°C

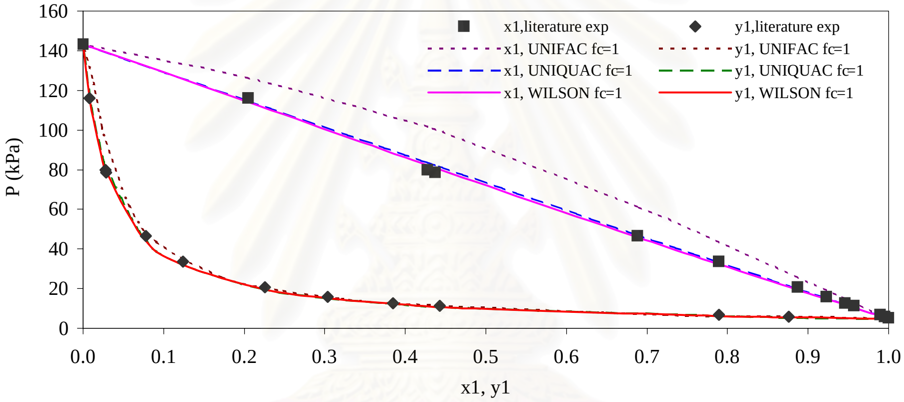

Figure 6.19 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of propylene glyco(*1*)l-water(*2*) system at 110°C

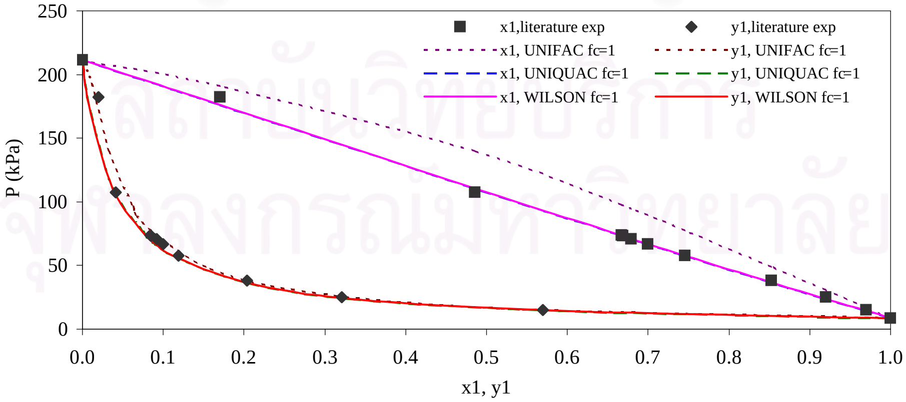

Figure 6.20 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of propylene glycol(*1*)-water(*2*) system at 122°C

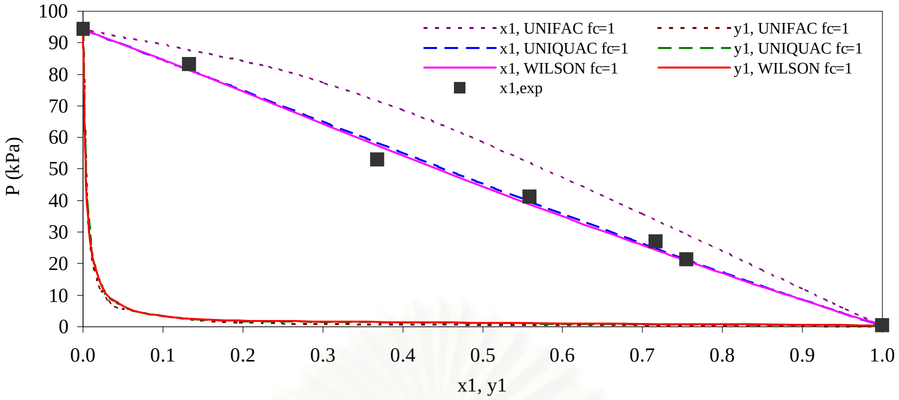

Figure 6.21 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of 1,4-butylene glycol(*1*)-water(*2*) system at 98°C

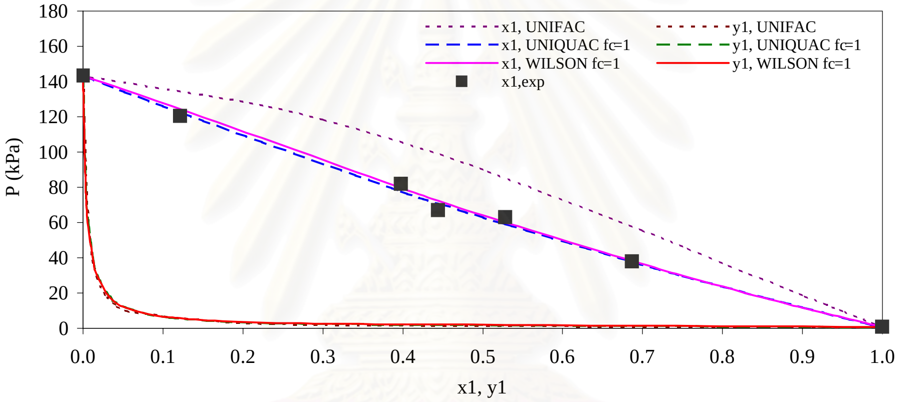

Figure 6.22 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of 1,4-butylene glycol(*1*)-water(*2*) system at 110°C

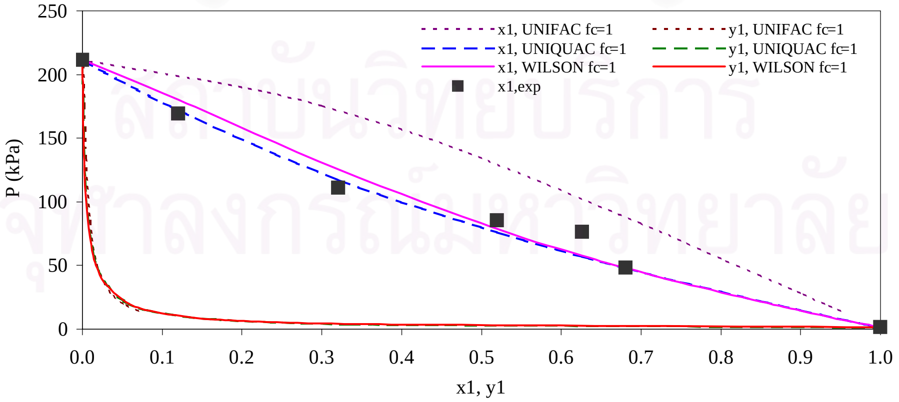

Figure 6.23 Comparison of UNIFAC, UNIQUAC and Wilson models estimations of 1,4-butylene glycol(*1*)-water(*2*) system at 122°C

When the parameters of each binary systems was determined, it can be used to predict pressure of each system by EOS and/or properties models. The %AAD is used in evaluating models as the objective function; the smaller the deviation, the better the model. As show in Table 6.6 and 6.7, the UNIQUAC model has %AAD in range of 1.9890-8.7003 where the Wilson model has the value in range of 1.9614-10.2832. Both give closely good estimated VLE data of glycols in water with slightly better estimation of UNIQUAC model.

6.10 Activity Coefficients

The activity coefficients estimated by using UNIQUAC or Wilson models in each of the three systems were also shown in Appendix F. The activity coefficient is different in each system and depends on the mole fraction and temperature of one system. In the studied glycol-water systems, the dependence of UNIQUAC estimated activity coefficients on the mole fraction is presented by Figures 6.24, 6.25 and 6.26 for 98, 110 and 122^{o}C of temperature respectively. The Figure 6.27 present the dependence on temperature of the activity coefficients of studied infinitely diluted glycols in water with the assumption of x_i = 1E-09 for the infinite dilution of species *i*.

The first set of figures show that the activity coefficients of glycol trended to increase when the glycol mole fraction is increased.

The Figure 6.27 presents that the infinite dilution activity coefficients of glycol decreased when the system temperature is increased. Besides, the results inform that the infinite dilution activity coefficients of straight chain glycol decrease when the molecular size of is increased.

Table 6.8 UNIQUAC estimated infinite dilution activity coefficient of glycols in water

Temperature (^{o}C)	Ethylene glycol	Propylene glycol	1,4-Butylene glycol
98	0.7856	1.1858	0.8419
110	0.5912	0.9472	0.4028
122	0.3474	0.9118	0.0988

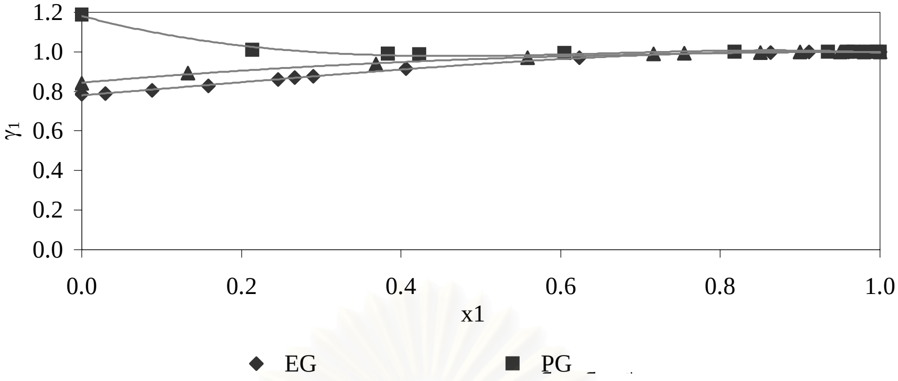

Figure 6.24 UNIQUAC estimated activity coeffcients of glycols (*1*) in water (*2*) at 98°C

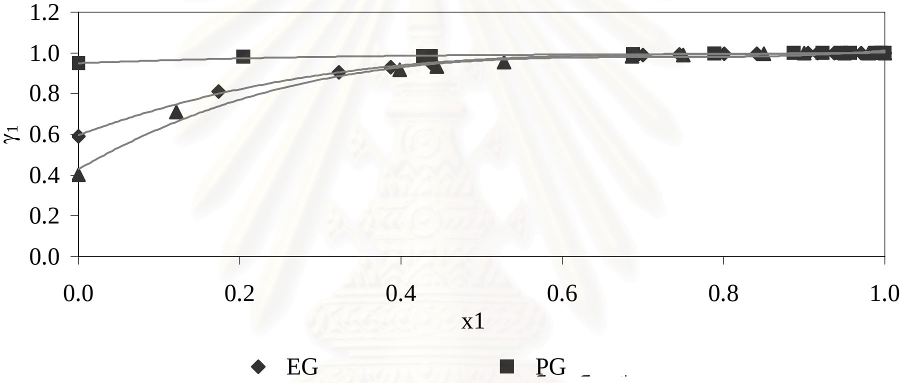

Figure 6.25 UNIQUAC estimated activity coeffcients of glycols (*1*) in water (*2*) at 110°C

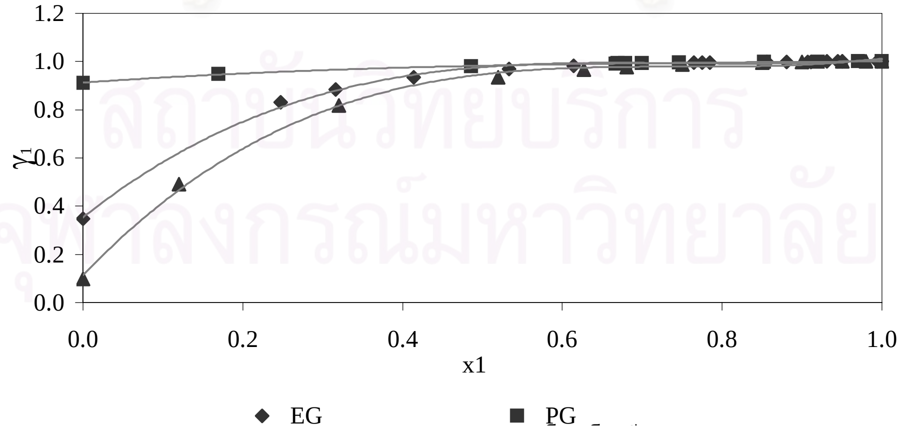

Figure 6.26 UNIQUAC estimated activity coeffcients of glycols (*1*) in water (*2*) at 122°C

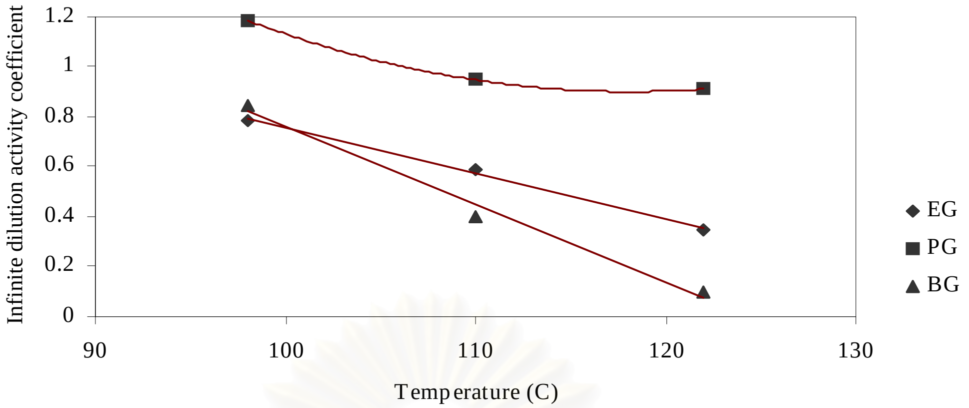

Figure 6.27 Infinite dilution activity coeffcients of glycols in water estimated by using UNIQUAC model

However, infinite dilution activity coefficient of branch chain is greater than that of straight chain glycol, not in agreement with the molecular size. The ethylene glycol and 1,4-butylene glycol have straight chain structures but the propylene glycol has branch structure. The molecular size (molecular weight) of ethylene glycol < propylene glycol < 1,4-butylene glycol.

Suleiman and Eckert (1994) suggested that this effect may be due to the interaction of component and tried to explain by using the normal boiling point of component in their results.

6.11 Comparison with Literature Researches

The calculated results of γ^{∞} of glycols in water by using τ_{12} and τ_{21} obtained by the work of Lancia et al. (1996) (Table 3.3) in the present UNIQUAC model are shown in Tables 6.9 and 6.10 for ethylene glycol and propylene glycol respectively. The results of glycols were then illustrated by Figures 6.28.

Table 6.9 γ^{∞} of water(*1*)-ethylene glycol(*2*) system calculated by using UNIQUAC interaction in the work of Lancia et al. (1996)

Temperautre (C)	98	110	122
γ_1^{∞}	1.7793	1.9464	2.0177
γ_2^{∞}	2.3571	2.2068	1.9800

Table 6.10 γ^{∞} of water(*1*)-propylene glycol(*2*) system calculated by using UNIQUAC interaction in the work of Lancia et al. (1996)

Temperautre (C)	98	110	122
γ_1^{∞}	1.6157	1.7365	1.8084
γ_2^{∞}	3.6741	3.7468	3.6319

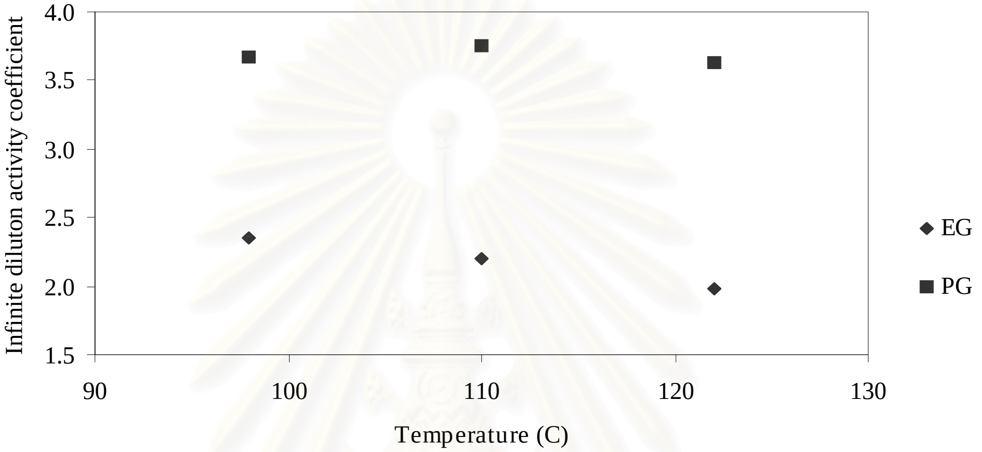

Figure 6.28 Calculated infinite dilution activity coeffcients of glycol in water by using UNIQUAC interaction in the work of Lancia et al (1996)

The Table 6.9 show that the γ^{∞} of ethylene glycol decrease when the system temperature is increased, in agreement with the results in this work. These confirm that the present computer programming give reliable estimation.

