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นางสาวจันจิรา หงส์รพิพัฒน์

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LIQUID-LIQUID EQUILIBRIA OF 1-HEXANOL-ETHANOL-WATER, 1-OCTANOL-ETHANOL-WATER, AND 1-DECANOL-ETHANOL-WATER

Miss Janjira Hongrapiput

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ข้อมูลสมดุลจากงานวิจัยนำมาฟิตด้วยโมเดล UNIQUAC พบว่าโมเดล UNIQUAC สามารถฟิตข้อมูลสมดุลของทุกระบบที่ศึกษาได้ดี ค่าพารามิเตอร์ของโมเดล UNIQUAC สัมพันธ์กับอุณหภูมิแบบเชิงเส้นและขึ้นกับน้ำหนักโมเลกุลของสารสกัด (เฮกซานอล, ออกทานอล และเดคานอล) ทั้งนี้เฮกซานอล, ออกทานอลและเดคานอลสามารถนำมาใช้เป็นสารสกัดเอทานอลจากสารละลายน้ำได้ดี เนื่องจากให้ค่าสัมประสิทธิ์ของการกระจายและค่าการเลือกมากกว่า 1

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สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา

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JANJIRA HONGRAPIPUT : LIQUID-LIQUID EQUILIBRIA OF 1-HEXANOL-ETHANOL-WATER, 1-OCTANOL-ETHANOL-WATER, 1-DECANOL-ETHANOL-WATER. THESIS ADVISOR : ASSOC. PROF. KROEKCHAI SUKANJANAJTEE, Ph.D., 140 pp. ISBN 974-03-1315-9.

Ternary liquid-liquid equilibria of 1-hexanol-ethanol-water, 1-octanol-ethanol-water, and 1-decanol-ethanol-water were studied in this research work at the temperature of 30, 40, 50, and 60°C. The apparatus was designed in this work for the liquid-liquid equilibrium analysis.

The liquid-liquid equilibrium data were fitted nicely with the UNIQUAC model. The UNIQUAC binary interaction parameters are linear function with temperature and dependent on molecular weight of solvent used (1-hexanol, 1-octanol, and 1-decanol). 1-hexanol, 1-octanol, and 1-decanol can be used as a good extractant for ethanol from aqueous solution, owing to the distribution coefficients were greater than 1 and the relative selectivity were much greater than 1.

Department Chemical Engineering Student's signature
Field of study Chemical Engineering Advisor's signature
Academic year 2001 Co-advisor's signature

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NOMENCLATURES

a	activity
a_{ij}	UNIQUAC binary interaction parameter
a_{mn}	group interaction parameter
f	fugacity
	partial fugacity
G	total Gibbs free energy
K_D	distribution coefficient of ethanol
K_{Di}	distribution coefficient for each species i
K_{Dj}	distribution coefficient for each species j
n_D	refractive index
P	pressure
Q	group area parameter
R	group volume parameter
RS	relative selectivity of ethanol over water
RS_{ij}	relative selectivity for any species i compared to another species j
S	entropy
T	temperature
u	energy of interaction between groups
V	volume
X	mole fraction of group
x	mole fraction
z	lattice coordination number

Subscripts

i	i th phase
j	j th phase
k, m, n	group type

Superscripts

I, II, N	phase type
C	combinatorial contribution
R	residual contribution

Greek letters

μ	chemical potential
ϕ	fugacity coefficient
	partial fugacity coefficient
γ	activity coefficient
θ, Θ	area fraction
Φ	segment fraction
τ	UNIQUAC binary interaction parameter
ψ	group interaction parameter

CHAPTER I

INTRODUCTION

Ethanol is produced from the fermentation of some local agricultural produce. The current fermentation step produces only a dilute aqueous concentration of ethanol due to end product inhibition. In order to concentrate the ethanol, traditional distillation processes are frequently used by the concept of boiling point or vapor pressure differences. But distillation process consumes relatively large amount of energy.

The liquid-liquid extraction process is primarily used when separation by distillation is ineffective, very difficult or, too expensive. The importance of liquid-liquid extraction in separation technology has increased steadily. This process separates the components based on the differences in chemical structure. Liquid-liquid extraction is now widely used in industries for removing or recovering valuable organic materials. There is advantage for removing ethanol from aqueous solutions because of its flexibility and it gains an important reduction of energy consumption in the overall process. The efficiency of extraction can be developed by using the appropriate extractant and more efficient-extraction operation. A variety of solvents are used as extractants. Such as alcohol, eater, amine, amide, ketone, hydrocarbon, etc.

There were many researches concerning the liquid-liquid extraction of ethanol from aqueous solutions. Several organic solvents were examined as potential separating agents such as normal alkanes from n-hexane (C_6) to n-hexadecane (C_{16})

(Roddy and Cloeman, 1981); 2-ethylhexanol (Ruiz, Gomis, and Botella, 1987); dichloromethane (Ruiz et al., 1988); amyl acetate, benzyl alcohol, and methyl isobutyl ketone (Solimo, 1989); phenolic (Arenson, Kertes, and King, 1990); oleic acid (Zhang, and Hill, 1991); diisopropyl ether (Letcher, Ravindran, and Radloff, 1992); a methyl substituted benzene (Letcher and Siswana, 1992); ethyl acetate and buthyl acetate (Arce, Alonso, and Vidal, 1999); isoamyl acetate, isooctyl alcohol, and n-butyl acetate (Koullas, Umealu, and Koukios, 1999); and 1-pentanol (Fernandez et al., 1999).

Roddy (1981) studied the distribution coefficient measurements for ethanol and water in several organic solvents. For the classes of compounds studied, the order of extractability of ethanol was alcohol = phosphate > ester > amine > ketone > ether > halocarbon = hydrocarbon.

In liquid-liquid extraction of ethanol, the equilibrium condition between the solvent and aqueous phases is very important for process calculation designed. The activity coefficients can be correlated with or without the experimental equilibrium data. The correlating models, the universal quasi-chemical equation (UNIQUAC) (Abrams and Praunitz, 1975), gives very satisfactory correlation of several experimental liquid-liquid systems. The predicting model, UNIFAC (UNIQUAC Functional group Activity Coefficients) (Fredenslund, Jones, and Prausnitz, 1975) also gives good result.

The objective of the present work was to experimentally determine three ternary liquid-liquid equilibria systems : (i) 1-hexanol-ethanol-water, (ii) 1-octanol-ethanol-water, and (iii) 1-decanol-ethanol-water at several temperatures and to test the capability of the various activity coefficient models to correlate these data. The experimental data were measured at 30, 40, 50, and 60°C and regressed by the UNIQUAC model. The resulted liquid-liquid equilibrium data were useful for indicating the dependent of liquid-liquid equilibrium on molecular size of straight chain alcohols.

CHAPTER II

THEORY

2.1 Liquid-Liquid Extraction

2.1.1 Liquid-Liquid Extraction process

Liquid-liquid extraction process is a mass transfer operation where a liquid solution (the feed) is contacted with an immiscible liquid (the extractant or solvent) in order to extract a desired component (the solute). The results are two output streams, the extract and raffinate. The extract is rich in solvent containing the desired solute and the raffinate is residual feed solution minus the extracted solute.

The process takes advantage of the different relative solubilities of solutes in immiscible feed and solvent. The solute dissolves more readily and becomes more concentrated in the solvent in which it has higher solubility.

2.1.2 The Extractant or Solvent

Important factors to consider suitable extractant for extraction are:

- Immissible with the liquid solution to be extracted.
- Dissolves the solute to be extracted.
- Does not dissolve impurities.
- High capacity for the solute.
- High selectivity for the solute over the feed solution.

- Volatile.
- Not toxic and not flammable.

2.2 Liquid-Liquid Equilibria

2.2.1 Introduction

The proper design of solvent extraction processes depends crucially upon an accurate knowledge of the relevant liquid-liquid equilibria. The latter must be either measured or predicted. This work is concerned with methods for the correlation of experimentally determined liquid-liquid equilibria and with methods for the prediction of unknown equilibria.

2.2.2 The Phase Rule

In an equilibrium system of two phases, the important intensive variables affecting the equilibrium of a solute are temperature, pressure and concentration. The phase rule provides a means of determining the number of intensive variables that can be independently varied (within limits) without changing the state of the system. The equilibrium between two phases in a given situation is restricted by the phase rule:

$$F = C - N + 2 \tag{2.1}$$

Where F is the number of intensive variables or degrees of freedom of the system, C the number of total components in the two phases, and N the number of phases at equilibrium.

The important assumptions in the derivation of this relation are that no chemical reactions occuring and the interfaces between phases are plane.

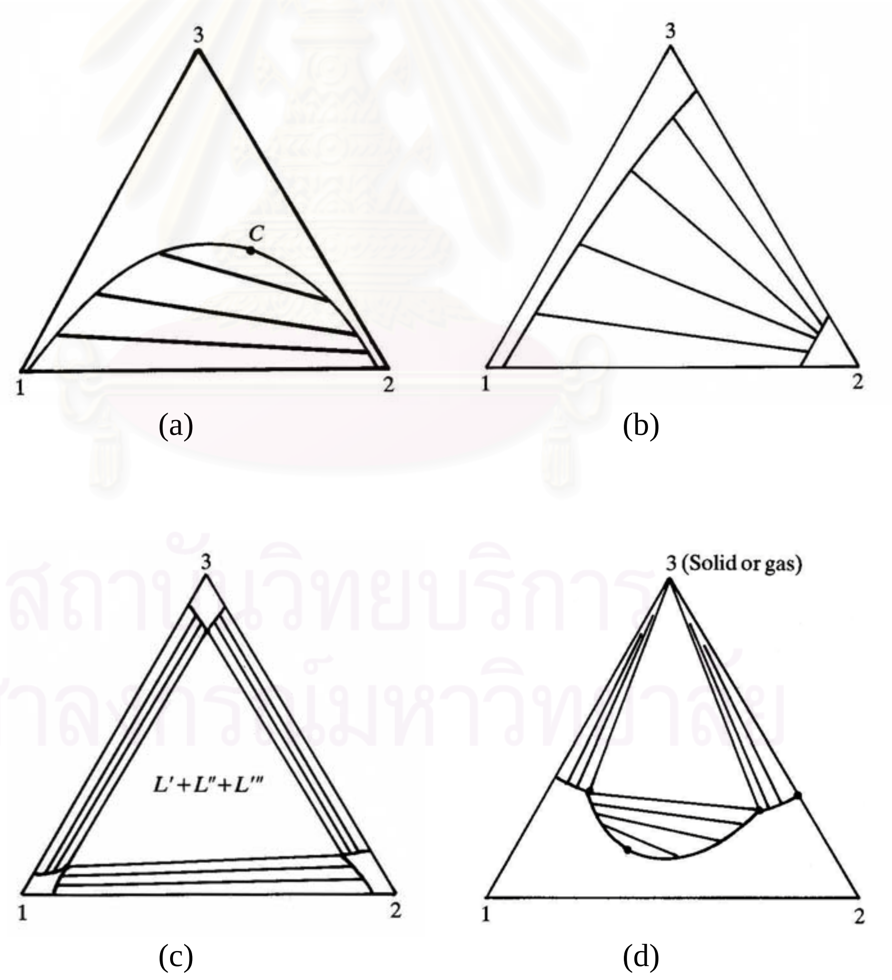
Generally in ternary liquid-liquid system we have three components and two phases in equilibrium. From phase rule equation (2.1), the number of degrees of freedom is 3. The variables are temperature, pressure, and four concentrations. Four concentrations occur because only two of the three mass fraction concentrations in a phase can be specified. The third must make the total mass or mole fractions total to 1.0. If pressure and temperature are set, which is the usual case at equilibrium, setting one concentration in either phase fixes the system.