6.12 Correlation of the Activity Coefficient and Molecular Size

We have found from the Figure 6.27 that the infinite dilution activity coefficients of straight chain glycol decrease when the molecular size is increased and that value of branch chain glycol is greater than of the straight chain. These inform that the activity coefficient depends on molecular size and structure of glycol in aqueous solution. These two effects may be explained together by interaction of components, which can be presented by boiling point of component because the boiling point also depends on both of those two effects.

Table 6.11 shows the change of the infinite dilution activity coefficients by the effects found in the research.

The molecular weight is used to represent the molecular size effect to the infinite dilution activity. It can not explain those 2 effects presented in this work as shows in Figure 6.29. The correlation of the infinite dilution activity of glycol in water and molecular weight is also suggested in the figure. The effects of molecular size together with molecular structure on the the infinite dilution activity of glycol in water are present by the normal boiling point (n.b.p.), the boiling point at 1 atm. of pressure that near to the studying pressures, as show in Figure 6.30.

Table 6.11 Infinite dilution activity coefficient correlate to molecular weight and normal boiling point

	MW	n.b.p. (^{o}C)	Infinite dilution activity coefficient		
			98 C	110 C	122 C
1,2-propylene glycol	76.095	189	1.1858	0.9472	0.9118
Ethylene glycol	62.068	197.2	0.7856	0.5912	0.3474
1,4-butylene glycol	90.122	230	0.8419	0.4028	0.0988

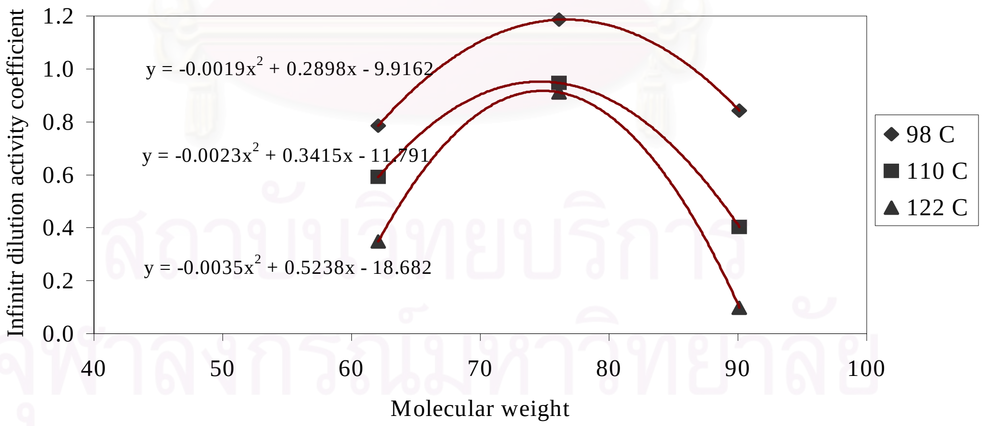

Figure 6.29 Effect of molecular size on the the infinite dilution activity coefficient of glycol in water

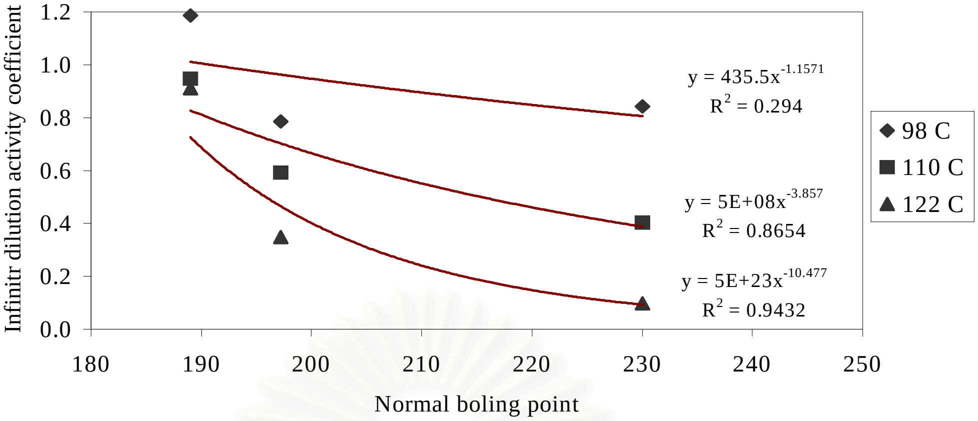

Figure 6.30 Effects of molecular size and structure on the the infinite dilution activity coefficient of glycol in water

Figures present that not only molecular size has effect on the infinite dilution activity coefficient γ^{∞} but the molecular structure and may others else also. These also support the interaction of component has effect on the γ^{∞}, the suggestion of Suleiman and Eckert (1994).

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The study of VLE for mixtures of glycols and water constitutes an interesting field of study in this research, both for theoretical and for applicative proposes. The interested glycols are ethylene glycol (ethanediol), propylene glycol (propanediol) and 1,4-butylene glycol (1,4-butanediol). The studied systems can use the assumption of $\phi = 1$ for gas at low pressure. The UNIQUAC and Wilson models have been successfully applied to such the binary mixtures in the temperature range of 98-122^{o}C. A satisfactory agreement has been found between models and experiment results. The binary parameters of each model can be evaluated from the VLE data, and then can be further used to predict properties of such the binary mixtures at other conditions of operation or to predict the equilibrium conditions for ternary mixtures containing the studied components.

Activity coefficients of each system were estimated by the correlated models. The values depended on temperature and composition (mole fraction) in each system. With in studied glycol-water systems, the activity coefficients were depended on molecular size and shape, as the literature (Suileiman and Eckert, 19894) found. The ethylene glycol and 1,4-butylene glycol have straight chain structures but the propylene glycol has branch structure. The molecular size (molecular weight) of ethylene glycol < propylene glycol < 1,4-butylene glycol. The research showed that the infinite dilution activity coefficients of glycols trended to decrease when the molecular size of the same structure was increased and the branch chain have the value of the infinite dilution activity coefficients greater than that of the straight chain.

However, in the small temperature range of study, the effect of molecular size of glycols in water can be more significantly presented by the parameters of both UNIQUAC and Wilson models. The molecular size of glycol increase, τ_{12} increase but the τ_{21} decrease whereas the Λ_{12} decrease but the Λ_{21} increase. Besides, the parameters were also depended on system temperature. When studied temperature is increased, the τ_{12} increase but the τ_{21} decreased whereas the Λ_{12} decrease but the Λ_{21} increase.

7.2 Recommendations for Future Studies

To eliminate the molecular structure effect on activity coefficients, it should study the 1,2-butylene glycol to learn only the molecular size effect.

To study the effect of molecular structure on activity coefficient, it should study the isomer of one molecular size, eg. comparison of 1,2- butylene glycol, 1,3- butylene glycol, 1,4- butylene glycol, and 2,3- butylene glycol etc.

To expand the VLE information to a wide range of conditions, future work may study at temperature out of range of 98-122^{o}C.

Future work may correlate VLE data with UNIQUAC using the new developed combination part of UNIQUAC and UNIFAC as follow in the work of Lancia et al. (1996) for the liquid phase calculation, and compare accuracy of the model.

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APPENDICES

APPENDIX A

PROPERTIES OF PURE COMPONENTS

Table A.1 Physical properties of pure components

Name	Other Names	Formular	Form and Color	M.W.	m.p. (^oC)	b.p. (^oC)	sp.gr. or Density	Solubility			Use
								Water	Alcohol	Other	
1,2-butylene glycol	α-butylene glycol; 1,2- or α-butanediol; 1,2-dihydroxy butane; Ethyl-ethylene glycol;	CH_3CH_2CH- $(OH)CH_2OH$	colorless liquid.	90.122		192	1.019	s.	s.		
1,3-butylene glycol	β-butylene glycol; 1,3- or β-butanediol; 1,3-dihydroxy butane; α-methyl-trimethylene glycol	$CH_3CH(OH)$- CH_2CH_2OH	colorless viscous liquid.	90.122	-77	207	$1.0259^{20/4}$ $1.0059^{20/20}$	s.	s.	sl.s. in ether	Polyesters, polyurethanes, surface-active agents, plasticizers, humectant, couping agent, solvent, food additive, flavoring.
1,4-butylene glycol	γ-butylene glycol; 1,4- or γ-butanediol; 1,4-dihydroxy butane; Tetramethylene glycol	CH_2OH- $(CH_2)_2CH_2OH$	colorless oily liquid.	90.122	16	230	$1.020^{20/4}$	s.	s.	sl.s. in ether	Solvents, humectant, intermediate for plasticizers, pharmaceuticals, cross-linking agent in polyurethane elastomers, manufacture of tetrahydrofuran, terephthalate plastics.

Name	Other Names	Formular	Form and Color	M.W.	m.p. (^oC)	b.p. (^oC)	sp.gr. or Density	Solubility			Use
								Water	Alcohol	Other	
2,3-butylene glycol	ψ- butylene glycol; 2,3- or ψ-butanediol; 2,3-dihydroxy butane; pseudobutylene glycol; dimethyl pinacol; *sym*-dimethylethylene glycol	$CH_3CH(OH)$- $CH(OH)CH_3$	colorless crystalline or liquid.	90.122	23	182	$1.045^{20/20}$ $1.048^{0/4}$	s.	s.	s. in ether	Resins, solvent for dyes, intermediate, blending agent.
Ethylene glycol	1,2-ethanediol; glycol; ethylene alcohol; glycol alcohol; glycohol alcohol; dihydroxyethane; monophenyl ether; phenoxetol	CH_2OHCH_2- OH	colorless, syrupy liquid; odorless; sweet taste.	62.068	-13.5	197.2	$1.1176^{15/15}$ $1.1155^{(20C)}$	s.	s.	s. in acetone	Coolant and antifreeze, heat-transfer agent, low-freezing dynamite, solvent, extractant, resin, lacquers, printing inks, adhesives, leather dyeing, textile processing, cosmetics, tobacco, foam stabilizer, etc.
1,2-propylene glycol	"propylene glycol"; 1,2-propanediol; 1,2-dihydroxy propane; methyl glycol; methylene glycol	$CH_2OHCHOH$ $-CH_3$	colorless, viscous liquid; odorless; test.less.	76.095	-60	189	$1.0381^{20/20}$ $1.040^{(15C)}$	s.	s.	s. in many org. solv.	Antifreeze, solvent, perfumes, colors, coolant in refrigerator, plasticizers, hydraulic fluids, emulsifier, preservative, suntan lotion, pharmaceuticals, break fluids, tobacco, etc.

Name	Other Names	Formular	Form and Color	M.W.	m.p. (°C)	b.p. (°C)	sp.gr. or Density	Solubility			Use
								Water	Alcohol	Other	
1,3-propylene glycol	1,3-propanediol; trimethylene glycol	$HOCH_2CH_2$-CH_2OH	colorless, viscous liquid; oderless.	76.095		210	$1.0537^{(25C)}$	s.	s.	s. in ether	Intermediate, especially for polyesters.
Water		H_2O	colorless liquid; odorless; test.less.	18.015	0	100	$1.00^{(4C)}$	s.	s.	s. in many org. solv.	Suspending agent, solvent, diluent, industial coolant, filtration, washing & scouring, mining, hydrolysis, hydraulic systems, power source, steam generation, food industry, source of hydrogen by electrolysis & thermochemical decomposition, etc.

Abbreviation :

b.p.	boiling point
m.p.	melting point
M.W.	Molecular weight
org. solv.	organic solvent
s.	soluble
sp.gr.	specific gravity
sl.s.	slightly soluble

Table A.2 Chemical and thermodynamic properties of pure components

Properties	1,3-Butylene glycol	1,4-Butylene glycol	2,3-Butylene glycol	Ethylene glycol	1,2-Proplene glycol	1,3-Propylene glycol	Water
Critical properties							
'Temperature, T_c (K)	643.00	667.00	611.00	645.00	626.00	658.00	647.13
'Pressure, P_c (bar)	50.00	48.80	51.30	75.30	61.00	59.20	220.55
'Volume, V_c (cm^3/mol)	292.0	297.0	267.0	191.0	239.0	217.0	56.0
'Compresibility factor, Z_c (-)	0.273	0.261	0.270	0.268	0.280	0.235	0.229
Acentric factor, ω (-)	1.146	1.189	1.106	1.137	1.107	1.152	0.345
Solubility parameter $(J/cm^3)^{0.5}$	26.974	27.958	25.95	19.493	29.516	31.173	47.813
Liquid volume (at 25°C) (cm^3/mol	89.913	88.987	90.63	65.634	73.694	72.364	18.069
Herry's Law constant for compound in water (H_i - atm/mole fraction) [$K_i = H_i/P_t$; $y_i = K_i x_i$]							
Temperature (°C)	-	20.0	-	25.0	-	-	-
H@T (atm/mole fraction)	-	2.8544E-05	-	1.0506E-04	-	-	-
H@T (atm/mol/m^3)	-	5.1378E-10	-	1.8911E-09	-	-	-
Dipole moment (Debye)	-	3.93 (liquid)	2.10 (in benzene)	2.31 (in dioxane)	3.63 (liquid)	2.52 (in dioxane)	1.85 (gas)

critical density, g/cm^3 $\rho_c = MW/V_c$

critical compressibility factor $z = P_c V_c / RT_c$

acentric factor $= \frac{3}{7} \frac{T_B/T_C}{1 - T_B/T_C} (\log P_C) - 1$

Table A.2 Chemical and thermodynamic properties of pure components (continue)

Properties	1,3-Butylene glycol	1,4-Butylene glycol	2,3-Butylene glycol	Ethylene glycol	1,2-Proplene glycol	1,3-Propylene glycol	Water
Liquid viscosity							
$^{\#}$regression coefficients for the correlation : $\log_{10} \eta_{liq} = A + B/T + CT + DT^2$ (η_{liq} - centipoise, T-K)							
temperature range	293 - 643	293 - 667	281 - 611	261 - 645	233 - 626	246 - 658	273 - 643
A	-24.0994	-14.3559	-6.0949	-16.9780	-29.4920	-7.9787	-10.2158
B	4.6841E+03	3.1423E+03	2.1560E+03	3.1886E+03	5.2456E+03	1.9800E+03	1.7925E+03
C	4.4009E-02	2.4253E-02	2.8597E-03	3.2537E-02	5.8169E-02	1.1850E-02	1.7730E-02
D	-3.0862E-05	-1.7544E-05	-1.0083E-06	-2.4480E-05	-4.2343E-05	-9.3205E-06	-1.2631E-05
η_{liq} @ 25°C	97.500	71.600	79.314	17.645	47.962	23.270	0.911
η_{liq} @ T_{max}	0.053	0.053	0.064	0.059	0.051	0.062	0.056
Density of liquid (saturated liquid density, g/ml)							
$^{\#}$regression coefficients for the correlation : density = $AB^{-(1-T/Tc)^{\wedge}n}$ (T-K)							
temperature range	196.15 - 643.00	293.05 - 667.00	280.75 - 611.00	260.15 - 645.00	213.15 - 626.00	246.45 - 658.00	273.16 - 647.13
A	0.32441	0.31558	0.33718	0.32503	0.31839	0.32832	0.34710
B	0.25980	0.25131	0.26990	0.25499	0.26106	0.25080	0.27400
n	0.28570	0.28570	0.28600	0.17200	0.20459	0.28570	0.28571
density @ 25°C	1.002	1.013	0.994	1.110	1.033	1.052	1.027