2.2.3 Phase Diagrams

The graphical representation of phase equilibria is facilitated by application of the phase rule. Thus, in a ternary liquid-liquid system, the degrees of freedom is 3 (F = 3) and the plane representation is only possible if two intensive variables are fixed-usually pressure and temperature. Ternary phase diagrams are often plotted on a Gibbs equilateral triangle where the pure components are represented by the vertices, the binary mixtures by the edges, and ternary mixture by points within the triangle.

A typical isothermal, isobaric phase diagram for a ternary mixture in which only one of the binary pairs is partially miscible is shown in Figure 2.1(a). This is known as a Type I system. The two branches of the phase boundary (the binodal curve) meet at the critical point C, which is also known as the plait point. Compositions of the liquid phases in equilibrium are connected by tie lines that are not horizontal in general. Type II and Type III systems also exist, in which there are two and three partially miscible binary pairs, respectively, as shown in Figure 2.1(b), (c). In the Type III system a three-phase region (L′+L″+L‴) exists for which the system is invariant ($F = 0$). The compositions of the three equilibrium phases are represented by three isolated points connected by a tie triangle. Both the type II and Type III systems can be considered to be formed by the merging of two or three Type I systems.

Ternary liquid-liquid regions can also be generated from a completely miscible binary system by contacting with a soluble solid (salting out) or a gas above its critical temperature (supercritical extraction). A typical phase diagram is shown in Figure 2.1(d) which is sometimes known as a Type IV system.

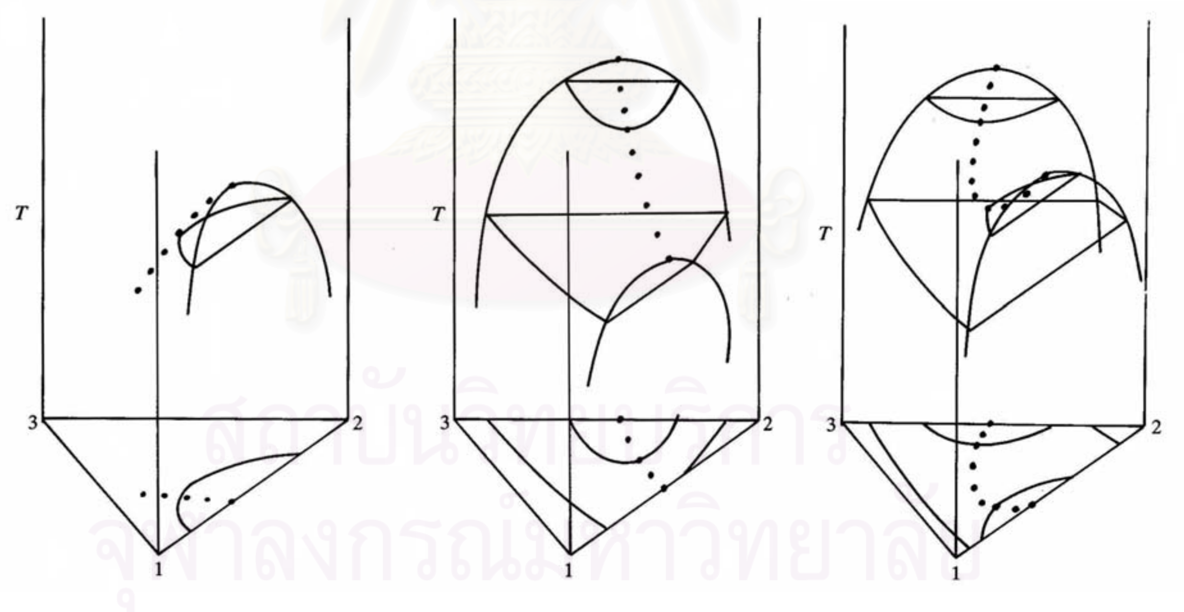


(a) (b)

(c) (d)

Figure 2.1 Ternary liquid-liquid systems. (a) Type I, (b) Type II, (c) Type III, and (d) Type IV.

The temperature dependence of these equilibria can be represented by plotting the temperature on the vertical axis of a triangular prism. Such a diagram is shown in Figure 2.2(a) for a Type I system. Also shown is the projection of an isothermal section and of the monotonic critical curve on the base plane of the prism. Systems having critical curves with maxima (or minima) also exist and these have closed phase boundaries in the ternary region over part of the temperature range. Figure 2.2(b) shows how a Type I binodal curve can intersect a binary face of the prism to generate a Type II system, and Figure 2.2(c) shows the merging of type I binodal curves to give a Type II system. In the former case the critical curve is monotonic and in the latter it has a minimum corresponding to the merging of two plait points.



(a) (b) (c)

Figure 2.2 Temperature dependence of ternary liquid-liquid equilibria, where • • • critical curve.

2.2.4 Thermodynamics of Equilibrium

2.2.4.1 Conditions of Equilibrium

The condition of phase equilibrium is that no driving force exist between phases to change properties of each phase. Thus, the criteria for equilibrium require that the temperature, pressure, and chemical potential of each component are uniform throughout the system.

The conditions for liquid-liquid equilibrium in a heterogeneous system comprising *N* phases and *C* components may be written as follows.

$$T^{\mathrm{I}} = T^{\mathrm{II}} = \ldots = T^{\mathrm{N}} \tag{2.2}$$

$$P^{\mathrm{I}} = P^{\mathrm{II}} = \ldots = P^{\mathrm{N}} \tag{2.3}$$

$$\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{II}} = \ldots = \mu_i^{\mathrm{N}} \qquad ; i = 1, 2, \ldots, C \tag{2.4}$$

The chemical potential (μ_i) of component *i* is related to the total Gibbs free energy G^α of any phase α by equation (2.5).

$$\mu_i^\alpha = (\partial G^\alpha / \partial n_i^\alpha)_{T, P, n_j^\alpha} \tag{2.5}$$

An alternative, thermodynamically equivalent, and sometimes more useful criterion for equilibrium is that at constant temperature and pressure the total Gibbs free energy of the entire system is at a minimum.

$$d\left(\sum_{\alpha=1}^{\phi} G^{\alpha}\right)_{T,P} = 0 \tag{2.6}$$

2.2.4.2 Fugacity and Fugacity Coefficient

The concept of fugacity arises from a consideration of the change in Gibbs energy (G). The Gibbs energy is particular importance in classical thermodynamics because of its unique relation to temperature and pressure through the equation (2.7).

$$dG = -SdT + VdP \tag{2.7}$$

Applied to one mole of a single-phase pure fluid i, this equation becomes the equation (2.8).

$$dG_i = -S_i\, dT + V_i\, dP \tag{2.8}$$

and restriction to constant T gives,

$$dG_i = V_i\, dP \qquad \text{(constant } T\text{)} \tag{2.9}$$

For an ideal gas, $V_i = RT/P$. Thus,

$$dG_i = (RT/P)\, dP \qquad \text{(constant } T\text{)} \tag{2.10}$$

or

$$dG_i = RT\, d\ln P \qquad \text{(constant } T\text{)} \tag{2.11}$$

Equation (2.11) provides an expression for the effect of pressure on the Gibbs energy of an ideal gas. Although valid only for an ideal gas, the simplicity of form of the equation suggests that it would be convenient to replace the pressure P by a new function, which by definition makes the equation universally valid. Thus,

$$dG_i = RT\, d \ln f_i \qquad \text{(constant } T\text{)} \tag{2.12}$$

where f_i, called the *fugacity* of pure fluid i, is a property of i with dimensions of pressure.

In view of the following auxiliary conditions, the fugacity of pure fluid i reduce to the pressure at low values.

$$\lim_{P\to 0} (f_i/P) = \lim_{P\to 0} \phi_i = 1 \tag{2.13}$$

where ϕ_i is called *fugacity coefficient* of pure fluid i.

$$\phi_i \equiv f_i/P \tag{2.14}$$

Definitions analogous to that for a pure material can be made for a *solution* and for a *component in solution*. For a solution, one merely deletes the subscript i on f and ϕ.

$$dG = RT\, d \ln f \qquad \text{(constant } T\text{)} \tag{2.15}$$

$$\lim_{P\to 0} (f/P) = \lim_{P\to 0} \phi = 1 \tag{2.16}$$

$$\phi \equiv f/P \tag{2.17}$$

For a component i in solution, the $\hat{f}_i$ is called *partial fugacity* and the $\hat{\phi}_i$ is called *partial fugacity coefficient*.

$$d\bar{G}_i = RT\, d \ln \hat{f}_i \qquad \text{(constant } T\text{)} \tag{2.18}$$

$$\lim_{P\to 0} (\hat{f}_i / x_i P) = \lim_{P\to 0} \hat{\phi}_i = 1 \tag{2.19}$$

$$\hat{\phi}_i \equiv \hat{f}_i / x_i P \tag{2.20}$$

2.2.4.3 Equality of Fugacities as a Criterion of Phase Equilibrium

In section 2.2.4.1 shown that the criterion for phase equilibrium for PVT systems of uniform *T* and *P* could be concisely states by equality of the chemical potentials as equation (2.4).

$$\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{II}} = \ldots = \mu_i^{\mathrm{N}} \qquad ; i = 1, 2, \ldots, C \tag{2.4}$$

This equation holds for each component *i* of an *C*-component system containing *N* phases at equilibrium. The relationship between the fugacity $\hat{f}_i$ and the chemical potential μ_i expressed in the definition in equation (2.18) allows to derive an alternative criterion for phase equilibrium which is often of greater practical utility than equation (2.4).