Table A.2 Chemical and thermodynamic properties of pure components (continue)

Properties	1,3-Butylene glycol	1,4-Butylene glycol	2,3-Butylene glycol	Ethylene glycol	1,2-Proplene glycol	1,3-Propylene glycol	Water
Vapor pressure							
[#] regression coefficients for the correlation : $\log_{10} P = A + B/T + C \log_{10} T + DT + ET^2$ (P-mmHg, T-K) [Antoine-type equation]							
temperature range	196.15 - 643.00	293.05 - 667.00	280.75 -611.00	260.15 - 645.00	213.15 - 626.00	246.45 - 658.00	273.16 - 647.13
A	109.4540	22.4549	46.6247	82.4062	90.2930	27.4723	29.8605
B	-7.4377E+03	-4.2023E+03	-4.7864E+03	-6.3472E+03	-6.6968E+03	-4.0200E+03	-3.1522E+03
C	-3.6627E+01	-4.2015E+00	-1.2792E+01	-2.5433E+01	-2.8109E+01	-6.2839E+00	-7.3037E+00
D	1.4845E-02	-7.4539E-10	-8.5522E-10	-2.3732E-09	-1.3326E-10	-6.7098E-10	2.4247E-09
E	-7.6634E-14	6.1761E-07	3.8460E-06	8.7467E-06	9.3651E-06	2.2952E-06	1.8090E-06
[##] regression coefficients for the correlation : $P = \exp [A + B/T + C \ln T + DT^E]$ (P-Pascal, T-K)							
temperature range	196.15 - 643.00	293.05 - 667.00		260.15 - 645.00	213.15 - 626.00	246.45 - 658.00	273.16 - 647.13
error	< 10%	< 10%		< 10%	< 10%	< 10%	< 10%
A	2.5692E+02	5.6597E+01		1.9464E+02	2.1280E+02	6.8150E+01	7.3649E+01
B	-1.7126E+04	-9.6762E+03		-1.4615E+04	-1.5420E+04	-9.2565E+03	-7.2582E+03
C	-3.6627E+01	-4.2015E+00		-2.5433E+01	-2.8108E+01	-6.2839E+00	-7.3037E+00
D	3.4182E-02	1.4221E-06		2.0140E-05	2.1564E-05	5.2749E-06	4.1653E-06
E	1.0000E+00	2.0000E+00		2.0000E+00	2.0000E+00	2.0000E+00	2.0000E+00

Table A.2 Chemical and thermodynamic properties of pure components (continue)

Properties	1,3-Butylene glycol	1,4-Butylene glycol	2,3-Butylene glycol	Ethylene glycol	1,2-Proplene glycol	1,3-Propylene glycol	Water
Second Virial coefficient (m^3/kmol)							
${}^{\#\#}$ regression coefficients for the correlation : $B_{ij} = A + B/T + C/T^3 + D/T^8 + E/T^9$ (T-K)							
temperature range	322.00 - 3212.00	333.00 - 3333.00		323.00 - 3223.00	313.00 - 3123.00	330.00 - 3290.00	323.64 - 3236.40
error	< 25%	< 25%		< 25%	< 25%	< 25%	< 25%
A	-4.4903E-02	-5.0576E-02		-1.1361E-01	-7.6351E-02	-8.2189E-02	-2.3040E-02
B	2.2210E+02	2.3069E+02		3.1111E+02	2.5985E+02	2.7156E+02	2.6860E+01
C	-1.8513E+08	-2.0923E+08		-1.6684E+08	-1.6097E+08	-1.8867E+08	-2.8170E+07
D	5.2158E+21	7.6049E+21		5.9180E+21	4.2654E+21	6.8989E+21	3.3408E+20
E	-2.2488E+24	-3.3116E+24		-2.4740E+24	-1.7792E+24	-2.9538E+24	-1.3837E+23

[#] Yaws (1999)

[##] Daubert and Danner (1989)

Table A.3 Temperature depending properties of pure components at studied temperatures

Properties	1,3-Butylene glycol	1,4-Butylene glycol	2,3-Butylene glycol	Ethylene glycol	1,2-Proplene glycol	1,3-Propylene glycol	Water
Liquid viscosity [#] correlation : $\log_{10} \eta_{liq} = A + B/T + CT + DT^2$ (η_{liq} - centipoise, T-K)							
At 98°C (371.15 K)	4.015	4.957	4.331	2.075	2.500	2.953	0.285
At 110°C (383.15 K)	2.866	3.650	3.019	1.648	1.862	2.296	0.252
At 122°C (395.15 K)	2.118	2.757	2.157	1.336	1.435	1.817	0.226
Density of liquid (saturated liquid density, g/ml) [#] correlation : density = $AB^{-(1-T/Tc)^n}$ (T-K)							
At 98°C (371.15 K)	0.931	0.943	0.919	1.057	0.973	0.978	0.958
At 110°C (383.15 K)	0.918	0.931	0.905	1.048	0.963	0.965	0.945
At 122°C (395.15 K)	0.906	0.919	0.892	1.038	0.952	0.952	0.933
Vapor pressure [#] correlation : $\log_{10} P = A + B/T + C \log_{10} T + DT + ET^2$ (P-mmHg, T-K) [Antoine-type equation]							
At 98°C (371.15 K)	6.4451E+00	2.6402E+00	2.4473E+01	1.4397E+01	2.0522E+01	6.4636E+00	7.0699E+02
At 110°C (383.15 K)	1.2848E+01	5.2939E+00	4.4732E+01	2.6399E+01	3.7467E+01	1.2124E+01	1.0736E+03
At 122°C (395.15 K)	2.4318E+01	1.0147E+01	7.8448E+01	4.6316E+01	6.5378E+01	2.1854E+01	1.5841E+03
[##] correlation : $P = \exp [A + B/T + C \ln T + DT^E]$ (P-Pascal, T-K)							
At 98°C (371.15 K)	8.5923E+02	3.5192E+02		1.9192E+03	2.7517E+03	8.6024E+02	9.4248E+04
At 110°C (383.15 K)	1.7129E+03	7.0565E+02		3.5191E+03	5.0239E+03	1.6134E+03	1.4312E+05
At 122°C (395.15 K)	3.2420E+03	1.3526E+03		6.1741E+03	8.7668E+03	2.9081E+03	2.1117E+05

Table A.3 Temperature depending properties of pure components at studied temperatures (continue)

Properties	1,3-Butylene glycol	1,4-Butylene glycol	2,3-Butylene glycol	Ethylene glycol	1,2-Proplene glycol	1,3-Propylene glycol	Water
Second Virial coefficient (m^3/kmol)	$^{\#\#}$ correlation :	$B_{ij} = A + B/T + C/T^3 + D/T^8 + E/T^9$ (T-K)					
At 98^{o}C (371.15 K)	-5.4092E+00	-7.1807E+00		-4.6153E+00	-3.9920E+00	-5.9835E+00	-6.0923E-01
At 110^{o}C (383.15 K)	-4.1634E+00	-5.4035E+00		-3.4283E+00	-3.0743E+00	-4.4724E+00	-5.1201E-01
At 122^{o}C (395.15 K)	-3.2828E+00	-4.1628E+00		-2.6072E+00	-2.4267E+00	-3.4222E+00	-4.3870E-01

APPENDIX B

UNIQUAC & UNIFAC GROUP PARAMETERS

Table B.1 Group volume and surface area parameters

Group number and name				Rk	Qk	Sample group assignment
1	CH_2	Alkane group				
	Subgroups:					
	1A	CH_3	end group of hydrocarbon chain	0.0011	0.848	Ethane: $2CH_3$
	1B	CH_2	middle group in hydrocarbon chai	0.6744	0.340	n-butane: $2CH_3$, $2CH_2$
	1C	CH	middle group in hydrocarbon chai	0.4469	0.228	iso-butane: $3CH_3$, 1CH
2	C=C		olefin group, α-olefin only	1.3454	1.176	α-butene: 1C=C, $1CH_2$, $1CH_3$
3	ACH		aromatic carbon group	0.5313	0.400	Benzene: 6ACH
4	$ACCH_2$		aromatic carbon -alkane group			
	Subgroups:					
	4A	$ACCH_2$	general case	1.0396	0.660	Ethylbenzene: 5ACH, $1ACCH_2$, $1CH_3$
	4B	$ACCH_3$	toluene group	1.2663	0.968	Toluene:5ACH, $1ACCH_3$
5	COH	alcohol group, includes nearest CH_2				
	Subgroups:					
	5A	COH	general case	1.2044	1.124	Ethanol: $1CH_3$, 1COH
	5B	MCOH	methanol	1.4311	1.432	Methanol: 1MCOH
	5C	CHOH	secondary alcohol	0.9769	0.812	Isopropanol: $2CH_3$, 1CHOH
6	H_2O	water		0.9200	1.400	Water:IH2O
7	ACOH	aromatic carbon-alcohol group		0.8952	0.680	Phenol: 5ACH 1ACOH
8	CO	cabonyl group		0.7713	0.640	Acetone: $2CH_3$, 1CO
9	CHO	aldehyde group		0.9980	0.948	Propionaldehyde: $1CH_3$, $1CH_2$, 1CHO

Table B.1 Group volume and surface area parameters (continue)

Group number and name				Rk	Qk	Sample group assignment
10	COO	ester group		1.0020	0.880	Methyl acetate:2CH3,ICOO
11	O	ether group		0.2439	0.240	Diethyl either: $2CH_3$, $2CH_2$, 1O
12	CNH_2	primary amine group,includes nearest CH_2				
	Subgroups:					
	12A	CNH_2	general case	1.3692	1.236	n-propylamine: $1CH_3$, $1CH_2$, $1CNH_2$
	12B	$MCNH_2$	methylamine	1.5959	1.544	Methylamine: $1MCNH_3$
13	NH	secondary amine group		0.5326	0.396	Diethylamine: $2CH_3$, $2CH_2$, 1NH
14	$ACNH_2$	aromatic carbon-amine group		1.0600	0.816	Aniline: 5ACH, $1ACNH_2$
15	CCN	nitrile group, includes nearest CH_2				
	Subgroups:					
	15A	MCCN	acetonitrile	1.8701	1.724	Acetonitrile: 1MCCN
	15B	CCN	general case	1.6434	1.416	Propionitrile: 1CCN, $1CH_3$
16	Cl	chloride group				
	Subgroups:					
	16A	Cl-1	Cl on end carbon	0.766	0.720	1,2 dichloroethane: $2CH_2$, 2Cl-1
	16B	Cl-2	Cl on middle carbon	0.8069	0.728	1,2,3 trichloropropane: $2CH_2$, 1CH, 2Cl-1, 2Cl-2
17	$CHCl_2$	dichloride group, end group only		2.0672	1.684	1,1 dichloroethane: $1CH_3$, $1CHCl_2$
18	ACCl	aromatic carbon-chloride group		1.1562	0.344	Chlorobenzene: 5ACH, 1ACCl

APPENDIX C

REFRACTIVE INDEX CALIBRATION OF 1,4-BUTYLENE GLYCOL IN WATER

Table B.2 Group interaction parameters, a_{mn} ^{o}K

m \ n	CH2	C=C	ACH	ACCH2	COH	H2O	ACOH	CO	CHO	
CH2	0.00	-200.00	32.08	26.78	931.20	1452.00	1860.00	1565.00	685.90	1
C=C	2520.00	0.00	651.60	1490.00	943.30	578.30	x	1400.00	x	2
ACH	15.26	-144.30	0.00	167.00	705.90	360.70	1310.00	851.10	x	3
ACCH2	-15.84	-309.20	-146.80	0.00	856.20	3000.00	740.00	3000.00	x	4
COH	169.70	254.20	83.50	92.61	0.00	-320.80	x	462.30	480.00	5
H2O	657.70	485.40	361.50	385.00	287.50	0.00	462.60	470.80	234.50	6
ACOH	3000.00	x	3000.00	3000.00	x	-558.20	0.00	x	x	7
CO	3000.00	3000.00	101.80	75.00	-106.50	-532.60	x	0.00	-49.24	8
CHO	343.20	x	x	x	3000.00	-226.40	x	39.47	0.00	9
COO	348.00	x	325.50	3000.00	167.50	x	-254.10	333.60	x	10
O	2160.00	x	-75.50	3000.00	-13.44	x	x	-39.81	x	11
CNH2	-16.74	90.37	-38.64	x	-109.80	-527.70	x	x	x	12
NH	3000.00	8.92	37.94	x	-700.00	-882.70	x	x	x	13
ACNH2	3000.00	x	3000.00	3000.00	x	236.80	x	x	x	14
CCN	27.31	43.03	-88.44	-150.00	337.90	227.00	x	447.70	x	15
Cl	-119.60	242.10	-90.43	52.69	357.00	618.20	x	62.00	x	16
CHCl2	31.06	-72.88	x	x	x	467.00	x	37.63	x	17
ACCl	121.10	x	1000.00	x	586.30	1472.00	x	x	x	18
	1	2	3	4	5	6	7	8	9	

Table B.2 Group interaction parameters, a_{mn} °K (continue)

m \ n	COO	O	CNH2	NH	ACNH2	CCN	Cl	CHCl2	ACCl	
CH2	687.50	472.60	422.10	800.00	1330.00	601.60	523.20	60.45	194.20	1
C=C	x	x	349.90	515.20	x	691.30	253.80	259.50	x	2
ACH	159.10	37.24	179.70	487.20	680.00	290.10	124.00	x	-99.90	3
ACCH2	110.00	680.00	x	x	640.00	3000.00	33.84	x	x	4
COH	174.30	-204.60	-166.80	3000.00	x	79.85	194.60	x	69.97	5
H2O	x	x	385.30	743.80	-314.60	118.50	158.40	247.20	190.60	6
ACOH	-470.20	x	x	x	x	x	x	x	x	7
CO	-180.10	475.50	x	x	x	-307.40	628.00	874.50	x	8
CHO	x	x	x	x	x	x	x	x	x	9
COO	0.00	-26.15	x	x	x	x	x	x	x	10
O	-290.00	0.00	x	x	x	x	x	x	x	11
CNH2	x	x	0.00	x	x	x	x	x	-10	12
NH	x	x	x	0.00	x	x	x	x	-60	13
ACNH2	x	x	x	x	0.00	x	x	x	3000	14
CCN	x	x	x	x	x	0.00	-100.00	x	25	15
Cl	x	x	x	x	x	100.00	0.00	-308.50	x	16
CHCl2	x	x	x	x	x	x	790.00	0.00	x	17
ACCl	x	x	3000.00	3000.00	1100.00	3000.00	x	x	0.00	18
	10	11	12	13	14	15	16	17	18	

Table C.1 Gravimetrically standard preparation of1-4,butylene glycol in aqueous solution

Mass of H_2O (g)	Mass (g) of supply 1,4-butylene glycol	Mass (g) of pure 1,4-butylene glycol	Mole fraction (z)
5.5140	3.0950	3.0641	0.1000
3.5654	4.4371	4.3927	0.1976
2.5054	5.4188	5.3646	0.2997
1.8537	6.0808	6.0200	0.3936
4.2672	21.2449	21.0325	0.4963
1.5238	11.3661	11.2524	0.5961
0.7436	8.2630	8.1804	0.6874
0.4521	8.0799	7.9991	0.7796
0.2031	9.1002	9.0092	0.8987

Table C.2 Calibration results of refractive index of1,4-butahylene glycol in aqueou solution

Mole fraction (x)	Refractive index (RI)
0.0000	1.3304
0.1000	1.3734
0.1976	1.3962
0.2997	1.4110
0.3936	1.4198
0.4963	1.4262
0.5961	1.4308
0.6874	1.4342
0.7796	1.4362
0.8987	1.4393
1.0000	1.4403

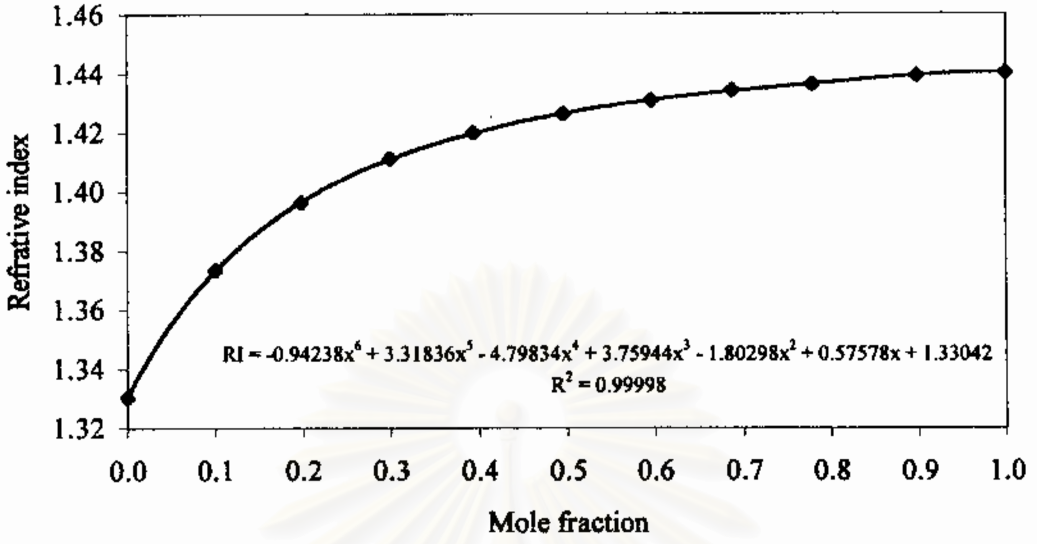

Figure C.1 Refractive index calibration curve of 1,4-buthylene glycol in water

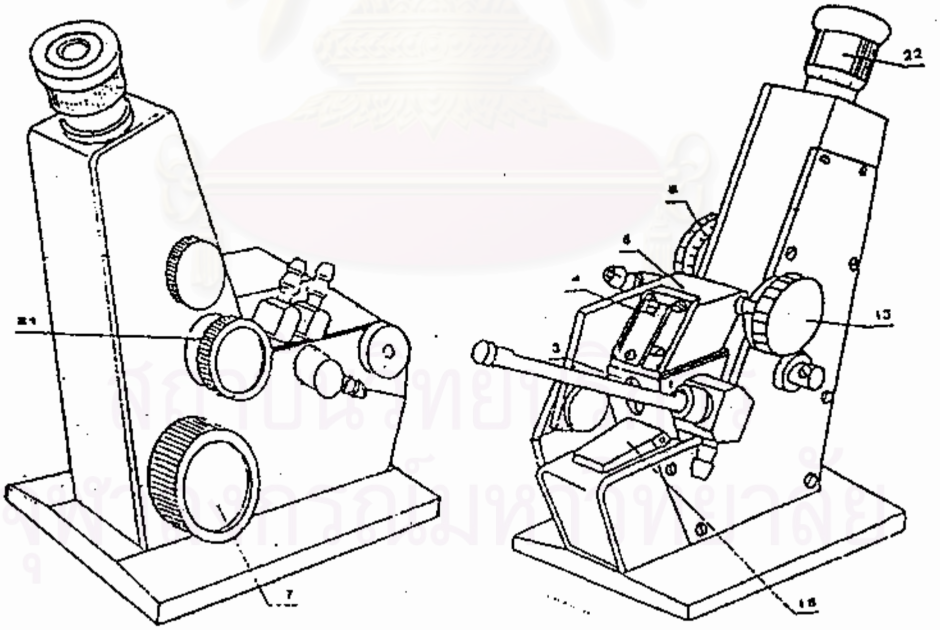

Figure C.2 Refractometer

APPENDIX D

GRAVIMETRICALLY PREPARATION OF CHARGE MIXTURES

Table D.1 Gravimetrically charge preparation of ethylene glycol in water

Approximated mole fraction (z_{app})	Mass of H_2O (g)	Mass (g) of supply ethylene glycol	Mass (g) of pure ethylene glycol	Mole fraction (z)
0.3	10.6534	14.5717	14.4988	0.2832
0.5	5.9739	19.3610	19.2642	0.4835
0.7	2.9869	22.4180	22.3059	0.6843
0.9	0.6970	14.5717	14.4988	0.8579

Table D.2 Gravimetrically charge preparation of1-4,butylene glycol in water

Approximated mole fraction (z_{app})	Mass of H_2O (g)	Mass (g) of supply 1,4-butylene glycol	Mass (g) of pure 1,4-butylene glycol	Mole fraction (z)
0.1	22.5693	12.6640	12.5374	0.0999
0.3	11.2273	24.3296	24.0863	0.3001
0.5	5.9215	29.0693	28.7786	0.4928
0.7	2.8020	33.0494	32.7189	0.7001
0.9	0.7668	35.1213	34.7701	0.9006

APPENDIX E

COMPUTER PROGRAMS

E.1 Program for UNIQUAC Interaction Parameters Evaluating

```
DECLARE SUB uniquac (acc!(), ncom%, x!(), comconst() AS ANY, comvalue!(), T!())
DECLARE FUNCTION rconst! (k$)
DECLARE FUNCTION qconst! (k$)
TYPE comgroup
        group AS STRING * 3
        number AS INTEGER
END TYPE

CLS

ncomponent% = 2
r = 8.314
DIM acc(ncomponent%) AS SINGLE
DIM comvalue(ncomponent%)
DIM T(ncomponent%, ncomponent%) AS SINGLE
DIM comconst(ncomponent%, 26) AS comgroup
DIM Pcal(20), O(ncomponent%) AS DOUBLE

'Select system
PRINT "  Select System"
PRINT "    1. 1,2-EthyleneGlycol-Water"
PRINT "    2. 1,3-PropyleneGlycol-Water"
PRINT "    3. 1,4-ButyleneGlycol-Water"
INPUT "  Type System (1,2,3) : ", sysno
        SELECT CASE sysno
        CASE 1
                seca(1) = -.11361
                secb(1) = 311.11
                secc(1) = -1.6684E+08
                secd(1) = 5.918E+21
                sece(1) = -2.474E+24

                vpa(1) = 194.96
                vpb(1) = -14615
                vpc(1) = -25.433
                vpd(1) = 2.014E-05
                vpe(1) = 2
```

```
          comvalue(1) = 1
          comconst(1, 1).group = "05A"
          comconst(1, 1).number = 2

CASE 2
          seca(1) = -.076351
          secb(1) = 259.85
          secc(1) = -1.6097E+08
          secd(1) = 4.2654E+21
          sece(1) = -1.7792E+24

          vpa(1) = 212.8
          vpb(1) = -15420!
          vpc(1) = -28.109
          vpd(1) = 2.1564E-05
          vpe(1) = 2

          comvalue(1) = 3
          comconst(1, 1).group = "01A"
          comconst(1, 1).number = 1
          comconst(1, 2).group = "05A"
          comconst(1, 2).number = 1
          comconst(1, 3).group = "05B"
          comconst(1, 3).number = 1

CASE 3
          seca(1) = -.050576
          secb(1) = 230.69
          secc(1) = -2.0923E+08
          secd(1) = 7.6049E+21
          sece(1) = -3.3116E+24

          vpa(1) = 56.597
          vpb(1) = -9676.2
          vpc(1) = -4.2015
          vpd(1) = 1.4221E-06
          vpe(1) = 2

          comvalue(1) = 2
          comconst(1, 1).group = "05A"
```

```
        comconst(1, 1).number = 2
        comconst(1, 2).group = "01B"
        comconst(1, 2).number = 2

    END SELECT

'Set value for water
    'Bi
    seca(2) = -.02304
    secb(2) = 26.86
    secc(2) = -2.817E+07
    secd(2) = 3.3408E+20
    sece(2) = -1.3837E+23

    'vaper pressure
    vpa(2) = 73.649
    vpb(2) = -7258.2
    vpc(2) = -7.3037
    vpd(2) = 4.1653E-06
    vpe(2) = 2

    comvalue(2) = 1
    comconst(2, 1).group = "06A"
    comconst(2, 1).number = 1

PRINT
'Select temperature
PRINT "  Select Temperature"
PRINT "    1. 371 K"
PRINT "    2. 383 K"
PRINT "    3. 395 K"
INPUT "  Type Temperature (1,2,3) : ", systempno
SELECT CASE systempno
CASE 1
    temp = 371
CASE 2
    temp = 383
CASE 3
    temp = 395
END SELECT
```

```
FOR i% = 1 TO ncomponent%
            B(i%) = (seca(i%) + secb(i%) / temp + secc(i%) / temp ^ 3 + secd(i%) / temp ^ 8 + sece(i%) / temp ^ 9) / 1000
            Psat(i%) = EXP(vpa(i%) + vpb(i%) / temp + vpc(i%) * LOG(temp) + vpd(i%) * temp ^ vpe(i%))
NEXT i%

T(1, 1) = 1
T(2, 2) = 1

INPUT "number of exp. point"; npoint%
FOR i% = 1 TO npoint%
       INPUT "Xexp(1)"; Xexp(i%)
       INPUT "Pexp"; Pi
       Pexp(i%) = Pi * 1000
       PRINT "-------------------------------"
NEXT i%
DIM Xexp(npoint%)
DIM Pexp(npoint%)
T12min = 0
T12max = 3
T21min = 0
T21max = 3
istep% = 10
errormin = 100000000

DO
dT12 = (T12max - T12min) / istep%
dT21 = (T21max - T21min) / istep%

FOR iii% = 0 TO istep%
            T(1, 2) = T12min + iii% * dT12
FOR jjj% = 0 TO istep%
            T(2, 1) = T21min + jjj% * dT21

FOR ii% = 1 TO npoint%
x(2) = Xexp(ii%)
x(1) = 1 - x(2)

CALL uniquac(acc(), ncomponent%, x(), comconst(), comvalue(), T())
```

```
iteri% = 0
DO
    iteri% = iteri% + 1
    Bm = 0
    FOR i% = 1 TO ncomponent%
    FOR j% = 1 TO ncomponent%
        Bij(i%, j%) = SQR(ABS(B(i%) * B(j%))) * (B(i%) + B(j%)) / ABS(B(i%) + B(j%))
        Bm = Bm + y(i%) * y(j%) * Bij(i%, j%)
    NEXT j%
    NEXT i%

    Pcalb = Pcal(ii%)
    FOR i% = 1 TO ncomponent%
        sumyiBij = 0
        FOR j% = 1 TO ncomponent%
            sumyiBij = sumyiBij + y(i%) * Bij(i%, j%)
        NEXT j%

        O(i%) = EXP((2 * sumyiBij - Bm) * Pcal(ii%) / r / temp)
    NEXT i%

    Pcal(ii%) = 0
    FOR i% = 1 TO ncomponent%
        yP(i%) = acc(i%) * x(i%) * Psat(i%) / O(i%)
        Pcal(ii%) = Pcal(ii%) + yP(i%)
    NEXT i%

sumy = 0
FOR i% = 1 TO ncomponent%
    y(i%) = yP(i%) / Pexp(ii%)
    sumy = sumy + y(i%)
NEXT i%
FOR i% = 1 TO ncomponent%
    y(i%) = y(i%) / sumy
NEXT i%
'PRINT Pcal(ii%), Psat(1), Psat(2)

LOOP UNTIL Pcal(ii%) = Pcalb OR iteri% > 1000

NEXT ii%
```

```
sumerror = 0
FOR ii% = 1 TO npoint%
        sumerror = sumerror + SQR((Pcal(ii%) - Pexp(ii%)) ^ 2)
NEXT ii%
sumerror = sumerror / npoint%
IF sumerror < errormin THEN
errormin = sumerror
T12b = T(1, 2)
T21b = T(2, 1)
END IF

PRINT "T12"; T(1, 2), ; "T21"; T(2, 1), errormin
'PRINT hat12b, hat21b, errormin
NEXT jjj%
NEXT iii%

T12min = T12b - dT12
T12max = T12b + dT12
T21min = T21b - dT21
T21max = T21b + dT21

IF T12min < 0 THEN T12min = 0
IF T21min < 0 THEN T21min = 0

LOOP UNTIL T12max = T12min AND T21max = T21min

PRINT T12b, T21b, errormin

FUNCTION qconst (k$)
SELECT CASE k$
CASE "01A"
        qconst = .848
CASE "01B"
        qconst = .54
CASE "01C"
        qconst = .228
CASE "05A"
        qconst = 1.124
CASE "05B"
        qconst = .812
```

```
CASE "06A"
        qconst = 1.4
CASE "08A"
        qconst = .64
END SELECT
END FUNCTION

FUNCTION rconst (k$)
SELECT CASE k$
CASE "01A"
        rconst = .9011
CASE "01B"
        rconst = .6744
CASE "01C"
        rconst = .4469
CASE "05A"
        rconst = 1.2044
CASE "05B"
        rconst = .9769
CASE "06A"
        rconst = .92
CASE "08A"
        rconst = .7713
END SELECT
END FUNCTION

SUB uniquac (acc(), ncom%, x(), comconst() AS comgroup, comvalue(), T())
DIM q(ncom%), r(ncom%), l(ncom%) AS SINGLE
DIM sa(ncom%), fe(ncom%) AS SINGLE
DIM lnaccc(ncom%), lnaccr(ncom%) AS SINGLE
z = 10
sumsa = 0
sumrx = 0
FOR i% = 1 TO ncom%
        q(i%) = 0
        r(i%) = 0
        FOR k% = 1 TO comvalue(i%)
                q(i%) = q(i%) + comconst(i%, k%).number * qconst(comconst(i%, k%).group)
                r(i%) = r(i%) + comconst(i%, k%).number * rconst(comconst(i%, k%).group)
        NEXT k%
```

```
        sumsa = sumsa + q(i%) * x(i%)
        sumrx = sumrx + r(i%) * x(i%)
NEXT i%

FOR i% = 1 TO ncom%
        l(i%) = z / 2 * (r(i%) - q(i%)) - (r(i%) - 1)
        sa(i%) = q(i%) * x(i%) / sumsa
        fe(i%) = r(i%) * x(i%) / sumrx
NEXT i%

FOR i% = 1 TO ncom%

'cal lnaccc(i%)
sumxl = 0
FOR j% = 1 TO ncom%
        sumxl = sumxl + x(j%) * l(j%)
NEXT j%
lnaccc(i%) = LOG(fe(i%) / x(i%)) + z / 2 * q(i%) * LOG(sa(i%) / fe(i%)) + l(i%) - fe(i%) / x(i%) *
sumxl

'cal lnaccr(i%)
sumsaTij = 0
FOR j% = 1 TO ncom%
        sumsaTij = sumsaTij + sa(j%) * T(j%, i%)
NEXT j%

sumfracsaTij = 0
FOR j% = 1 TO ncom%
        sumsaTkj = 0
        FOR k% = 1 TO ncom%
                sumsaTkj = sumsaTkj + sa(k%) * T(k%, j%)
        NEXT k%
sumfracsaTij = sumfracsaTij + sa(j%) * T(i%, j%) / sumsaTkj
NEXT j%

        lnaccr(i%) = q(i%) * (1 - LOG(sumsaTij) - sumfracsaTij)
        acc(i%) = EXP(lnaccc(i%) + lnaccr(i%))
NEXT i%
END SUB
```