Applied the equation (2.21) to each component *i* in each phase α.

$$\mu_i^{\alpha}(\text{final}) - \mu_i^{\alpha}(\text{initial}) = \text{RT} \ln \frac{\hat{f}_i^{\alpha}(final)}{\hat{f}_i^{\alpha}(initial)} \tag{2.21}$$

Since equation (2.21) is valid both for changes in composition and for changes in physical state, we can without loss of generality let the “initial” state be the same for all phases, namely that of component *i* as its exists in the *N*th phases at equilibrium conditions. Thus, for $i = 1, 2, \ldots, C$.

$$\mu_i^{\alpha}(\text{initial}) = \mu_i^{\mathrm{N}}$$

$$\hat{f}_i^{\alpha}(\text{initial}) = \hat{f}_i^{N}$$

and equation (2.21) yields the following equations for μ_i in each of the phases I through N-1.

$$\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{N}} + RT \ln (\hat{f}_i^{I} / \hat{f}_i^{N})$$

$$\mu_i^{\mathrm{II}} = \mu_i^{\mathrm{N}} + RT \ln (\hat{f}_i^{II} / \hat{f}_i^{N})$$

$$\begin{array}{ll} . & . \\ . & . \\ . & . \end{array}$$

$$\mu_i^{\mathrm{N-1}} = \mu_i^{\mathrm{N}} + RT \ln (\hat{f}_i^{N-1} / \hat{f}_i^{N})$$

Substitution of these equations in equation (2.4) and rearrangement gives.

$$\ln (\hat{f}_i^{I} / \hat{f}_i^{N}) = \ln (\hat{f}_i^{II} / \hat{f}_i^{N}) = \ldots = \ln (\hat{f}_i^{N-1} / \hat{f}_i^{N}) = 0$$

from which we obtain

$$\hat{f}_i^{I} = \hat{f}_i^{II} = \ldots = \hat{f}_i^{N} \quad ; i = 1, 2, \ldots, C \qquad (2.22)$$

Thus the fugacity $\hat{f}_i$ of a component in a multicomponent, multiphase system must be the same in all phases in which it is present at equilibrium.

2.2.4.4 Activity and activity coefficient

Certain choices of reference or standard states have been found convenient and are widely accepted. The fugacity are especially important because of the relation of fugacity to Gibbs energy. For a process from state 1 to state 2,

$$\Delta G = G_2 - G_1 = RT (\ln f_2 - \ln f_1)$$

$$= RT \Delta \ln f = RT \ln (f_2/f_1) \qquad (2.23)$$

In terms of a standard state, designated by a superscript *0*, for a pure substance,

$$G \;=\; G^0 + RT \ln (f/f^{\,0}) \tag{2.24}$$

And for a component of a mixture

$$\bar{G}_i \;=\; G_i^0 + RT \ln (\hat{f}_i / f_i^0) \;=\; G_i^0 + RT \ln a_i \tag{2.25}$$

where a_i is called *relative fugacity* or *activity*. The activity a_i of species i in solution is the ratio of partial fugacity of a component to its fugacity in some defined standard state.

$$a_i \;\equiv\; \hat{f}_i / f_i^0 \tag{2.26}$$

Since at phase equilibrium, the value of f_i^0 is the same for each phase, substitution of equation (2.26) into equation (2.22) gives another alternative condition for phase equilibria,

$$a_i^{\mathrm{I}} \;=\; a_i^{\mathrm{II}} \;=\; \dots \;=\; a_i^{\mathrm{N}} \qquad ;\, i \;=\; 1, 2, \dots, C \tag{2.27}$$

For an ideal solution, $a_i = x_i$.

To represent departure of activities from mole fractions when solutions are nonideal, *activity coefficients* based on concentrations in mole fractions are defined by,

$$\gamma_i \;\equiv\; \frac{a_i}{x_i} \;\equiv\; \frac{\hat{f}_i}{x_i f_i^0} \tag{2.28}$$

For describing nonideal solution system.

$$\hat{f}_i \;=\; \gamma_i x_i f_i^0 \tag{2.29}$$

At phase equilibrium of the system composed C component and N phases , introducing activity coefficients into equation (2.22),

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} f_i^0 \;=\; \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} f_i^0 \;=\; \dots \;=\; \gamma_i^{\mathrm{N}} x_i^{\mathrm{N}} f_i^0 \quad ; i \;=\; 1, 2, \dots, C \quad (2.30)$$

The last equation becomes.

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} \;=\; \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} \;=\; \dots \;=\; \gamma_i^{\mathrm{N}} x_i^{\mathrm{N}} \qquad ; i \;=\; 1, 2, \dots, C \quad (2.31)$$

For convenient reference, thermodynamic quantities that are useful in phase equilibria calculations are summarized in Table 2.1.

Table 2.1 Thermodynamic quantities for phase equilibria

Thermodynamic Quantity	Definition	Physical Significance	Limiting Value for Ideal Solution
Chemical potential	$\mu_i \equiv \left(\dfrac{\partial G}{\partial N_i}\right)_{P,T,N_j}$	Partial molar free energy, $\bar{g}_i$	$\mu_i = \bar{g}_i$
Partial fugacity	$\hat{f}_i \equiv C \exp\left(\dfrac{\mu_i}{RT}\right)$	Thermodynamic pressure	$\hat{f}_i = x_i P_i^s$
Fugacity coefficient of a pure species	$\phi_i \equiv \dfrac{f_i}{P}$	Deviation to fugacity due to pressure	$\phi_i = \dfrac{P_i^s}{P}$
Partial fugacity coefficient of a species in a mixture	$\hat{\phi}_i \equiv \dfrac{\hat{f}_i}{x_i P}$	Deviation to fugacity due to pressure and composition	$\hat{\phi}_i = \dfrac{P_i^s}{P}$
Activity	$a_i \equiv \dfrac{\hat{f}_i}{f_i^0}$	Relative thermodynamic pressure	$a_i = x_i$
Activity coefficient	$\gamma_i \equiv \dfrac{a_i}{x_i}$	Deviation to fugacity due to composition	$\gamma_i = 1.0$

2.2.4.5 The Equilibrium Distribution Coefficient

The capacity of extractant or solvent can be described by the equilibrium distribution coefficient (K_{Di}). The distribution coefficient is defined as the ratio of the mole fraction of solute in the solvent to that in the liquid feed solution at equilibrium. The distribution coefficient for each species *i* between phase I and phase II is defined as.

$$K_{Di} = x_i^{\mathrm{I}} / x_i^{\mathrm{II}} = \gamma_i^{\mathrm{II}} / \gamma_i^{\mathrm{I}} \qquad (2.32)$$

It is desirable to have a high distribution coefficient to minimize the quantity of solvent required to extract a given amount of solute.

2.2.4.6 The Relative Selectivity

The ability to selectively remove the solute over the liquid feed solution may be described by the relative selectivity. Once accurate distribution coefficients are known it is then easy to express the relative selectivity for any species *i* compared to another species *j* via.

$$RS_{ij} = K_{Di} / K_{Dj} \qquad (2.33)$$

A high relative selectivity is desired to reduce any further concentration step needed to remove the solute from the feed solution.

2.3 Correlation and Prediction of Activity Coefficients

2.3.1 The Correlating UNIQUAC Model

A large number of semi-empirical equations have been proposed for the correlation of the activity coefficients of mixtures of non-electrolytes. All of these can provide useful correlations of experimental data for binary mixtures, but in many cases their extension to multicomponent mixtures is not successful unless additional parameters are included. The latter can only be obtained from measurements on the multicomponent mixture. Consequently, the most widely used correlations are those which can be accurately extended to multicomponent mixtures using only binary parameters. Such equations then become predictive when applied to a multicomponent system.

For liquid-liquid systems the most accurate correlation are know to be the UNIQUAC model of Abrams and Prausnitz (1975).

Abrams and Prausnitz (1975) show that the UNIQUAC model gives good representation of both vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolytes such as hydrocarbons, ketones, esters, water, amines, alcohol, nitriles, etc.

The UNIQUAC equation for the activity coefficient have two parts. The first is a combinatorial part (γ_i^C) that essentially due to differences in size and shape of the molecules in the mixture. The second is a residual part (γ_i^R) that essentially due to energetic interactions.

In multicomponent mixture, the UNIQUAC equation for the activity coefficient of (molecular) component *i* is

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{2.34}$$

where

$$\ln\gamma_i^C = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_j x_j l_j \tag{2.35}$$

and

$$\ln\gamma_i^R = q_i\left[1 - \ln\sum_j \theta_j \tau_{ji} - \sum_j (\theta_j \tau_{ij} / \sum_k \theta_k \tau_{kj})\right] \tag{2.36}$$

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

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}; \quad \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

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

In these equations, x_i is the mole fraction of component *i* and the summation in Equation (2.35) and (2.36) are over all components, including component *i*. The lattice coordination number *z* is given a value of 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 are 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 parameters (R_k) and the group area parameters (Q_k). Some data of R_k and Q_k are given in Table B.1.

$$r_i = \sum_k \nu_k^{(i)} R_k \qquad \text{and} \qquad q_i = \sum_k \nu_k^{(i)} Q_k \tag{2.37}$$

where $\nu_k^{(i)}$ is the number of groups of type k in component i, always an integer. The group parameters R_k and Q_k can be determined from values of the van der Waals group volume and surface areas V_{wk} and A_{wk} given by Bondi (1968) using the following relations

$$R_k = V_{wk}/15.17 \qquad \text{and} \qquad Q_k = A_{wk}/(2.5 \cdot 10^9) \tag{2.38}$$

The two adjustable binary parameters τ_{ij} and τ_{ji} appearing in equation (2.36) must be evaluated from experimental phase equilibrium data. In general, $(u_{ji} - u_{ii})$ and $(u_{ij} - u_{jj})$ are linear functions of temperature and $u_{ji} - u_{ij}$ so $\tau_{ii} = \tau_{jj} = 1$. These two adjustable parameters can be used for ternary or multicomponent systems, no ternary or higher parameters are required.

2.3.2 The Predictive UNIFAC Model

In the absence of experimental data with which to obtain the parameters of the UNIQUAC equation, resort must be made to purely predictive model. The UNIFAC model is discussed below.

The UNIFAC model was first developed by Fredenslund, Jones, and Prausnitz (1975). This model is a group-contribution method which combines the solution-of-functional-groups concept with the UNIQUAC equation. The resulting UNIFAC (UNIQUAC Functional group Activity Coefficients) model represented the mixture by a mixture of the constituent functional groups. Since the number of groups ($-CH_3$, $-OH$, $-CO_2H$, etc.) that are encountered is much smaller than the number of different mixtures that have to be modeled. This method is a powerful and often predicted activity coefficients of binary and multicomponent mixtures with good accuracy.

The UNIFAC method provides a simple procedure for calculating activity coefficients in terms of constants reflecting the sizes and surface areas of individual functional groups, and parameters representing energetic interactions between groups.

The activity coefficients have a combinatorial contribution (γ_i^C) that depends upon the size and shape of molecules and a residual contribution (γ_i^R) that characterizes the energetic interactions between molecules.

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (2.34)$$

where the combinatorial part of the UNIFAC model can be used directly from the UNIQUAC model as in equation (2.35). Only pure component properties enter into this equation.

For the residual part of activity coefficient, the solution-of-groups concept is used as follows.

$$\ln\gamma_i^R = \sum_k \nu_k^{(i)} \left[\ln\Gamma_k - \ln\Gamma_k^{(i)} \right] \qquad (2.39)$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group *k* in a reference solution containing only molecules of type *i*. The latter definition is necessary to attain the normalization so that $\gamma_i \rightarrow 1$

as $x_i \rightarrow 1$. The group residual activity coefficient Γ_k is found from an expression similar to equation (2.36) of the UNIQUAC model.

$$\ln \Gamma_k = Q_k \left[1 - \ln(\sum_m \Theta_m \psi_{mk}) - \sum_m (\Theta_m \psi_{km} / \sum_n \Theta_n \psi_{nm}) \right] \qquad (2.40)$$

Equation (2.40) also holds for $\ln\Gamma_k^{(i)}$. Θ_m is the area fraction of group m and the sums are over all different groups. Θ_m is calculated in the same manner as θ_i.

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad (2.41)$$

and the mole fraction of group m in the mixture X_m is given by

$$X_m = \frac{\sum_j \upsilon_m^{(j)} x_j}{\sum_j \sum_n \left(\upsilon_n^{(j)} x_j \right)} \qquad (2.42)$$

The group interaction parameter ψ_{mn} have a temperature dependent form

$$\psi_{mn} = \exp\left[\frac{u_{mn} - u_{nn}}{RT} \right] = \exp-(a_{mn} / T) \qquad (2.43)$$

Where u_{mn} is a measure of the energy of interaction between groups m and n. The group interaction parameters a_{mn} are the parameters which must be evaluated from experimental phase equilibrium data. Note that a_{mn} has units of degrees Kelvin and $a_{mn} \neq a_{nm}$. However, when $m = n$, $a_{mn} = 0$ and $\psi_{mn} = 1$. The Table B.2 show a few a_{mn} parameters that obtained from a database using a wide range of experimental results.

CHAPTER III

LITERATURE REVIEW

The liquid-liquid extraction of ethanol from aqueous solutions has been studied for a long time. The knowledge of the phase equilibrium data is required for the development of liquid extraction process and the design of corresponding equipment.

Many research groups have studied the liquid-liquid equilibrium of ethanol, water, and several organic solvents. They were examined as potential separating agents for ethanol separation. Some of researches are reviewed forward.

Roddy and Coleman (1981) determined distribution coefficient for ethanol and water between a series of straight-chain alkanes from n-hexane (C_6) to n-hexadecane (C_{16}). They were measured at 25°C and varying concentration of ethanol solutions from 0.02 to 10M. The ethanol distribution coefficient values for each alkanes were all low, ≤ 0.02 . They were essentially constant for each alkane over a wide concentration range, 0.02 to about 5M, then increased sharply at 7 and 10M. The ethanol distribution coefficients were much lower, but increased with increasing ethanol concentration, so that the ethanol/water separation factors dropped from about 4500 at 0.1M to 20 at 10M ethanol concentration.

In the same year, Roddy (1981) measured distribution coefficients of ethanol and water from ethanol-water mixtures to several organic liquids. Study was done at 20, 25, and 40°C from 0.1 and 1.0M ethanol by a tracer counting technique. It was found that the order of extractability of ethanol was alcohol = phosphate > ester > amine > ketone > ether > halocarbon = hydrocarbon. Branching on the alcohol solvent molecules appears to be of benefit; the highest distribution coefficient for ethanol is obtained when the hydroxyl group is located on a primary carbon. These highest coefficient was 0.69 for 2-ethyl-1-butanol solvent. Separation factors were calculated for each liquid. Better separation factors were obtained with the alcohols without loss in extraction ability for ethanol.

Liquid-liquid equilibrium data for two ternary systems, water-ethanol-2-ethylhexanol (Ruiz et al., 1987), and water-ethanol-dichloromethane (Ruiz et al., 1988) were reported. The solvents for extraction of ethanol from aqueous solutions are 2-ethylhexanol and dichloromethane. These solvents are less volatile and more volatile than ethanol, respectively. Data for the binodal curves of the ternary systems were determined by using the cloud-point method. Tie-line data were obtained by analyzing both phases by means of gas chromatography. The liquid-liquid equilibrium data were correlated simultaneously together with vapor-liquid equilibrium data by using the UNIQUAC equation. The results indicate that the UNIQUAC equation gives a good correlation of the data. The obtained UNIQUAC parameters allowed the calculation of vapor-liquid equilibrium, liquid-liquid equilibrium, and vapor-liquid-liquid equilibrium data for these two ternary systems.

Experimental mutual solubility and tie-line data were examined for three ternary liquid-liquid systems composed of water-ethanol-amyl acetate, water-ethanol-benzyl alcohol, and water-ethanol-metyl isobuthyl ketone (Solimo, 1989). The studies were determined at 298.15K in order to obtain complete phase diagrams and to determine the most suitable solvent for ethanol extraction from aqueous solutions.

The binodal curves were obtained by using titrating method and measuring their densities. The equilibrium compositions were obtained with the aid of a calibrating curve density and weight fraction of ethanol. The plait points were determined by using the Othmer and Tobias method. Experimental results showed that the selectivity of amyl acetate higher than methyl isobutyl ketone and benzyl alcohol, indicating that amyl acetate is the best of the three solvents. However, all distribution coefficients of the systems were less than 1 except for water-ethanol-benzyl alcohol up to 15% ethanol. The equilibrium data were correlated with the UNIFAC group contribution method. The equilibrium data were in qualitative agreement with UNIFAC method.

The extraction of ethanol from dilute aqueous solutions with solvents composed of phenol derivatives at 25°C was investigated. Distribution ratio for extraction with m-cresol at 0 and 50°C were also measured (Arenson et al., 1990). The gas chromatography was used to measure the equilibrium compositions. They suggests that the extraction of ethanol is due almost completely to hydrogen bonding between the hydroxy functionalities of ethanol and the phenol. The effect of temperature on the distribution ratio over the temperature range from 0 to 50°C is relatively small .

Zhang and Hill (1991) presented equilibrium concentration data for the system of water-oleic acid-ethanol at 20, 30, 45, and 60°C. The results indicate that the mole fraction of ethanol in the solvent phase increases to between twice and four times that in the aqueous phase. The concentrations of ethanol and water in solvent phase increases with temperature at the expense of concentrations in the aqueous phase. The solvent phase is very insoluble in the aqueous phase, but its solubility increases with temperature. The concentration data are shown to be well represented by the NRTL model for predicting liquid-liquid equilibria. But the UNIQUAC model gave poorer results. Since oleic acid is a better solvent for ethanol extraction than observations made by Roddy and Coleman (1981) for long-chained alkanes.

Letcher, Ravindran et al. (1992) presented the tie-lines and liquid-liquid equilibrium of an alkanol-diisopropyl ether-water at 25°C. The alkanols are methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2- butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol. Their results for binodal curves show that the solubility of water in diisopropyl ether + an alcohol is very much dependent on the type of alcohol. Water is most soluble in the systems containing ethanol or 2-propanol or tertiary butanol. A similar result was obtained by Letcher, Sewry, and Naran (1989b) for mixtures of ethyl ether-water-an alcohol. A comparison of the results reported here for the diisopropyl ether systems with the results reported earlier by Letcher et al, (1989b) for the ethyl ether systems, show that for a particular alcohol water is less soluble in diisopropyl ether mixtures than in ethyl ether mixtures.

Tie-lines and liquid-liquid equilibrium data of an alkanol-toluene or mesitylene-water at 25°C were experimented (Lether and Siswana, 1992). The alkanols are methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2- butanol, 2-methyl-1-propanol and 2-methyl-2-propanol. Tie-lines and liquid-liquid equilibrium data of 2-propanol-o-xylene or m-xylene-water were also measured. The propose of this study was to analyse the effect of substituted methyl groups of benzene on the tie-lines and liquid-liquid equilibrium data. The results were compared with data which had been reported for related ternary mixtures containing p-xylene (Letcher, 1989), benzene (Letcher, Sewry, and Radloff, 1990) cyclohexane and hexane (Letcher, Siswana, and Radloff, 1991). The conclusions demonstrated that the partitioning of an alkanol between water and any methyl-substituted benzene compound is dependent on the length and structure of the carbon chain of the alkanol. The effect of the alkyl chain length of the alkanol is more pronounced than the effect of the number of methyl-substituted benzene.

Arce et al. (1994) were reported liquid-liquid equilibrium data and binodal curves for the systems water-methanol-1-octanol and water-ethanol-1-octanol at 25, 35, and 45°C. The data were fitted to the NRTL and UNIQUAC equations. The NRTL and UNIQUAC equations are equally satisfactory for corrlation if the NRTL nonrandomness parameter (α) is set to 0.1 for water-methanol-1-octanol and to 0.2 for water-ethanol-1-octanol.

The interest of aqueous systems containing alcohols and esters stems from the use of these compounds in food technology as aromas and extractants. The equilibrium data are required for liquid-liquid extraction processes. The base ternary systems studied were the type I systems ethyl acetate-ethanol-water and butyl acetate-ethanol-water, and the type II system ethyl acetate- butyl acetate-water (Arce et al., 1999). Experiment were done at 25, 35, and 45°C and at atmospheric pressure. The experimental data were correlated by the NRTL and UNIQUAC models by two difference approaches: a) system by system correlation, affording system specific binary interaction parameters; and b) correlation of the combined data for three systems, affording common binary interaction parameters. Both models satisfactorily correlated the data. The result binary interaction parameters will be useful for predicting the activity coefficients and liquid-liquid equilibrium data of diverse multicomponent systems.

Several organic solvents were examined as potential separating agent for ethanol recovery from aqueous solutions by liquid-liquid extraction. Liquid-liquid equilibrium data at 25°C for the three promising solvents, isoamyl acetate, isooctyl alcohol, and n-butyl acetate with ethanol-water systems were collected by Koullas et al. (1999). The results confirm that at this stage of the work, isoamyl acetate and isooctyl alcohol were found to be very good separating agents. Where as n-butyl acetate was found to be of interior potential solvent.

Liquid-Liquid equilibrium data for 1-pentanol-ethanol-water at 25, 50, 85, and 95°C have been determined by Torres et al.(1999). The results have been correlated simultaneously by the UNIQUAC method obtaining two sets of interaction parameters. One of them independent of the temperature and the other with a linear dependence. Both sets of parameters fit the experimental results well and have a little difference of root mean square deviation in phase composition. Then it seems unnecessary to use the temperature–dependent parameters instead of those simultaneously correlated temperature – independent parameters.

CHAPTER IV

EXPERIMENTS

4.1 Chemicals

All chemicals used were analytical reagent grade and used without further purification.