E.2 Program for Phase Compositions & Activity Coefficients Estimating by Correlated Wilson Model

```
DECLARE SUB wilson (acc!(), ncomponent%, x!(), hat!())

CLS
PRINT
"========================================================================
======"
PRINT "CALCULATING SIMULATION FOR ACTIVITY COEFFICIENTS OF AQUEOUS
SOLUTION OF GLYCOL"
PRINT "                            BY WILSON EQUATION"
PRINT
"========================================================================
======"
PRINT

'Select system
PRINT "  Select System"
PRINT "    1. 1,2-EthyleneGlcol(1) -Water(2)"
PRINT "    2. 1,2-PropyleneGlcol(1)-Water(2)"
PRINT "    3. 1,4-ButyleneGlcol(1) -Water(2)"
INPUT "  Type System No. (1,2,3) : ", sysno

        SELECT CASE sysno
        CASE 1
                seca(1) = -.11361
                secb(1) = 311.11
                secc(1) = -1.6684E+08
                secd(1) = 5.918E+21
                sece(1) = -2.474E+24
                vpa(1) = 194.96
                vpb(1) = -14615
                vpc(1) = -25.433
                vpd(1) = 2.014E-05
                vpe(1) = 2
        CASE 2
                seca(1) = -.076351
                secb(1) = 259.85
```

```
                secc(1) = -1.6097E+08
                secd(1) = 4.2654E+21
                sece(1) = -1.7792E+24

                vpa(1) = 212.8
                vpb(1) = -15420!
                vpc(1) = -28.109
                vpd(1) = 2.1564E-05
                vpe(1) = 2

        CASE 3
                seca(1) = -.050576
                secb(1) = 230.69
                secc(1) = -2.0923E+08
                secd(1) = 7.6049E+21
                sece(1) = -3.3116E+24

                vpa(1) = 56.597
                vpb(1) = -9676.2
                vpc(1) = -4.2015
                vpd(1) = 1.4221E-06
                vpe(1) = 2
        CASE ELSE
        END SELECT

'Set value for water
        'Bi
        seca(2) = -.02304
        secb(2) = 26.86
        secc(2) = -2.817E+07
        secd(2) = 3.3408E+20
        sece(2) = -1.3837E+23
        'vaper pressure
        vpa(2) = 73.649
        vpb(2) = -7258.2
        vpc(2) = -7.3037
        vpd(2) = 4.1653E-06
        vpe(2) = 2

PRINT
'Select temperature
PRINT "  Select Temperature"
```

```
PRINT "    1. 371.15 K  ( 98 C)"
PRINT "    2. 383.15 K  (110 C)"
PRINT "    3. 395.15 K  (122 C)"
INPUT "  Type Temperature No. (1,2,3) : ", systempno
        SELECT CASE systempno
        CASE 1
                systemp = 371.15

                SELECT CASE sysno
                CASE 1
                        hat(1, 1) = 1
                        hat(1, 2) = .8910639
                        hat(2, 1) = 1.392897
                        hat(2, 2) = 1
                CASE 2
                        hat(1, 1) = 1
                        hat(1, 2) = .679598
                        hat(2, 1) = 1.568164
                        hat(2, 2) = 1
                CASE 3
                        hat(1, 1) = 1
                        hat(1, 2) = .5272951
                        hat(2, 1) = 1.90539
                        hat(2, 2) = 1
                END SELECT

        CASE 2
                systemp = 383.15

                SELECT CASE sysno
                CASE 1
                        hat(1, 1) = 1
                        hat(1, 2) = .7761081
                        hat(2, 1) = 1.583332
                        hat(2, 2) = 1
                CASE 2
                        hat(1, 1) = 1
                        hat(1, 2) = .5726682
                        hat(2, 1) = 1.6730035#
                        hat(2, 2) = 1
```

```
                CASE 3
                        hat(1, 1) = 1
                        hat(1, 2) = .4048714
                        hat(2, 1) = 2.410022
                        hat(2, 2) = 1
                END SELECT

        CASE 3
                systemp = 395.15

                SELECT CASE sysno
                CASE 1
                        hat(1, 1) = 1
                        hat(1, 2) = .6683057
                        hat(2, 1) = 1.781017
                        hat(2, 2) = 1
                CASE 2
                        hat(1, 1) = 1
                        hat(1, 2) = .4524984
                        hat(2, 1) = 1.864681
                        hat(2, 2) = 1
                CASE 3
                        hat(1, 1) = 1
                        hat(1, 2) = .3557532
                        hat(2, 1) = 3.220192
                        hat(2, 2) = 1
                END SELECT

        CASE ELSE
        END SELECT

R = 8.314
ncomponent% = 2
DIM acc(ncomponent%), x(ncomponent%) AS SINGLE

FOR i% = 1 TO ncomponent%
        B(i%) = (seca(i%) + secb(i%) / systemp + secc(i%) / systemp ^ 3 + secd(i%) / systemp ^ 8 +
sece(i%) / systemp ^ 9) / 1000
        Psat(i%) = EXP(vpa(i%) + vpb(i%) / systemp + vpc(i%) * LOG(systemp) + vpd(i%) *
systemp ^ vpe(i%))
```

```
NEXT i%

PRINT
PRINT "  Input Liquid Phase Mole Fraction of Glycol (x1)"
PRINT "    { for exit type x1 > 1 }"

DO

INPUT "  x1"; x(i)
x(1) = x(i)
x(2) = 1 - x(1)

CALL wilson(acc(), ncomponent%, x(), hat())

        DO

        Bm = 0
        FOR i% = 1 TO ncomponent%
        FOR j% = 1 TO ncomponent%
                Bij(i%, j%) = SQR(ABS(B(i%) * B(j%))) * (B(i%) + B(j%)) / ABS(B(i%) + B(j%))
                Bm = Bm + y(i%) * y(j%) * Bij(i%, j%)
        NEXT j%
        NEXT i%

        Pcalb = Pcal
        FOR i% = 1 TO ncomponent%
                sumyiBij = 0
                FOR j% = 1 TO ncomponent%
                        sumyiBij = sumyiBij + y(i%) * Bij(i%, j%)
                NEXT j%

                O(i%) = 1
                'EXP((2 * sumyiBij - Bm) * Pcal / R / systemp)
        NEXT i%

        Pcal = 0
        FOR i% = 1 TO ncomponent%
                yp(i%) = acc(i%) * x(i%) * Psat(i%) / O(i%)
                Pcal = Pcal + yp(i%)
        NEXT i%
```

```
          sumy = 0
          FOR i% = 1 TO ncomponent%
                    y(i%) = yp(i%) / Pcal
                    sumy = sumy + y(i%)
          NEXT i%

          LOOP UNTIL Pcal = Pcalb

PRINT "  Pcal(kPa)", " i    "; " x", " y", " acc"
FOR i% = 1 TO ncomponent%
          y(i%) = y(i%) / sumy
PRINT "   "; Pcal / 1000, i%; "   "; x(i%), y(i%), acc(i%)
NEXT i%

PRINT "  --------------------------------------------------"

LOOP UNTIL x(1) < 0 OR x(1) > 1
PRINT
PRINT "== EXIT =="

SUB wilson (acc(), ncomponent%, x(), hat())

FOR i% = 1 TO ncomponent%
          sumxhatij = 0
          FOR j% = 1 TO ncomponent%
                    sumxhatij = sumxhatij + x(j%) * hat(i%, j%)
          NEXT j%
          sumfrac = 0
          FOR k% = 1 TO ncomponent%
          sumxhatkj = 0
                    FOR j% = 1 TO ncomponent%
                              sumxhatkj = sumxhatkj + x(j%) * hat(k%, j%)
                    NEXT j%
                    sumfrac = sumfrac + x(k%) * hat(k%, i%) / sumxhatkj
          NEXT k%
          acc(i%) = EXP(1 - LOG(sumxhatij) - sumfrac)
NEXT i%

END SUB
```

E.3 Program for Liquid Phase Composition & Activity Coefficients Estimating from Experimental Measured Pressures Using UNIFAC Method

```
DECLARE SUB setcom (ncom%, comvalue!(), comconst() AS ANY)
DECLARE SUB unifac (acc!(), ncom%, x!(), comconst() AS ANY, comvalue!(), temp!)
DECLARE FUNCTION rconst! (k$)
DECLARE FUNCTION qconst! (k$)
DECLARE FUNCTION amn! (m$, n$)
TYPE comgroup
        group AS STRING * 3
        number AS INTEGER
        x AS SINGLE
END TYPE
ncomponent% = 2
R = 8.314
DIM acc(ncomponent%), x(ncomponent%) AS SINGLE
DIM comvalue(ncomponent%)
DIM T(ncomponent%, ncomponent%) AS SINGLE
DIM comconst(ncomponent%, 26) AS comgroup
CLS
PRINT "  ============================================================================="
PRINT "  CALCULATING SIMULATION FOR ACTIVITY COEFFICIENT OF AQUEOUS
SOLUTION OF GLYCOL"
PRINT "  ============================================================================="
PRINT

'Select system
PRINT "  Select System"
PRINT "    1. 1,2-EthyleneGlycol-Water"
PRINT "    2. 1,2-PropyleneGlycol-Water"
PRINT "    3. 1,4-ButyleneGlycol-Water"
INPUT "  Type System (1,2) : ", sysno
        SELECT CASE sysno
        CASE 1
                seca(1) = -.11361
                secb(1) = 311.11
                secc(1) = -1.6684E+08
                secd(1) = 5.918E+21
                sece(1) = -2.474E+24

                vpa(1) = 194.96
```

```
        vpb(1) = -14615
        vpc(1) = -25.433
        vpd(1) = 2.014E-05
        vpe(1) = 2

        comvalue(1) = 1
        comconst(1, 1).group = "05A"
        comconst(1, 1).number = 2

CASE 2
        seca(1) = -.076351
        secb(1) = 259.85
        secc(1) = -1.6097E+08
        secd(1) = 4.2654E+21
        sece(1) = -1.7792E+24

        vpa(1) = 212.8
        vpb(1) = -15420!
        vpc(1) = -28.109
        vpd(1) = 2.1564E-05
        vpe(1) = 2

        comvalue(1) = 3
        comconst(1, 1).group = "01A"
        comconst(1, 1).number = 1
        comconst(1, 2).group = "05A"
        comconst(1, 2).number = 1
        comconst(1, 3).group = "05B"
        comconst(1, 3).number = 1

CASE 3
        seca(1) = -.050576
        secb(1) = 230.69
        secc(1) = -2.0923E+08
        secd(1) = 7.6049E+21
        sece(1) = -3.3116E+24

        vpa(1) = 56.597
        vpb(1) = -9676.2
        vpc(1) = -4.2015
        vpd(1) = 1.4221E-06
        vpe(1) = 2

        comvalue(1) = 2
        comconst(1, 1).group = "05A"
```

```
                comconst(1, 1).number = 2
                comconst(1, 2).group = "01B"
                comconst(1, 2).number = 2

        CASE ELSE
        END SELECT

'Set value for water
        'Bi
        seca(2) = -.02304
        secb(2) = 26.86
        secc(2) = -2.817E+07
        secd(2) = 3.3408E+20
        sece(2) = -1.3837E+23

        'vaper pressure
        vpa(2) = 73.649
        vpb(2) = -7258.2
        vpc(2) = -7.3037
        vpd(2) = 4.1653E-06
        vpe(2) = 2

        comvalue(2) = 1
        comconst(2, 1).group = "06A"
        comconst(2, 1).number = 1

PRINT
'Select temperature
PRINT "  Select Temperature"
PRINT "    1. 371.15 K"
PRINT "    2. 383.15 K"
PRINT "    3. 395.15 K"
INPUT "  Type Temperature (1,2,3) : ", systempno
SELECT CASE systempno
CASE 1
        temp = 371.15
CASE 2
        temp = 383.15
CASE 3
        temp = 395.15
END SELECT

FOR i% = 1 TO ncomponent%
    B(i%) = (seca(i%) + secb(i%) / temp + secc(i%) / temp ^ 3 + secd(i%) / temp ^ 8 + sece(i%) / temp ^ 9) / 1000
```

```
    Psat(i%) = EXP(vpa(i%) + vpb(i%) / temp + vpc(i%) * LOG(temp) + vpd(i%) * temp ^ vpe(i%))
NEXT i%
DO
INPUT "X1 "; x(1)
x(2) = 1 - x(1)
CALL setcom(ncomponent%, comvalue(), comconst())
CALL unifac(acc(), ncomponent%, x(), comconst(), comvalue(), temp)
  DO
        Bm = 0
        FOR i% = 1 TO ncomponent%
        FOR j% = 1 TO ncomponent%
                Bij(i%, j%) = SQR(ABS(B(i%) * B(j%))) * (B(i%) + B(j%)) / ABS(B(i%) + B(j%))
                Bm = Bm + y(i%) * y(j%) * Bij(i%, j%)
        NEXT j%
        NEXT i%

        FOR i% = 1 TO ncomponent%
                sumyiBij = 0
                FOR j% = 1 TO ncomponent%
                        sumyiBij = sumyiBij + y(i%) * Bij(i%, j%)
                NEXT j%
                O(i%) = 1
                        'EXP((2 * sumyiBij - Bm) * Pcal / R / temp)
        NEXT i%
        Pcalb = Pcal
        Pcal = 0
        FOR i% = 1 TO ncomponent%
                yP(i%) = acc(i%) * x(i%) * Psat(i%) / O(i%)
                Pcal = Pcal + yP(i%)
        NEXT i%
        FOR i% = 1 TO ncomponent%
                y(i%) = yP(i%) / Pcal
        NEXT i%
  LOOP UNTIL Pcal = Pcalb
PRINT "Pcal    ", " i   ", "acc    ", "x    ", "y       "
FOR i% = 1 TO ncomponent%
PRINT Pcal, i%, acc(i%), x(i%), y(i%)
NEXT i%
PRINT "---------------------------------------------"
LOOP UNTIL x(1) = 0
FUNCTION amn (m$, n$)
```

```
DIM a(26, 26)
mm% = VAL(LEFT$(m$, 2))
nn% = VAL(LEFT$(n$, 2))
a(1, 1) = 0
a(1, 5) = 931.2
a(1, 6) = 1452
a(1, 8) = 1565
a(5, 1) = 169.7
a(5, 5) = 0
a(5, 6) = -320.8
a(5, 8) = 462.3
a(6, 1) = 657.7
a(6, 5) = 287.5
a(6, 6) = 0
a(8, 1) = 3000
a(8, 8) = 0
amn = a(mm%, nn%)
END FUNCTION

FUNCTION qconst (k$)
SELECT CASE k$
CASE "01A"
        qconst = .848
CASE "01B"
        qconst = .54
CASE "01C"
        qconst = .228
CASE "05A"
        qconst = 1.124
CASE "05B"
        qconst = .812
CASE "06A"
        qconst = 1.4
CASE "08A"
        qconst = .64
END SELECT
END FUNCTION

FUNCTION rconst (k$)
SELECT CASE k$
CASE "01A"
```

```
    rconst = .9011
CASE "01B"
    rconst = .6744
CASE "01C"
    rconst = .4469
CASE "05A"
    rconst = 1.2044
CASE "05B"
    rconst = .9769
CASE "06A"
    rconst = .92
CASE "08A"
    rconst = .7713
END SELECT
END FUNCTION

SUB setcom (ncom%, comvalue(), comconst() AS comgroup)
FOR i% = 1 TO ncom%
    SELECT CASE i%
    CASE 1
        FOR j% = 1 TO comvalue(i%)
          comconst(0, j%).group = comconst(1, j%).group
          comconst(0, j%).number = comconst(1, j%).number
        NEXT j%
        comvalue(0) = comvalue(1)
    CASE ELSE
        FOR j% = 0 TO comvalue(i%)
         IF comconst(0, j%).group = comconst(i%, j%).group THEN
         comconst(0, j%).number = comconst(i%, j%).number + comconst(i%, j%).number
         ELSE
         comvalue(0) = comvalue(0) + 1
         comconst(0, comvalue(0)).group = comconst(i%, j%).group
         comconst(0, comvalue(0)).number = comconst(i%, j%).number
         END IF
        NEXT j%
    END SELECT
NEXT i%
FOR i% = 1 TO ncom%
    sumn = 0
    FOR j% = 1 TO comvalue(i%)
        sumn = sumn + comconst(i%, j%).number
```

```
        NEXT j%
                FOR j% = 1 TO comvalue(i%)
                comconst(i%, j%).x = comconst(i%, j%).number / sumn
        NEXT j%
NEXT i%
END SUB

SUB unifac (acc(), ncom%, x(), comconst() AS comgroup, comvalue(), temp)
DIM q(ncom%), R(ncom%), l(ncom%) AS SINGLE
DIM sa(ncom%), fe(ncom%), sap(26), sam(comvalue(0))  AS SINGLE
DIM lnaccc(ncom%), lnaccr(ncom%), lnTm(comvalue(0)), lnTp(ncom%, 26)  AS SINGLE
z = 10
sumqx = 0
sumrx = 0
FOR i% = 1 TO ncom%
        q(i%) = 0
        R(i%) = 0
        FOR k% = 1 TO comvalue(i%)
                q(i%) = q(i%) + comconst(i%, k%).number * qconst(comconst(i%, k%).group)
                R(i%) = R(i%) + comconst(i%, k%).number * rconst(comconst(i%, k%).group)
        NEXT k%
        sumqx = sumqx + q(i%) * x(i%)
        sumrx = sumrx + R(i%) * x(i%)
NEXT i%
FOR i% = 1 TO ncom%
        l(i%) = z / 2 * (R(i%) - q(i%)) - (R(i%) - 1)
        sa(i%) = q(i%) * x(i%) / sumqx
        fe(i%) = R(i%) * x(i%) / sumrx
NEXT i%
'cal lnaccc(i%)
FOR i% = 1 TO ncom%
        sumxl = 0
        FOR j% = 1 TO ncom%
                sumxl = sumxl + x(j%) * l(j%)
        NEXT j%
lnaccc(i%) = LOG(fe(i%) / x(i%)) + z / 2 * q(i%) * LOG(sa(i%) / fe(i%)) + l(i%) - fe(i%) / x(i%) *
sumxl
NEXT i%
'cal lnaccr(i%)
'in mixture
sumsumvx = 0
```

```
FOR i% = 1 TO ncom%
    FOR j% = 1 TO comvalue(i%)
        sumsumvx = sumsumvx + comconst(i%, j%).number * x(i%)
    NEXT j%
NEXT i%
FOR i% = 1 TO comvalue(0)
    sumvx = 0
    FOR j% = 1 TO ncom%
        FOR k% = 1 TO comvalue(j%)
        IF comconst(j%, k%).group = comconst(0, i%).group THEN sumvx = sumvx + comconst(j%, k%).number * x(j%)
        NEXT k%
    NEXT j%
    comconst(0, i%).x = sumvx / sumsumvx
NEXT i%
sumxqm = 0
FOR i% = 1 TO comvalue(0)
    sumxqm = sumxqm + comconst(0, i%).x * qconst(comconst(0, i%).group)
NEXT i%
FOR i% = 1 TO comvalue(0)
    sam(i%) = comconst(0, i%).x * qconst(comconst(0, i%).group) / sumxqm
NEXT i%
FOR i% = 1 TO comvalue(0)
    sumsamY = 0
    FOR j% = 1 TO comvalue(0)
        sumsamY = sumsamY + sam(j%) * EXP(-amn(comconst(0, j%).group, comconst(0, i%).group) / temp)
    NEXT j%
    sumfracsumsamY = 0
    FOR j% = 1 TO comvalue(0)
        fracsumsamY = 0
        FOR k% = 1 TO comvalue(0)
            fracsumsamY = fracsumsamY + sam(k%) * EXP(-amn(comconst(0, k%).group, comconst(0, j%).group) / temp)
        NEXT k%
        sumfracsumsamY = sumfracsumsamY + sam(j%) * EXP(-amn(comconst(0, i%).group, comconst(0, j%).group) / temp) / fracsumsamY
    NEXT j%
lnTm(i%) = qconst(comconst(0, i%).group) * (1 - LOG(sumsamY) - sumfracsumsamY)
NEXT i%
```

```
'in molacule
FOR i% = 1 TO ncom%
        sumsap = 0
        FOR j% = 1 TO comvalue(i%)
                sumsap = sumsap + comconst(i%, j%).x * qconst(comconst(i%, j%).group)
        NEXT j%
        FOR j% = 1 TO comvalue(i%)
                sap(j%) = comconst(i%, j%).x * qconst(comconst(i%, j%).group) / sumsap
        NEXT j%
        FOR j% = 1 TO comvalue(i%)
                sumsaY = 0
                FOR k% = 1 TO comvalue(i%)
                        sumsaY = sumsaY + sap(k%) * EXP(-amn(comconst(i%, k%).group,
comconst(i%, j%).group) / temp)
                NEXT k%
                sumfracsaY = 0
                FOR k% = 1 TO comvalue(i%)
                        fracsaY = 0
                        FOR kk% = 1 TO comvalue(i%)
                                fracsaY = fracsaY + sap(kk%) * EXP(-amn(comconst(i%,
kk%).group, comconst(i%, k%).group) / temp)
                        NEXT kk%
                        sumfracsaY = sumfracsaY + sap(j%) * EXP(-amn(comconst(i%, k%).group,
comconst(i%, j%).group) / temp) / fracsaY
                NEXT k%
                lnTp(i%, j%) = qconst(comconst(i%, j%).group) * (1 - LOG(sumsaY) - sumfracsaY)
        NEXT j%
        FOR j% = 1 TO comvalue(i%)
                FOR k% = 1 TO comvalue(0)
                IF comconst(i%, j%).group = comconst(0, k%).group THEN lnaccr(i%) = lnaccr(i%)
+ comconst(i%, j%).number * (lnTm(k%) - lnTp(i%, j%))
                NEXT k%
        NEXT j%
NEXT i%
FOR i% = 1 TO ncom%
        acc(i%) = EXP(lnaccc(i%) + lnaccr(i%))
NEXT i%
END SUB
```