- 1-Hexanol was supplied by Fluka.
- 1-Octanol was supplied by AJAX.
- 1-Decanol was supplied by Merck.
- Ethanol was supplied by CARLO ERBA.
- The three times-distilled water was supplied by The Government Pharmaceutical Organization, Ministry of Public Health.

The properties of source chemicals are showed in Table 4.1

Table 4.1 Properties of pure chemicals used in this work

Chemicals	Structural	Molecular Weight	Minimum Assay (%)	Boiling Point (°C)	Density (20°C/4°C) (g/mL)
1-Hexanol	$CH_3(CH_2)_5OH$	-	99.0	156-157	0.820
1-Octanol	$CH_3(CH_2)_7OH$	-	99.5	-	0.820
1-Decanol	$CH_3(CH_2)_9OH$	158.29	99.0	228-235	0.829-0.830
Ethanol	CH_3CH_2OH	46.07	99.8	78.5	0.7896
Distilled water	H_2O	18.02	100.0	100	1.00

4.2 Experimental Apparatus

4.2.1 Constant Temperature Water Bath

The constant temperature water bath consists of a water bath, a heater which is controlled by a thermostat. The thermostat used are FCS-13A-R/M automatic controller with thermocouple of type Pt100 that have scale range –199.9 to 850.0°C. The temperature range for the thermostat was 25.6 to 149.0°C with a controller accuracy of ± 0.1 °C.

4.2.2 Refractometer

The Abbe refractometer used is the ATAGO refractometer type 1T. The refractive index scale range is 1.3000 – 1.7000 with an accuracy of ± 0.0005. The main parts of refractometer are shown in Figure 4.1.

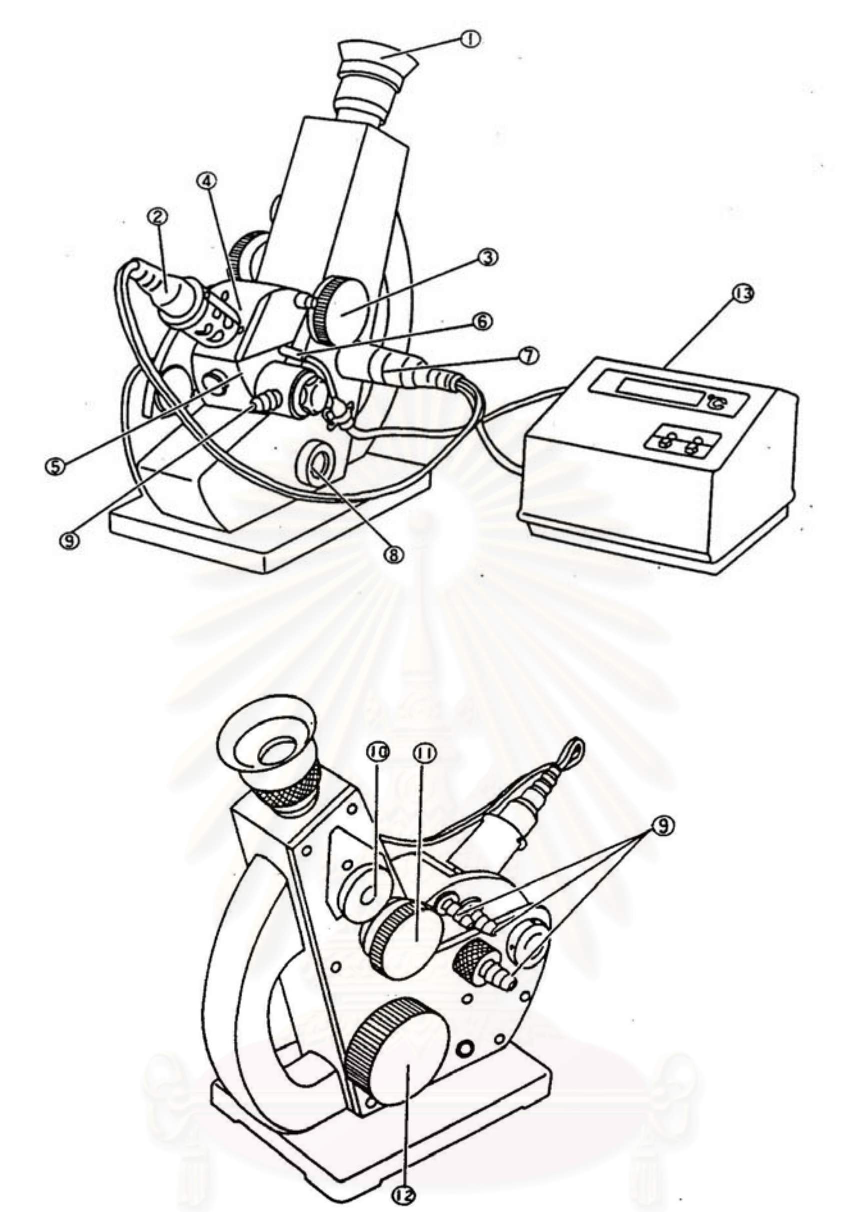
Table 4.2 Experimental and literature values for the refractive indexes of the pure chemicals used

Chemical	n_D at 20°C		n_D at 25°C	
	experiment	literature (a)	experiment	literature (b)
1-Hexanol	1.4135	1.4178	1.4131	1.4161
1-Octanol	1.4250	1.4295	1.4242	1.4276
1-Decanol	1.4330	1.4372	1.4320	1.4350
1-Ethanol	1.3601	1.3611	1.3565	1.3594
Distilled Water	1.3304	1.3330 (c)	1.3300	1.3325

(a) Lide, D. R. , and Frederikse, H. P. R., eds.,1994: 3-1 – 3-330

(b) Yaws, C. L., Wang, X. M., and Satyro, M. A., 1999: 239-260

(c) Liley et al., 1997: 2-27



1. Eyepiece
2. Specimen illuminator assembly
3. Prism open-shut handles
4. Secondary prism
5. Main prism
6. Thermistor head
7. Scale field of vision illuminator assembly
8. Dessicant case
9. Temperature control water inlet-outlet nozzles
10. Scale adjustment screw
11. Color compensator knob
12. Measurement knob
13. Thermometer

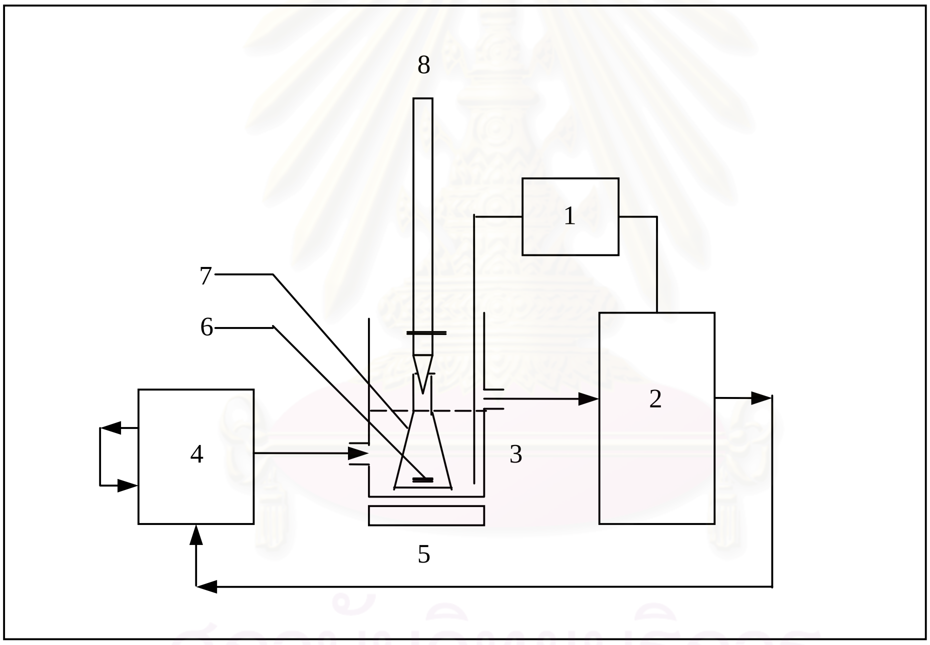
Figure 4.1 Main parts of ATAGO refractometer

4.2.3 Electronic Balance

The METTLER TOLEDO electronic balance model AB204 was used to weight the liquid solutions for calculation of mole fraction of the components. Its weighting limits are at the minimum of 10 mg and the maximum of 210g.

4.2.4 Apparatus Setup for Determination of Binodal Curves

Figure 4.2 shown schematic diagram of apparatus setup for determining the binodal curves.

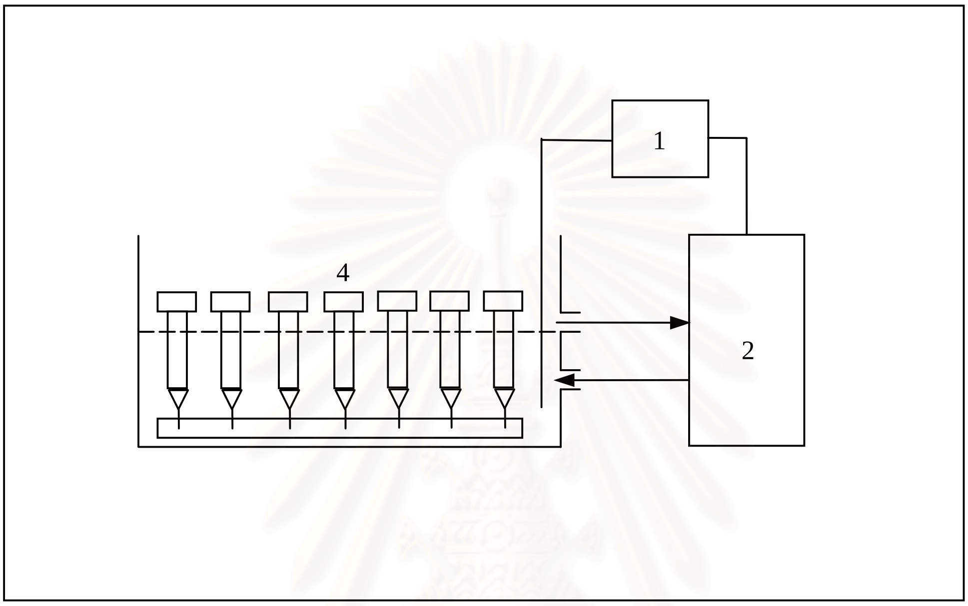


1. Thermostat
2. Heater with circulating pump
3. Constant temperature water bath
4. Refractometer
5. Stirrer
6. Magnetic stirrer
7. Conical flask
8. Buret

Figure 4.2 Schematic diagram of apparatus setup for determination of binodal curves

4.2.5 Apparatus Setup for Determination of Tie-Lines

Glass-syringe of 10 ml. made of glasses to serve as phase equilibrium cell. The schematic diagram of apparatus setup for determination of tie-lines is shown in Figure 4.3.