APPENDIX F

PROGRAM ESTIMATED DATA

Table F.1 Calculated liquid phase composition of ethylene glycol-water at 98°C by UNIQUAC

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.3	47.5133	0.4767	0.0248	47.5133
0.5	39.6740	0.5581	0.0356	39.6740
0.7	23.3720	0.7381	0.0823	23.3720
0.9	14.0869	0.8498	0.1587	14.0869

Table F.2 Calculated liquid phase composition of ethylene glycol-water at 110°C by UNIQUAC

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.3	79.9634	0.4091	0.0232	79.9634
0.5	70.5669	0.4750	0.0312	70.5669
0.7	49.6754	0.6294	0.0603	49.6754
0.9	21.2037	0.8583	0.1957	21.2037

Table F.3 Calculated liquid phase composition of ethylene glycol-water at 122°C by UNIQUAC

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.3	140.6032	0.2771	0.0143	140.6032
0.5	69.7180	0.6296	0.0755	69.7180
0.7	39.4750	0.8062	0.1731	39.4750
0.9	23.7832	0.9028	0.3225	23.7832

Table F.4 Calculated liquid phase composition of ethylene glycol-water at 98°C by Wilson equation

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.3	47.5133	0.4739	0.0246	47.5133
0.5	39.6740	0.5565	0.0353	39.6740
0.7	23.3720	0.7380	0.0817	23.3720
0.9	14.0869	0.8499	0.1575	14.0869

Table F.5 Calculated liquid phase composition of ethylene glycol-water at 110°C by Wilson equation

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.3	79.9634	0.4181	0.0232	79.9634
0.5	70.5669	0.4822	0.0309	70.5669
0.7	49.6754	0.6312	0.0594	49.6754
0.9	21.2037	0.8551	0.1933	21.2037

Table F.6 Calculated liquid phase composition of ethylene glycol-water at 122°C by Wilson equation

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.3	140.6032	0.3140	0.0166	140.6032
0.5	69.7180	0.6498	0.0767	69.7180
0.7	39.4750	0.8130	0.1728	39.4750
0.9	23.7832	0.9047	0.3208	23.7832

Table F.7 Program estimated data using Virial EOS & UNIQUAC model of ethylene glycol-water at 98^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	2.6612	1.00000	0.77931
0.974	0.026	0.5752	0.4248	4.5067	0.99996	0.78186
0.961	0.039	0.4703	0.5297	5.4378	0.99990	0.78315
0.911	0.089	0.2668	0.7332	9.0726	0.99946	0.78824
0.863	0.137	0.1810	0.8190	12.6464	0.99863	0.79335
0.623	0.377	0.0506	0.9494	32.0135	0.98483	0.82387
0.406	0.594	0.0190	0.9810	52.7104	0.93776	0.86512
0.290	0.710	0.0101	0.9899	65.9200	0.87413	0.89734
0.267	0.733	0.0087	0.9913	68.7977	0.85529	0.90491
0.246	0.754	0.0075	0.9925	71.5132	0.83560	0.91220
0.159	0.841	0.0036	0.9964	83.7521	0.72102	0.94612
0.088	0.912	0.0014	0.9986	94.8861	0.57361	0.97619
0.030	0.970	0.0003	0.9997	104.1169	0.40964	0.99610
1E-07	1.000	0.0000	1.0000	108.3144	0.31269	1.00000

Table F.8 Program estimated data using Virial EOS & UNIQUAC model of ethylene glycol-water at 110^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	4.8917	1.00000	0.73989
0.988	0.012	0.7921	0.2079	6.1192	0.99999	0.74118
0.971	0.029	0.6066	0.3934	7.8296	0.99994	0.74303
0.945	0.055	0.4399	0.5601	10.5027	0.99977	0.74592
0.937	0.063	0.4041	0.5959	11.3329	0.99969	0.74682
0.917	0.083	0.3336	0.6664	13.4246	0.99945	0.74911
0.905	0.095	0.3007	0.6993	14.6911	0.99927	0.75051
0.841	0.159	0.1895	0.8105	21.5969	0.99776	0.75827
0.801	0.199	0.1492	0.8508	26.0517	0.99629	0.76342
0.745	0.255	0.1108	0.8892	32.4865	0.99335	0.77112
0.700	0.300	0.0889	0.9111	37.8419	0.99006	0.77778
0.438	0.562	0.0269	0.9731	73.5362	0.93878	0.82975
0.387	0.613	0.0208	0.9792	81.7707	0.91640	0.84386
0.174	0.826	0.0047	0.9953	124.4420	0.70080	0.92688
1E-07	1.000	0.0000	1.0000	169.3157	0.23992	1.00000

Table F.9 Program estimated data using Virial EOS & UNIQUAC model of ethylene glycol-water at 110^oC

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	8.6090	1.00000	0.67933
0.994	0.006	0.9090	0.0910	9.4141	1.00000	0.68006
0.950	0.050	0.5303	0.4697	15.4117	0.99977	0.68549
0.945	0.055	0.5047	0.4953	16.1040	0.99971	0.68612
0.931	0.069	0.4433	0.5567	18.0544	0.99954	0.68791
0.911	0.089	0.3749	0.6251	20.8714	0.99922	0.69053
0.907	0.093	0.3633	0.6367	21.4406	0.99914	0.69106
0.881	0.119	0.3001	0.6999	25.1717	0.99854	0.69456
0.856	0.144	0.2543	0.7457	28.8240	0.99778	0.69805
0.785	0.215	0.1689	0.8311	39.5717	0.99448	0.70861
0.775	0.225	0.1602	0.8398	41.1335	0.99386	0.71019
0.765	0.235	0.1522	0.8478	42.7080	0.99319	0.71179
0.533	0.467	0.0517	0.9483	83.7200	0.95775	0.75820
0.414	0.586	0.0290	0.9710	109.6281	0.91070	0.79263
0.316	0.684	0.0165	0.9835	135.1339	0.83937	0.83002
0.247	0.753	0.0100	0.9900	156.3847	0.75911	0.86298
1E-07	1.000	0.0000	1.0000	258.6884	0.15174	1.00000

Table F.10 Calculated liquid phase composition of1,4-butylene glycol-water at 98^{o}C by UNIQUAC

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.1	83.1730	0.1157	0.0004	83.1730
0.3	53.0190	0.4229	0.0027	53.0190
0.5	41.1994	0.5437	0.0045	41.1993
0.7	26.8870	0.6947	0.0090	26.8870
0.9	21.3928	0.7548	0.0123	21.3928

Table F.11 Calculated liquid phase composition of1,4-butylene glycol-water at 110^{o}C by UNIQUAC

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.1	120.3351	0.1330	0.0005	120.3351
0.3	81.8575	0.3716	0.0029	81.8574
0.5	66.8729	0.4733	0.0047	66.8729
0.7	62.9266	0.5010	0.0053	62.9266
0.9	37.8082	0.6867	0.0126	37.8082

Table F.12 Calculated liquid phase composition of1,4-butylene glycol-water at 122^{o}C by UNIQUAC

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.1	169.1953	0.1300	0.0005	169.1953
0.3	111.0171	0.3496	0.0036	111.0170
0.5	85.3092	0.4726	0.0069	85.3091
0.7	76.1910	0.5201	0.0086	76.1909
0.9	48.0590	0.6806	0.0287	48.0589

Table F.13 Calculated liquid phase composition of1,4-butylene glycol-water at 98^{o}C by Wilson equation

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.1	83.1730	0.1092	0.0004	83.1730
0.3	53.0190	0.4095	0.0025	53.0191
0.5	41.1994	0.5311	0.0043	41.1994
0.7	26.8870	0.6853	0.0088	26.8870
0.9	21.3928	0.7471	0.0121	21.3928

Table F.14 Calculated liquid phase composition of1,4-butylene glycol-water at 110^{o}C by Wilson equation

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.1	120.3351	0.1424	0.0006	120.3351
0.3	81.8575	0.3810	0.0029	81.8575
0.5	66.8729	0.4792	0.0047	66.8730
0.7	62.9266	0.5060	0.0053	62.9266
0.9	37.8082	0.6867	0.0124	37.8082

Table F.15 Calculated liquid phase composition of1,4-butylene glycol-water at 122^{o}C by Wilson equation

$Z_{1,app}$	P_{exp}	$x_{1,cal}$	$y_{1,cal}$	P_{cal}
0.1	169.1953	0.1573	0.0007	169.1953
0.3	111.0171	0.3758	0.0037	111.0171
0.5	85.3092	0.4881	0.0068	85.3093
0.7	76.1910	0.5315	0.0085	76.1910
0.9	48.0590	0.6806	0.0183	48.0590