1. Thermostat
2. Heater with circulating pump
3. Constant temperature water bath
4. Glass-syringe

Figure 4.3 Schematic diagram of apparatus setup for determination of tie-lines

4.3 Experimental Procedure

4.3.1 Determination of Binodal Curves

The binodal curves or solubility isotherms for the systems of 1-hexanol-ethanol-water, 1-octanol-ethanol-water, and 1-decanol-ethanol-water were determined by the cloud-point method.

The procedure for gravimetrical determination of binodal curves were as follows.

1. Mix the weighted water-solvent in a closed conical flask with a capacity of 125 cm^3. The closed glass equipped with magnetic stirrer and a jacket for circulation of the isothermal fluid. The water jacket was thermostatically controlled using thermostat with accuracy ± 0.1 °C.
2. The third component (ethanol) was added from a buret until transition from turbidity to a clear solution was observed. In this way, the portions of the binodal curves were obtained.
3. Weighing the mixture after the transition point was reached to obtained the quantities of the third component.
4. The refractive index of the ternary mixtures were measured with ATAGO refractometer. And with a calibrating curve of refractive index vs mole fraction, the points of the binodal curve were obtained.

4.3.2 Determination of Tie-Lines

The tie-lines data were determined with an experimental device maintained at the constant temperature of T ± 0.1°C in a thermostated vessel.

Determination of tie-line were done by the following steps.

1. Different weighted ternary mixtures with compositions situated inside the heterogeneous region were prepared and placed in the equilibrium cell.
2. The liquid mixtures was shaken at 15 minutes intervals for 2 hours and allowed to settle for another 2 hours. The times for shaking and settling were sufficient to establish equilibrium. This was proved in preliminary experiments, which show that the longer times for shaking and settling gave the same results in the phase composition.
3. Samples were taken from each phase for analysis.
4. The analysis of the conjugated phase was carried out by the measurement of its refractive indexes at experimental temperature.
5. Step 1 to 4 were repeated at various temperatures.

CHAPTER V

DATA REDUCTION

The UNIQUAC model was used to correlate experimental liquid-liquid equilibria data and the evaluation of binary interaction parameters of model were done. The UNIFAC model was used to predict the liquid-liquid equilibria data of the interested system. The back calculation method and some mathematic methods were also used. The computer programs were written in Borland C++ 5.02. Flow charts of the programs were also presented.

5.1 Back Calculation Method

When experimental data on temperature and liquid-liquid equilibria phase compositions are available, the binary interaction parameters of UNIQUAC model can be evaluated by back calculation method.

The objective function chosen were in terms of the root mean square (rms) deviation in phase composition.

$$\text{rms} = \left(\sum_{k}^{M} \sum_{j}^{2} \sum_{i}^{3} \left(x_{ijk} - \hat{x}_{ijk} \right)^{2} / \ 6M \right)^{\frac{1}{2}}$$

where *M* is the number of tie lines, *x* indicates the experimental mole fraction, $\hat{x}$ the calculated mole fractions, and the subscript *i* indexes components, *j* phases and *k* tie lines. The mathematical tool required is the region elimination method.

5.2 Region Elimination Method

Region elimination method for a six-dimensional search make it possible to delete a calculated portion of the range of *x* from consideration on each successive stage of the search for an extremum of *f(x)*. When the remaining subinterval is sufficiently small, the search terminates.

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

In each dimension search, the range of parameters was divide into 5 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 5 sections again and decreased again by the same route until a range of parameters was with in acceptable value.

5.3 Computer Program

The research consists of two main programs and two subprograms which are described as follow.

5.3.1 Main Program for Evaluation of Binary Interaction Parameters

The binary interaction parameters of UNIQUAC model were evaluated from the experimental liquid-liquid equilibria compositions data. The flow chart of this main program was illustrated in Figure 5.1.

5.3.2 Main program for Calculation of Liquid-Liquid Equilibria Phase Compositions

From the phase rule as describe in 2.2.2. The number of degrees of freedom for the ternary liquid-liquid system is 3. The data of pressure and temperature are available, only one composition in either phase can fix the state of the system. The liquid-liquid phase compositions were obtained by input temperature and x_3^I, where superscript I indexes the aqueous phase and subscript 3 indexes water component.

For UNIQUAC model, the binary interaction parameters obtained by 5.3.1 were used for the calculation. The flow chart of this main program was illustrated in Figure 5.2.

5.3.3 Subprogram of UNIQUAC and UNIFAC Models

The flow charts of subprogram UNIQUAC and UNIFAC models were illustrated in Figures 5.3 and 5.4, respectively.

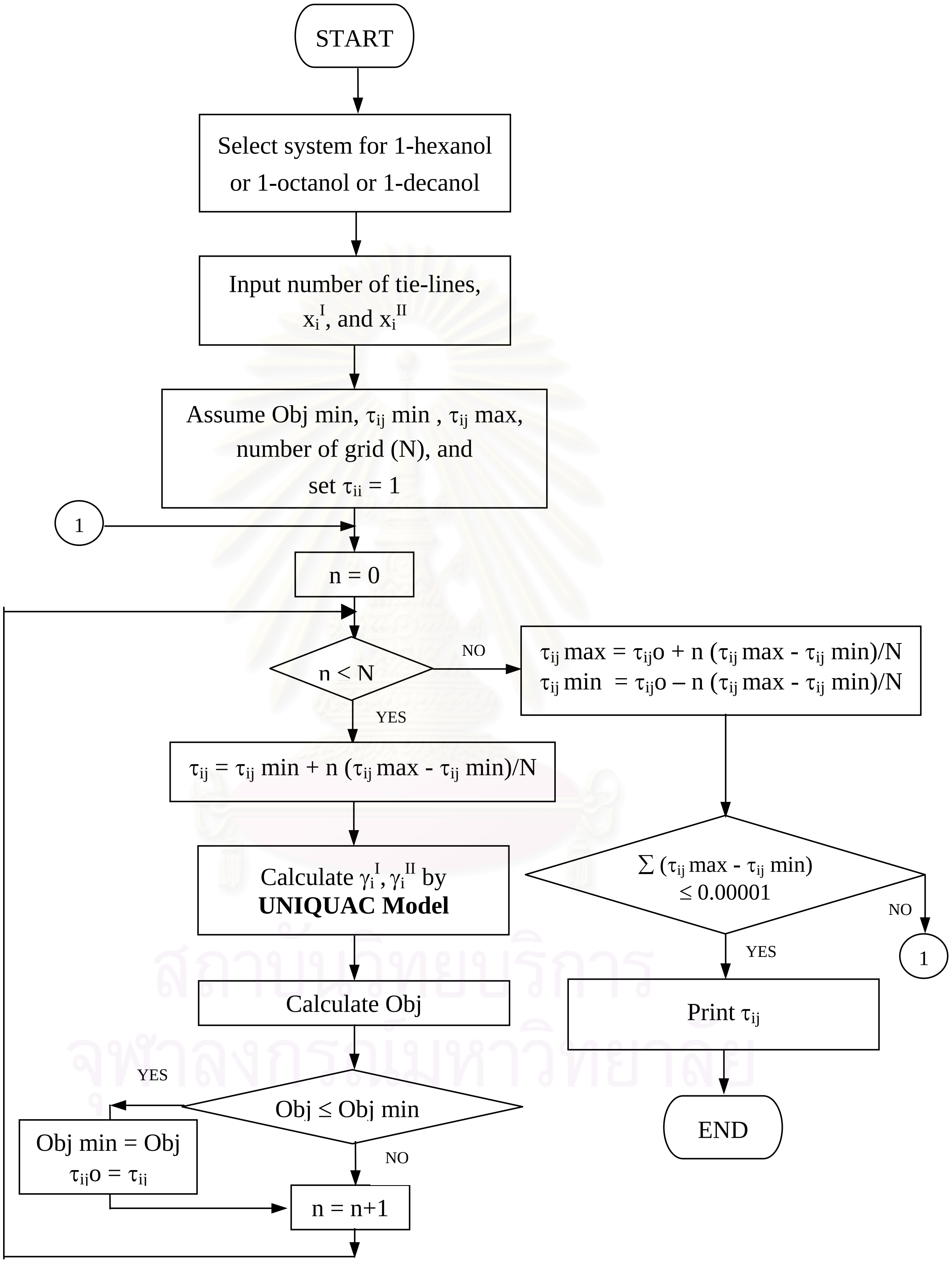


Figure 5.1 Flow chart of main program for evaluation of binary interaction parameters (τ_{ij})

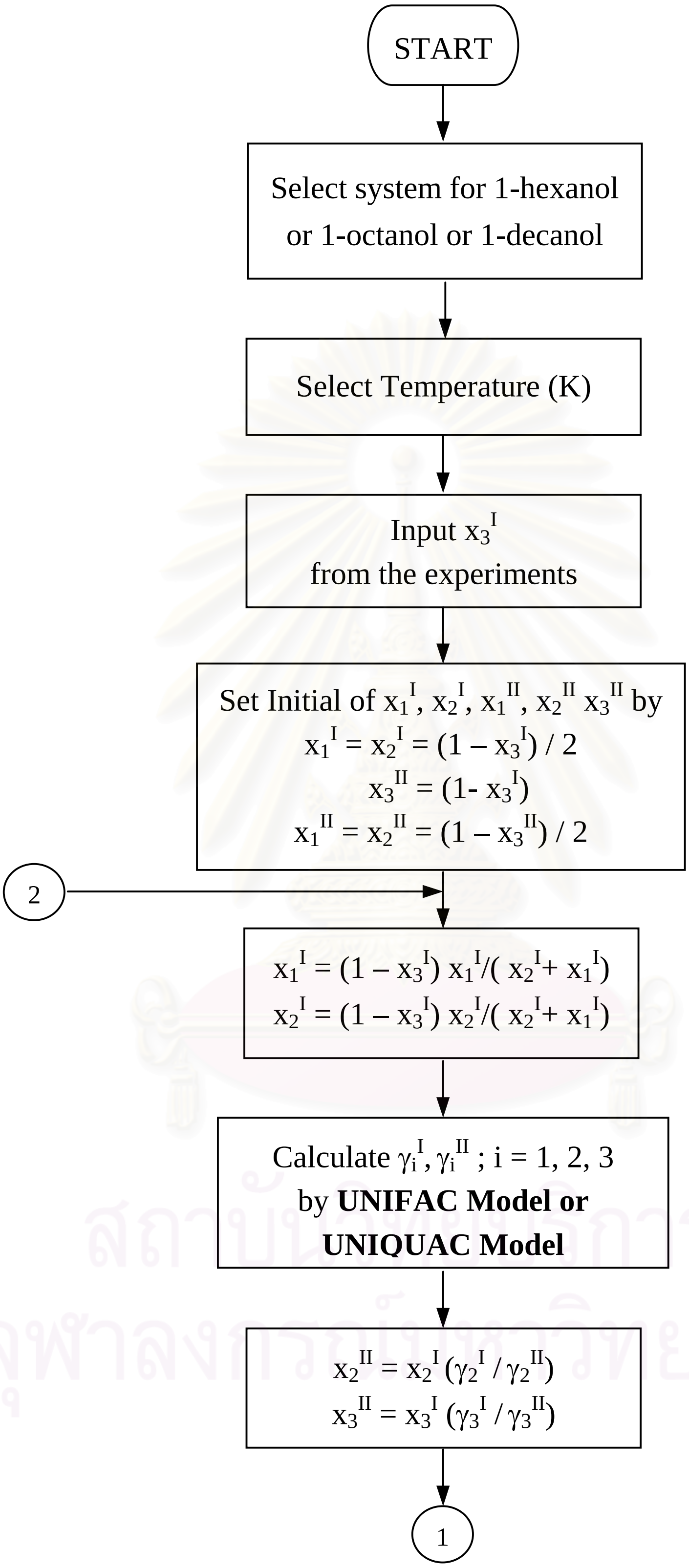


Figure 5.2 Flow chart of main program for calculation of liquid-liquid equilibria phase compositions

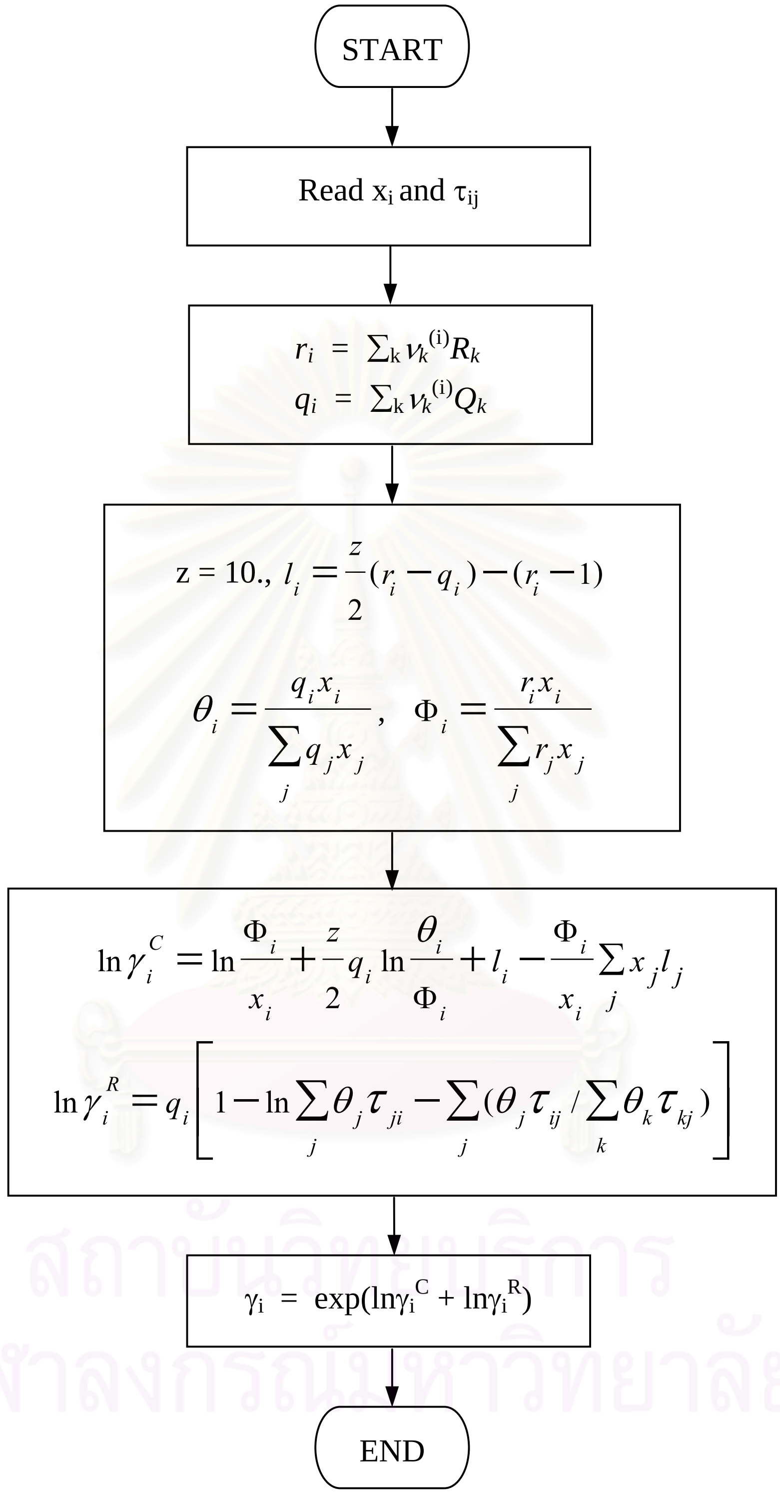


Figure 5.3 Flow chart of subprogram UNIQUAC

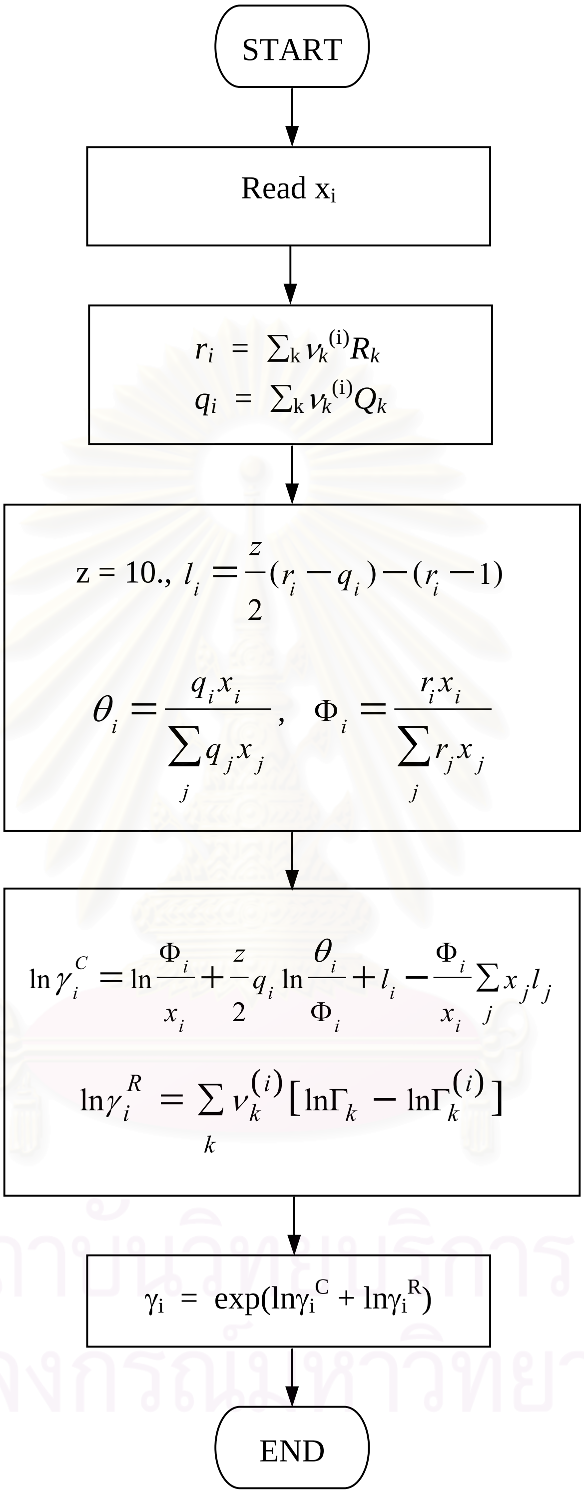


Figure 5.4 Flow chart of subprogram UNIFAC

CHAPTER VI

RESULTS AND DISCUSSION

6.1 Comparison of Binodal Curves

The experimental binodal points and tie-lines data of all system obtained in this work are presented in Table C.1 to C.24 in Appendix C and Figures 6.1 and 6.2. The binodal curves for the system of 1-octanol-ethanol-water at 30, 40, 50, and 60°C were drawn together with the binodal curve of Arce et al. (1994) at 45°C as shown in Figure 6.1. It is found that the binodal curve at the temperature of 45°C (Arce et al.'s work) lined between the experimental curves at the temperature of 40 and 50°C.

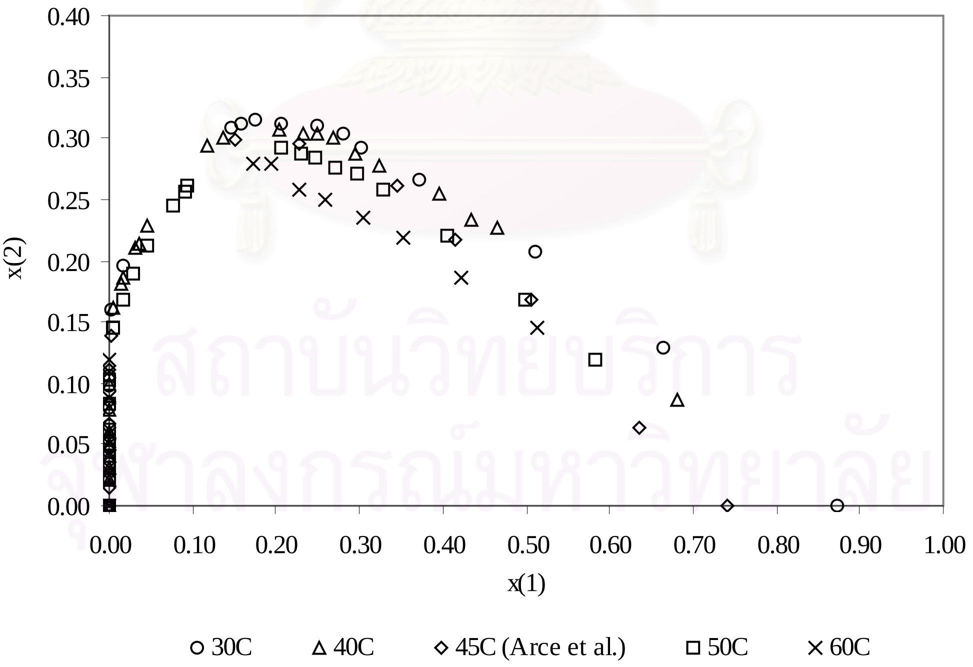


Figure 6.1 Comparison of experimental binodal curves of 1-octanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C with literature at 45°C

Figure 6.2 shows the comparison of the experimental binodal curves of solvents(1-hexanol, 1-octanol, 1-decanol)-ethanol-water and the binodal curve of 1-pentanol-ethanol-water in the work of Torres et al. (1999). The Figure presented correctly the order of binodal curves with respect to solvents.