Table F.16 Program estimated data by UNIFAC method of ethylene glycol(1)-water(2) at 98°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	2.6430	1.00000	0.91922
0.974	0.026	0.5330	0.4670	4.8298	0.99998	0.92046
0.961	0.039	0.4286	0.5714	5.9254	0.99996	0.92108
0.911	0.089	0.2371	0.7629	10.1531	0.99979	0.92343
0.863	0.137	0.1602	0.8398	14.2319	0.99948	0.92566
0.623	0.377	0.0469	0.9531	34.9374	0.99502	0.93716
0.406	0.594	0.0194	0.9806	54.3005	0.98033	0.95115
0.290	0.710	0.0113	0.9887	65.1365	0.95821	0.96242
0.267	0.733	0.0100	0.9900	67.3472	0.95133	0.96514
0.246	0.754	0.0088	0.9912	69.3871	0.94383	0.96778
0.159	0.841	0.0048	0.9952	78.0722	0.89624	0.98023
0.088	0.912	0.0022	0.9978	85.4024	0.82528	0.99134
0.030	0.970	0.0006	0.9994	91.3514	0.73076	0.99861
1E-09	1.000	0.0000	1.0000	94.2484	0.66380	1.00000

Table F.17 Program estimated data by UNIFAC method of ethylene glycol(1)-water(2) at 110°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	4.8463	1.00000	0.93971
0.988	0.012	0.7478	0.2522	6.0288	1.00000	0.94018
0.971	0.029	0.5465	0.4535	8.6107	0.99998	0.94083
0.945	0.055	0.3818	0.6182	11.9932	0.99994	0.94181
0.937	0.063	0.3483	0.6517	13.0354	0.99992	0.94210
0.917	0.083	0.2840	0.7160	15.6436	0.99986	0.94283
0.905	0.095	0.2548	0.7452	17.2105	0.99981	0.94327
0.841	0.159	0.1592	0.8408	25.5904	0.99946	0.94551
0.801	0.199	0.1257	0.8743	30.8472	0.99915	0.94688
0.745	0.255	0.0943	0.9057	38.2316	0.99857	0.94875
0.700	0.300	0.0766	0.9234	44.1869	0.99796	0.95026
0.438	0.562	0.0264	0.9736	79.3749	0.98903	0.96071
0.387	0.613	0.0214	0.9786	86.3888	0.98478	0.96360
0.333	0.667	0.0168	0.9832	93.9143	0.97818	0.96723
0.174	0.826	0.0067	0.9933	116.9291	0.93079	0.98244
1E-09	1.000	0.0000	1.0000	143.1239	0.72483	1.00000

Table F.18 Program estimated data by UNIFAC method of ethylene glycol(1)-water(2) at 122°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	8.5025	1.00000	0.95904
0.994	0.006	0.8743	0.1257	9.6669	1.00000	0.95922
0.950	0.050	0.4434	0.5566	18.2182	0.99996	0.96047
0.945	0.055	0.4187	0.5813	19.1913	0.99996	0.96061
0.931	0.069	0.3611	0.6389	21.9174	0.99993	0.96098
0.911	0.089	0.3000	0.7000	25.8155	0.99988	0.96151
0.907	0.093	0.2899	0.7101	26.5955	0.99987	0.96161
0.881	0.119	0.2365	0.7635	31.6698	0.99979	0.96226
0.856	0.144	0.1990	0.8010	36.5546	0.99970	0.96285
0.785	0.215	0.1322	0.8678	50.4559	0.99934	0.96442
0.775	0.225	0.1256	0.8744	52.4169	0.99928	0.96463
0.765	0.235	0.2295	0.7705	54.3787	0.99922	0.96483
0.614	0.386	0.0619	0.9381	84.0913	0.99785	0.96775
0.533	0.467	0.0451	0.9549	100.1152	0.99657	0.96941
0.414	0.586	0.0282	0.9718	123.8524	0.99280	0.97263
0.316	0.684	0.0184	0.9816	143.7230	0.98542	0.97671
0.247	0.753	0.0130	0.9870	158.0060	0.97477	0.98081
1E-09	1.000	0.0000	1.0000	211.1683	0.78453	1.00000

Table F.19 Program estimated data by UNIFAC method of propylene glycol (1)-water(2) at 98°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	2.7637	1.01031	1.31236
0.996	0.004	0.8477	0.1523	3.2473	1.01031	1.31223
0.984	0.016	0.5789	0.4211	4.6977	1.01031	1.31181
0.967	0.033	0.3324	0.6676	7.9566	1.01034	1.31066
0.960	0.040	0.3493	0.6507	7.5949	1.01034	1.31080
0.935	0.065	0.2437	0.7563	10.6064	1.01039	1.30949
0.818	0.182	0.0922	0.9078	24.5555	1.01155	1.29958
0.605	0.395	0.0349	0.9651	48.6691	1.02492	1.26176
0.423	0.577	0.0187	0.9813	66.6734	1.07465	1.20317
0.384	0.616	0.0164	0.9836	70.0604	1.09653	1.18691
0.214	0.786	0.0094	0.9906	82.3320	1.32287	1.10095
1E-09	1.000	0.0000	1.0000	94.2484	4.17600	1.00000

Table F.20 Program estimated data by UNIFAC method of propylene glycol (1)-water(2) at 110°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	5.0579	1.01276	1.33736
0.995	0.005	0.84024	0.1598	5.9895	1.01276	1.33711
0.990	0.010	0.72353	0.2765	6.9207	1.01276	1.33685
0.957	0.043	0.37076	0.6292	13.0559	1.01281	1.33487
0.946	0.054	0.31698	0.6830	15.0960	1.01284	1.33410
0.923	0.077	0.24128	0.7587	19.3522	1.01293	1.33233
0.887	0.113	0.17274	0.8273	25.9829	1.01319	1.32904
0.789	0.211	0.0914	0.9086	43.7634	1.01508	1.31671
0.688	0.312	0.05703	0.9430	61.4718	1.02033	1.29810
0.437	0.563	0.02335	0.9766	100.6009	1.07655	1.21932
0.428	0.572	0.02269	0.9773	101.8204	1.08098	1.21551
0.205	0.795	0.01113	0.9889	126.4527	1.38524	1.09897
1E-09	1.000	0.0000	1.0000	143.1239	4.35312	1.00000

Table F.21 Program estimated data by UNIFAC method of propylene glycol (1)-water(2) at 122^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	8.8456	1.0150	1.3607
0.970	0.030	0.4993	0.5007	17.1864	1.0151	1.3585
0.920	0.080	0.2625	0.7375	31.0118	1.0153	1.3539
0.853	0.147	0.1531	0.8469	49.3292	1.0161	1.3458
0.746	0.254	0.0852	0.9148	77.8389	1.0196	1.3276
0.700	0.300	0.0654	0.9346	89.7084	1.0226	1.3176
0.679	0.321	0.0638	0.9362	95.0309	1.0244	1.3125
0.667	0.333	0.0608	0.9392	98.0425	1.0255	1.3095
0.486	0.514	0.0321	0.9679	140.1626	1.0631	1.2499
0.170	0.830	0.0118	0.9882	191.5078	1.5306	1.0797
1E-09	1.000	0.0000	1.0000	211.1683	4.5134	1.0000

Table F.22 Program estimated data by UNIFAC method of1,4-butylene glycol (1)-water(2) at 98^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	0.2829	0.80395	1.24710
0.990	0.010	0.1923	0.8077	1.4566	0.80395	1.24826
0.950	0.050	0.0435	0.9565	6.1715	0.80386	1.25258
0.930	0.070	0.0308	0.9692	8.5397	0.80378	1.25454
0.900	0.100	0.0210	0.9790	12.1034	0.80362	1.25719
0.850	0.150	0.0133	0.9867	18.0645	0.80330	1.26079
0.800	0.200	0.0094	0.9906	24.0376	0.80297	1.26323
0.750	0.250	0.0071	0.9929	30.0022	0.80278	1.26433
0.700	0.300	0.0055	0.9945	35.9339	0.80289	1.26390
0.500	0.500	0.0024	0.9976	58.6771	0.81359	1.24212
0.400	0.600	0.0017	0.9983	68.8384	0.83619	1.21524
0.300	0.700	0.0012	0.9988	77.5751	0.89242	1.17442
0.200	0.800	0.0001	0.9999	84.3783	1.03913	1.11812
1E-09	1.000	0.0000	1.0000	94.2841	4.81184	1.00000

Table F.23 Program estimated data by UNIFAC method of1,4-butylene glycol (1)-water(2) at 110^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	0.5702	0.80809	1.27066
0.990	0.010	0.2367	0.7633	2.3846	0.80809	1.27170
0.950	0.050	0.0560	0.9440	9.6694	0.80794	1.27551
0.930	0.070	0.0398	0.9602	13.3260	0.80781	1.27719
0.900	0.100	0.0273	0.9727	18.8245	0.80776	1.27415
0.850	0.150	0.0173	0.9827	28.0123	0.80756	1.28224
0.800	0.200	0.0123	0.9877	37.2051	0.80736	1.28383
0.750	0.250	0.0092	0.9908	46.3698	0.80733	1.28399
0.700	0.300	0.0072	0.9928	55.4674	0.80769	1.28253
0.500	0.500	0.0032	0.9968	90.1489	0.82061	1.25569
0.400	0.600	0.0023	0.9977	105.4929	0.84581	1.22568
0.300	0.700	0.0016	0.9984	118.5552	0.90712	1.18143
0.200	0.800	0.0012	0.9988	128.5820	1.06524	1.12168
1E-09	1.000	0.0000	1.0000	143.1239	5.03867	1.00000

Table F.24 Program estimated data by UNIFAC method of1,4-butylene glycol (1)-water(2) at 122^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	1.0986	0.81225	1.29258
0.990	0.010	0.2848	0.7152	3.8191	0.81224	1.29350
0.950	0.050	0.0708	0.9292	14.7359	0.81218	1.29681
0.930	0.070	0.0505	0.9495	20.2117	0.81212	1.29823
0.900	0.100	0.0348	0.9652	28.4410	0.81202	1.30003
0.850	0.150	0.0222	0.9778	42.1776	0.81183	1.30210
0.800	0.200	0.0157	0.9843	55.9026	0.81175	1.30285
0.750	0.250	0.0118	0.9882	69.5646	0.81189	1.30211
0.700	0.300	0.0093	0.9907	83.1033	0.81248	1.29966
0.500	0.500	0.0042	0.9958	134.4375	0.82750	1.26797
0.400	0.600	0.0029	0.9971	156.9420	0.85517	1.23503
0.300	0.700	0.0021	0.9979	175.9243	0.92127	1.18761
0.200	0.800	0.0015	0.9985	190.3033	1.09014	1.12475
1E-09	1.000	0.0000	1.0000	211.1683	5.24594	1.00000

Table F.25 Program estimated data by UNIQUAC method of ethylene glycol(1)-water(2) at 98°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	2.6430	1.0000	0.7944
0.974	0.026	0.5671	0.4329	4.5386	0.9999	0.8017
0.961	0.039	0.4617	0.5383	5.4968	0.9997	0.8054
0.911	0.089	0.2591	0.7409	9.2792	0.9985	0.8196
0.863	0.137	0.1744	0.8256	13.0327	0.9964	0.8333
0.623	0.377	0.0475	0.9525	33.6200	0.9692	0.9013
0.406	0.594	0.0181	0.9820	54.4895	0.9165	0.9557
0.290	0.710	0.0102	0.9898	66.1274	0.8775	0.9782
0.267	0.733	0.0090	0.9910	68.4394	0.8691	0.9818
0.246	0.754	0.0079	0.9921	70.5457	0.8613	0.9848
0.159	0.841	0.0044	0.9956	79.1751	0.8290	0.9945
0.088	0.912	0.0022	0.9978	86.0293	0.8048	0.9987
0.030	0.970	0.0007	0.9993	91.4748	0.7900	0.9999
1E-09	1.000	0.0000	1.0000	94.2484	0.7856	1.0000

Table F.26 Program estimated data by UNIQUAC method of ethylene glycol(1)-water(2) at 110^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	4.8463	1.00000	0.81716
0.988	0.012	0.7729	0.2271	6.1947	0.99999	0.81900
0.971	0.029	0.5798	0.4202	8.1156	0.99992	0.82163
0.945	0.055	0.4133	0.5867	11.0780	0.99970	0.82568
0.937	0.063	0.3784	0.6216	11.9954	0.99961	0.82694
0.917	0.083	0.3105	0.6895	14.3020	0.99931	0.83010
0.905	0.095	0.2792	0.7208	15.6946	0.99908	0.83202
0.841	0.159	0.1749	0.8251	23.2350	0.99727	0.84241
0.801	0.199	0.1378	0.8622	28.0476	0.99556	0.84907
0.745	0.255	0.1026	0.8974	34.9200	0.99228	0.85864
0.700	0.300	0.0827	0.9173	40.5612	0.98879	0.86654
0.438	0.562	0.0265	0.9735	75.7670	0.94517	0.91702
0.387	0.613	0.0210	0.9790	83.1453	0.92950	0.92782
0.323	0.677	0.0153	0.9847	92.6701	0.90449	0.94179
0.174	0.826	0.0059	0.9941	115.9324	0.81166	0.97486
1E-09	1.000	0.0000	1.0000	143.1239	0.59120	1.00000

Table F.27 Program estimated data by UNIQUAC method of ethylene glycol(1)-water(2) at 122^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	8.50255	1.00000	0.77408
0.994	0.006	0.8959	0.1041	9.4331	1.00000	0.77476
0.950	0.050	0.4952	0.5048	16.3091	0.99981	0.77978
0.945	0.055	0.4699	0.5301	17.0963	0.99977	0.78036
0.931	0.069	0.4098	0.5902	19.3071	0.99963	0.78200
0.911	0.089	0.3443	0.6557	22.4825	0.99937	0.78438
0.907	0.093	0.3333	0.6667	23.1201	0.99931	0.78486
0.881	0.119	0.2742	0.7258	27.2844	0.99883	0.78803
0.856	0.144	0.2319	0.7681	31.3228	0.99823	0.79115
0.785	0.215	0.1546	0.8454	42.9878	0.99566	0.80047
0.775	0.225	0.1469	0.8531	44.6555	0.99518	0.80184
0.765	0.235	0.1396	0.8604	46.3398	0.99467	0.80323
0.614	0.386	0.0707	0.9293	72.5038	0.98158	0.82663
0.533	0.467	0.0502	0.9498	87.3865	0.96845	0.84163
0.414	0.586	0.0297	0.9703	110.7227	0.93500	0.86817
0.316	0.684	0.0181	0.9819	131.7153	0.88526	0.89544
0.247	0.753	0.0118	0.9882	147.7535	0.82966	0.91825
1E-09	1.000	0.0000	1.0000	211.1683	0.34742	1.00000

Table F.28 Program estimated data by UNIQUAC method of propylene glycol (1)-water(2) at 98^oC

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	2.7355	1.00000	0.79442
0.996	0.004	0.8804	0.1196	3.0948	1.00000	0.98199
0.984	0.016	0.6448	0.3552	4.1747	0.99998	0.98343
0.967	0.033	0.4632	0.5368	5.7100	0.99993	0.98545
0.960	0.040	0.4139	0.5861	6.3440	0.99990	0.98628
0.935	0.065	0.2967	0.7033	8.6168	0.99974	0.98917
0.818	0.182	0.1150	0.8850	19.4141	0.99798	1.00162
0.605	0.395	0.0415	0.9585	39.5393	0.99162	1.01800
0.423	0.577	0.0201	0.9799	56.7576	0.98782	1.02268
0.384	0.616	0.0172	0.9828	60.3880	0.98841	1.02227
0.214	0.786	0.0078	0.9922	75.7292	1.00906	1.01430
1E-09	1.000	0.0000	1.0000	94.2484	1.18584	1.00000

Table F.29 Program estimated data by UNIQUAC method of propylene glycol (1)-water(2) at 110^oC

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	4.9942	1.00000	0.95112
0.995	0.005	0.8795	0.1205	5.6503	1.00000	0.95171
0.990	0.010	0.7839	0.2161	6.3072	0.99999	0.95229
0.957	0.043	0.4482	0.5518	10.6631	0.99989	0.95611
0.946	0.054	0.3897	0.6103	12.1228	0.99982	0.95736
0.923	0.077	0.3034	0.6966	15.1870	0.99963	0.95994
0.887	0.113	0.2212	0.7788	20.0148	0.99920	0.96386
0.789	0.211	0.1179	0.8821	33.3368	0.99723	0.97378
0.688	0.312	0.0722	0.9278	47.2936	0.99405	0.98261
0.437	0.563	0.0260	0.9740	82.4512	0.98362	0.99660
0.428	0.572	0.0251	0.9749	83.7114	0.98328	0.99686
0.205	0.795	0.0088	0.9912	114.6558	0.98018	0.99885
1E-09	1.000	0.0000	1.0000	143.1239	0.94721	1.00000

Table F.30 Program estimated data by UNIQUAC method of propylene glycol (1)-water(2) at 122^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	8.7146	1.00000	0.92560
0.970	0.030	0.5894	0.4106	14.3412	0.99994	0.92952
0.920	0.080	0.3364	0.6636	23.8248	0.99954	0.93593
0.853	0.147	0.2021	0.7979	36.7320	0.99841	0.94422
0.746	0.254	0.1120	0.8880	57.7799	0.99514	0.95663
0.700	0.300	0.0905	0.9095	66.9754	0.99317	0.96158
0.679	0.321	0.0825	0.9175	71.1995	0.99216	0.96376
0.669	0.331	0.0790	0.9210	73.2163	0.99165	0.96478
0.667	0.333	0.0783	0.9217	73.6200	0.99155	0.96498
0.486	0.514	0.0375	0.9625	110.6129	0.97974	0.98086
0.170	0.830	0.0080	0.9920	176.0797	0.94786	0.99661
1E-09	1.000	0.0000	1.0000	211.1683	0.91177	1.00000

Table F.31 Program estimated data by UNIQUAC method of1,4-butylene glycol (1)-water(2) at 98^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.0E-09	1.0000	0.0000	1.0000	94.2484	0.8419	1.0000
0.1327	0.8673	0.0005	0.9995	81.5345	0.8913	0.9970
0.3686	0.6314	0.0021	0.9979	58.3913	0.9392	0.9792
0.5587	0.4413	0.0048	0.9952	39.7457	0.9715	0.9510
0.7162	0.2838	0.0101	0.9899	24.9081	0.9889	0.9219
0.7548	0.2452	0.0123	0.9877	21.3928	0.9919	0.9143
0.8500	0.1500	0.0230	0.9770	12.9528	0.9971	0.8951
0.9000	0.1000	0.0365	0.9635	8.6562	0.9987	0.8849
0.9500	0.0500	0.0750	0.9250	4.4557	0.9997	0.8746
0.9800	0.0200	0.1740	0.8260	1.9818	1.0000	0.8684
1.0000	1.0E-09	1.0000	0.0000	0.3519	1.0000	0.8643

Table F.32 Program estimated data by UNIQUAC method of1,4-butylene glycol (1)water(2) at 110^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.0E-09	1.0000	0.0000	1.0000	143.1239	0.4028	1.0000
0.1213	0.8787	0.0005	0.9995	122.4242	0.7099	0.9726
0.3982	0.6018	0.0033	0.9967	77.8921	0.9162	0.9010
0.4447	0.5553	0.0041	0.9959	70.9670	0.9321	0.8898
0.5281	0.4719	0.0060	0.9940	59.1213	0.9547	0.8699
0.6867	0.3133	0.0126	0.9874	37.8082	0.9826	0.8325
0.7500	0.2500	0.0176	0.9824	29.7895	0.9894	0.8179
0.8500	0.1500	0.0338	0.9662	17.6698	0.9965	0.7952
0.9000	0.1000	0.0535	0.9465	11.8562	0.9985	0.7841
0.9500	0.0500	0.1080	0.8920	6.2026	0.9996	0.7731
0.9800	0.0200	0.2396	0.7604	2.8859	0.9999	0.7666
1.0000	1.0E-09	1.0000	0.0000	0.7056	1.0000	0.7623

Table F.33 Program estimated data by UNIQUAC method of1,4-butylene glycol (1)-water(2) at 122^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.0E-09	1.0000	0.0000	1.0000	211.1683	0.0988	1.0000
0.1202	0.8798	0.0005	0.9995	172.3642	0.4907	0.9273
0.3206	0.6794	0.0030	0.9970	117.6260	0.8181	0.8174
0.5199	0.4801	0.0086	0.9914	76.2344	0.9348	0.7455
0.6266	0.3734	0.0143	0.9857	57.1143	0.9656	0.7140
0.6806	0.3194	0.0187	0.9813	48.0590	0.9764	0.6992
0.7500	0.2500	0.0271	0.9729	36.9650	0.9866	0.6812
0.8500	0.1500	0.0521	0.9479	21.9549	0.9956	0.6570
0.9000	0.1000	0.0818	0.9182	14.8461	0.9981	0.6455
0.9500	0.0500	0.1609	0.8391	7.9827	0.9996	0.6344
0.9800	0.0200	0.3332	0.6668	3.9774	0.9999	0.6279
1.0000	1.0E-09	1.0000	0.0000	1.3526	1.0000	0.6237

Table F.34 Program estimated data by Wilson equation of ethylene glycol(1)-water(2) at 98°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	2.6430	1.0000	0.8006
0.974	0.026	0.5652	0.4348	4.5540	0.9999	0.8088
0.961	0.039	0.4598	0.5402	5.5229	0.9997	0.8117
0.911	0.089	0.2576	0.7424	9.3325	0.9985	0.8260
0.863	0.137	0.1733	0.8267	13.1128	0.9965	0.8395
0.623	0.377	0.0474	0.9526	33.7255	0.9708	0.9042
0.406	0.594	0.0182	0.9818	54.3984	0.9224	0.9540
0.290	0.710	0.0103	0.9897	65.9200	0.8855	0.9750
0.267	0.733	0.0091	0.9909	68.2185	0.8772	0.9785
0.246	0.754	0.0080	0.9920	70.3171	0.8615	0.9919
0.159	0.841	0.0044	0.9956	78.9727	0.8340	0.9919
0.088	0.912	0.0022	0.9978	85.9199	0.8018	0.9974
0.030	0.970	0.0007	0.9993	91.4541	0.7732	0.9997
1E-09	1.000	0.0000	1.0000	94.2484	0.7576	1.0000

Table F.35 Program estimated data by Wilson equation of ethylene glycol(1)-water(2) at 110°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	4.8463	1.00000	0.79007
0.988	0.012	0.7785	0.2215	6.1505	0.99998	0.79328
0.971	0.029	0.5869	0.4131	8.0166	0.99986	0.79785
0.945	0.055	0.4194	0.5806	10.9131	0.99947	0.80486
0.937	0.063	0.3841	0.6159	11.8146	0.99930	0.80703
0.917	0.083	0.3150	0.6850	14.0898	0.99878	0.81244
0.905	0.095	0.2836	0.7164	15.4696	0.99839	0.81569
0.841	0.159	0.1763	0.8237	23.0146	0.99532	0.83307
0.801	0.199	0.1381	0.8619	27.8897	0.99251	0.84394
0.745	0.255	0.1021	0.8979	34.9200	0.98732	0.85913
0.700	0.300	0.0818	0.9182	40.7407	0.98201	0.87126
0.438	0.562	0.0254	0.9746	77.4155	0.92745	0.93798
0.387	0.613	0.0201	0.9799	85.0163	0.91141	0.94953
0.333	0.667	0.0147	0.9853	94.6955	0.88843	0.96295
0.174	0.826	0.0059	0.9941	117.4748	0.82176	0.98783
1E-09	1.000	0.0000	1.0000	143.1239	0.71902	1.00000

Table F.36 Program estimated data by Wilson equation of ethylene glycol(1)-water(2) at 122°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	8.5025	1.0000	0.78232
0.994	0.006	0.8948	0.1052	9.4446	1.0000	0.7838
0.950	0.050	0.4903	0.5097	16.4688	0.9996	0.7951
0.945	0.055	0.4647	0.5353	17.2800	0.9995	0.7964
0.931	0.069	0.4043	0.5957	19.5656	0.9992	0.8000
0.911	0.089	0.3383	0.6617	22.8673	0.9986	0.8052
0.907	0.093	0.3272	0.6728	23.5329	0.9985	0.8062
0.881	0.119	0.2678	0.7322	27.9014	0.9975	0.8130
0.856	0.144	0.2254	0.7746	32.1718	0.9963	0.8195
0.785	0.215	0.1484	0.8516	44.6779	0.9914	0.8383
0.775	0.225	0.1404	0.8596	46.4846	0.9905	0.8410
0.765	0.235	0.1333	0.8667	48.3026	0.9895	0.8437
0.614	0.386	0.0656	0.9344	77.1187	0.9687	0.8841
0.533	0.467	0.0461	0.9539	93.6086	0.9516	0.9055
0.414	0.586	0.0271	0.9729	119.0222	0.9172	0.9357
0.316	0.684	0.0168	0.9832	140.8136	0.8794	0.9585
0.247	0.753	0.0114	0.9886	156.4517	0.8470	0.9727
1.0E-09	1.000	0.0000	1.0000	211.1682	0.6852	1.0000

Table F.37 Program estimated data by Wilson equation of propylene glycol (1)-water(2) at 98°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	2.7355	1.00000	0.87853
0.996	0.004	0.8915	0.1085	3.0560	1.00000	0.87919
0.984	0.016	0.6695	0.3305	4.0204	0.99998	0.88115
0.967	0.033	0.4903	0.5097	5.3942	0.99990	0.88394
0.960	0.040	0.4404	0.5596	5.9624	0.99985	0.88508
0.935	0.065	0.3194	0.6806	8.0039	0.99959	0.88917
0.818	0.182	0.1252	0.8748	17.8087	0.99659	0.90821
0.605	0.395	0.0443	0.9557	36.6800	0.98185	0.94163
0.423	0.577	0.0206	0.9794	53.7104	0.95692	0.96730
0.384	0.616	0.0174	0.9826	57.4423	0.94976	0.97223
0.214	0.786	0.0072	0.9928	73.8801	0.90950	0.99012
1E-09	1.000	0.0000	1.0000	94.2484	0.83368	1.00000

Table F.38 Program estimated data by Wilson equation of propylene glycol (1)-water(2) at 110°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	4.9942	1.00000	0.91641
0.995	0.005	0.8833	0.1167	5.6254	1.00000	0.91702
0.990	0.010	0.7901	0.2099	6.2576	0.99999	0.91763
0.957	0.043	0.4573	0.5427	10.4508	0.99988	0.92161
0.946	0.054	0.3984	0.6016	11.8567	0.99980	0.92294
0.923	0.077	0.3111	0.6889	14.8094	0.99959	0.92570
0.887	0.113	0.2274	0.7726	19.4665	0.99911	0.92998
0.789	0.211	0.1214	0.8786	32.3580	0.99674	0.94143
0.688	0.312	0.0743	0.9258	45.9563	0.99250	0.95278
0.437	0.563	0.0262	0.9738	80.9154	0.97231	0.97784
0.428	0.572	0.0253	0.9748	82.1933	0.97129	0.97863
0.205	0.795	0.0084	0.9916	114.1017	0.93786	0.99436
1E-09	1.000	0.0000	1.0000	143.1239	0.89087	1.00000

Table F.39 Program estimated data by Wilson equation of propylene glycol (1)-water(2) at 122^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1.000	1E-09	1.0000	0.0000	8.7146	1.00000	0.92720
0.970	0.030	0.5890	0.4110	14.3497	0.99994	0.93086
0.920	0.080	0.3361	0.6639	23.8409	0.99956	0.93687
0.853	0.147	0.2020	0.7980	36.7485	0.99849	0.94473
0.746	0.254	0.1120	0.8880	57.7851	0.99534	0.95670
0.700	0.300	0.0905	0.9095	66.9764	0.99340	0.96158
0.679	0.321	0.0825	0.9175	71.1995	0.99239	0.96374
0.669	0.331	0.0790	0.9210	73.2162	0.99189	0.96476
0.667	0.333	0.0780	0.9220	73.6200	0.99178	0.96496
0.486	0.514	0.0375	0.9625	110.6704	0.97951	0.98140
0.170	0.830	0.0080	0.9921	.176.3616	0.94647	0.99823
1E-09	1.000	0.0000	1.0000	211.1683	0.93080	1.00000

Table F.40 Program estimated data by Wilson equation of1,4-butylene glycol (1)-water(2) at 98^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1E-09	1.000	0.0000	1.0000	94.2484	0.7669	1.0000
0.133	0.867	0.0005	0.9995	81.2656	0.8415	0.9937
0.369	0.631	0.0021	0.9979	57.3850	0.9296	0.9623
0.559	0.441	0.0049	0.9951	38.7902	0.9701	0.9281
0.716	0.284	0.0103	0.9897	24.2550	0.9889	0.8975
0.755	0.245	0.0127	0.9873	20.8288	0.9919	0.8899
0.850	0.150	0.0236	0.9764	12.6143	0.9972	0.8712
0.900	0.100	0.0375	0.9625	8.4347	0.9988	0.8614
0.950	0.050	0.0769	0.9231	4.3476	0.9997	0.8517
0.980	0.020	0.1778	0.8222	1.9393	1.0000	0.8458
1.000	1E-09	1.0000	0.0000	0.3519	1.0000	0.8420

Table F.41 Program estimated data by Wilson equation of1,4-butylene glycol (1)-water(2) at 110^{o}C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1E-09	1.000	0.0000	1.0000	143.1239	0.6030	1.0000
0.121	0.879	0.0005	0.9995	124.4250	0.7243	0.9889
0.398	0.602	0.0032	0.9968	79.5868	0.8996	0.9211
0.445	0.555	0.0040	0.9960	72.4197	0.9180	0.9076
0.528	0.472	0.0059	0.9941	59.9955	0.9450	0.8831
0.687	0.313	0.0125	0.9875	38.0008	0.9789	0.8369
0.750	0.250	0.0175	0.9825	29.8253	0.9872	0.8189
0.850	0.150	0.0340	0.9660	17.5886	0.9958	0.7915
0.900	0.100	0.0539	0.9461	11.7708	0.9982	0.7781
0.950	0.050	0.1090	0.8910	6.1453	0.9996	0.7651
0.980	0.020	0.2418	0.7582	2.8596	0.9999	0.7574
1.000	1E-09	1.0000	0.0000	0.7056	1.0000	0.7524

Table F.42 Program estimated data by Wilson equation of1,4-butylene glycol (1)-water(2) at 122°C

x_1	x_2	y_1	y_2	P (kPa)	γ_1	γ_2
1E-09	1.000	0.0000	1.0000	211.1683	0.3052	1.0000
0.120	0.880	0.0005	0.9995	180.4266	0.5080	0.9707
0.321	0.679	0.0026	0.9974	125.3959	0.7615	0.8717
0.520	0.480	0.0081	0.9919	78.9557	0.9046	0.7725
0.627	0.373	0.0140	0.9860	57.9770	0.9486	0.7251
0.681	0.319	0.0184	0.9816	48.2861	0.9450	0.7027
0.750	0.250	0.0271	0.9729	36.6622	0.9798	0.6756
0.850	0.150	0.0534	0.9466	21.4005	0.9934	0.6396
0.900	0.100	0.0845	0.9155	14.3648	0.9975	0.6228
0.950	0.050	0.1670	0.8330	7.6903	0.9993	0.6067
0.980	0.020	0.3444	0.6556	3.8487	0.9999	0.5975
1.000	1E-09	1.0000	0.0000	1.3526	1.0000	0.5914

VITA

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