Figure 6.2 Comparison of experimental binodal curves of solvent(1)-ethanol(2)-water (3) at 50°C

Thus, Figures 6.1 and 6.2 confirm that the experimental liquid-liquid equilibrium results of this work were reliable.

6.2 Effect of Temperature and Molecular Size of Solvents on Binodal Curves

6.2.1 Effect of Temperature on Binodal Curves

The Figures 6.3 to 6.5 illustrate the effect of temperature on binodal curves for the three systems, ie., 1-hexanol-ethanol-water, 1-octanol-ethanol-water, and 1-decanol-ethanol-water systems. It is found that, when the temperature is increased, the molecular kinetic energy of solvent and water are increased, so that they can overcome the intermolecular force of the molecules. Therefore, the solubility of solvent in water increases with the increasing temperature and consequently, the amount of ethanol in liquid-liquid equilibrium is decreased.

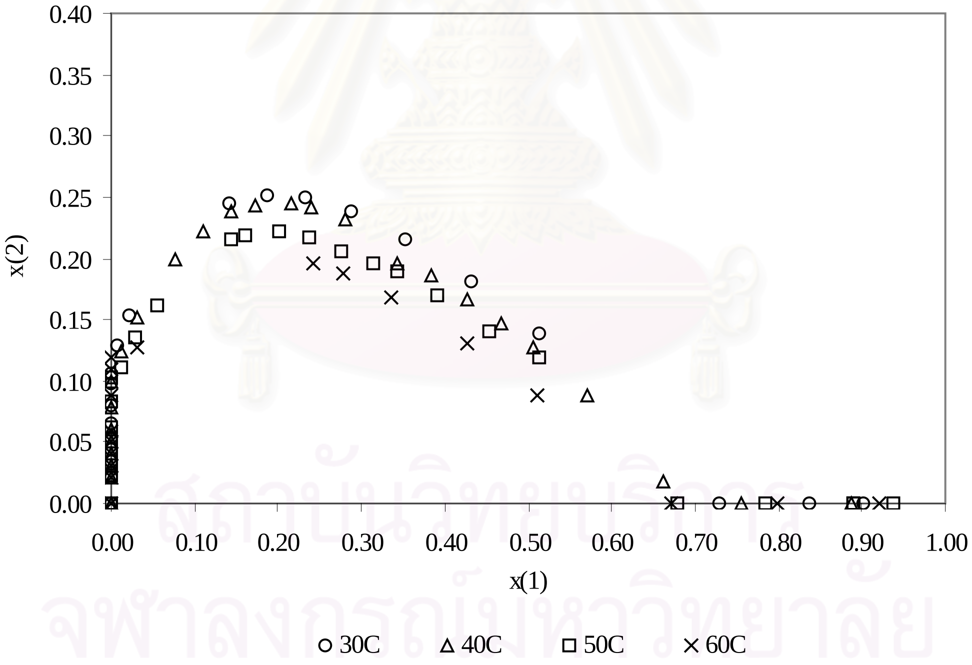


Figure 6.3 Experimental binodal curves of 1-hexanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

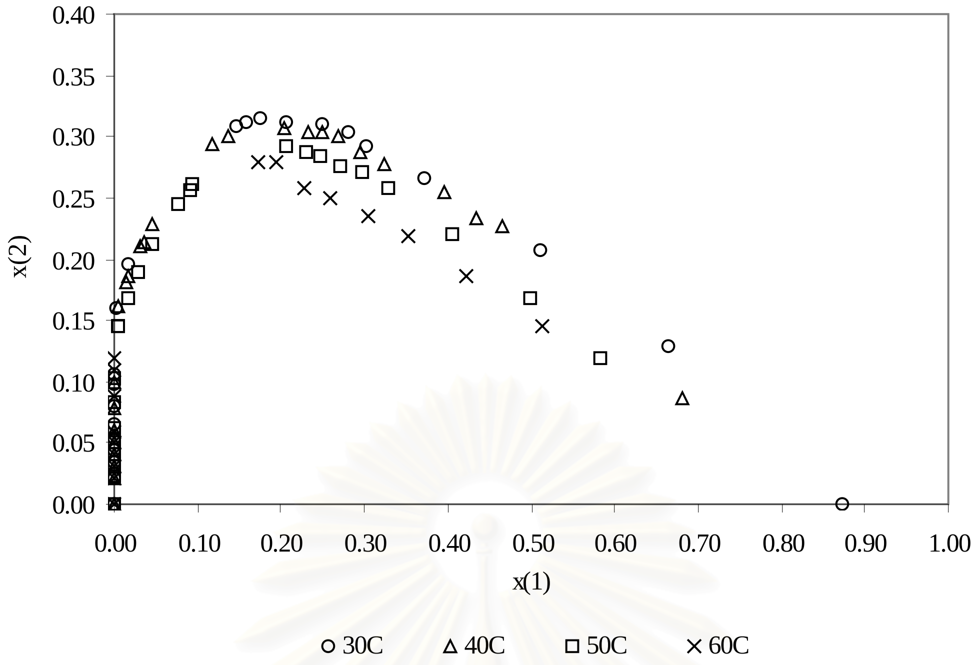


Figure 6.4 Experimental binodal curves of 1-octanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

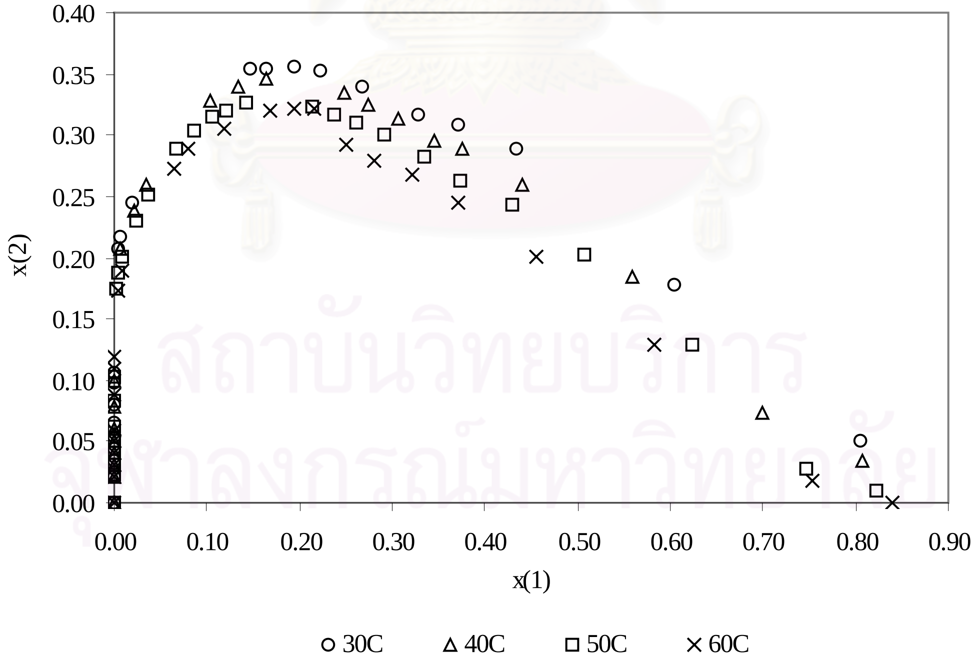


Figure 6.5 Experimental binodal curves of 1-decanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

6.2.2 Effect of Molecular Size of Solvents on Binodal Curves

Figures 6.6 to 6.9 show the influence of the molecular size of the solvents on binodal curves. From these figures, it is found that, when the molecular size becomes bigger, the solubility of solvent in water becomes lower. According to the concept of solubility, the polar molecule can dissolve in polar molecule more easily, in the same way, the non polar molecule like to dissolve in non polar molecule. Water and solvent are polar molecules. The solvent molecule composes of two parts, the alkyl group ($CH_3(CH_2)_n$-) being non polar, and the hydroxyl group (-OH) being polar. As the alkyl group increases in size, while the hydroxyl group is not increased, the net charge becomes lower, so they can dissolve less in water. Consider the Figures 6.6 to 6.9, hexanol is more soluble in water than octanol and decanol, respectively.

The solubility of the solvent also agrees with the value of dipole moment (Table 6.1). Dipole moments of molecules involved the electric charge density of the compound. Therefore, for the longer chain of alkyl group in solvent, non-polar part is bigger, so that net electric charge is lower.

Table 6.1 Dipole moment of various pure chemicals used

Chemicals	Water	Ethanol	1-Hexanol	1-Octanol	1-Decanol
Dipole moment (debye)	1.85	1.69	1.65	1.65	1.62

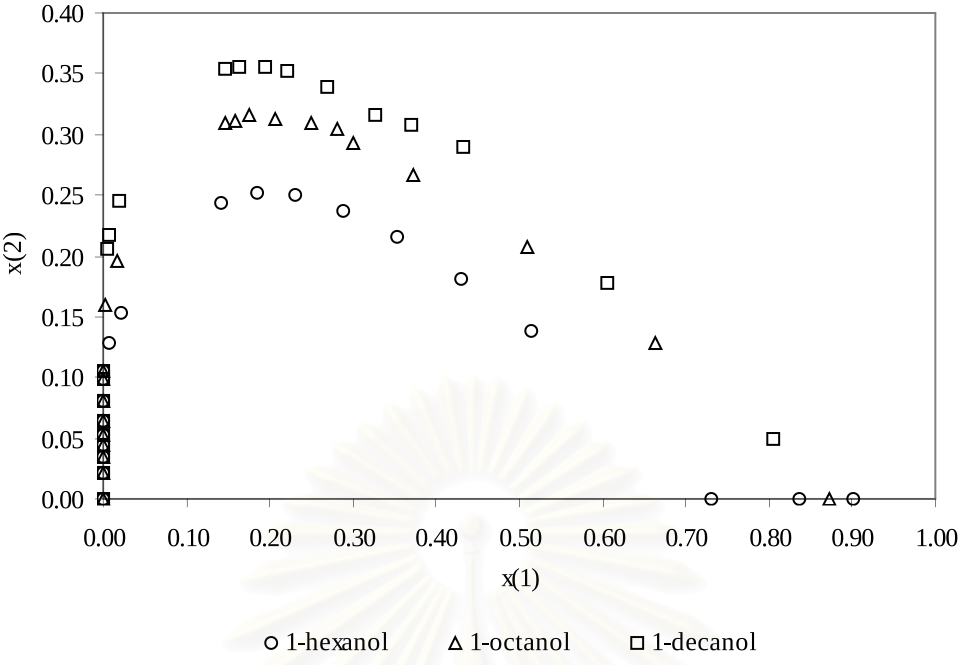


Figure 6.6 Experimental binodal curves of solvent(1)-ethanol(2)-water (3) at 30°C

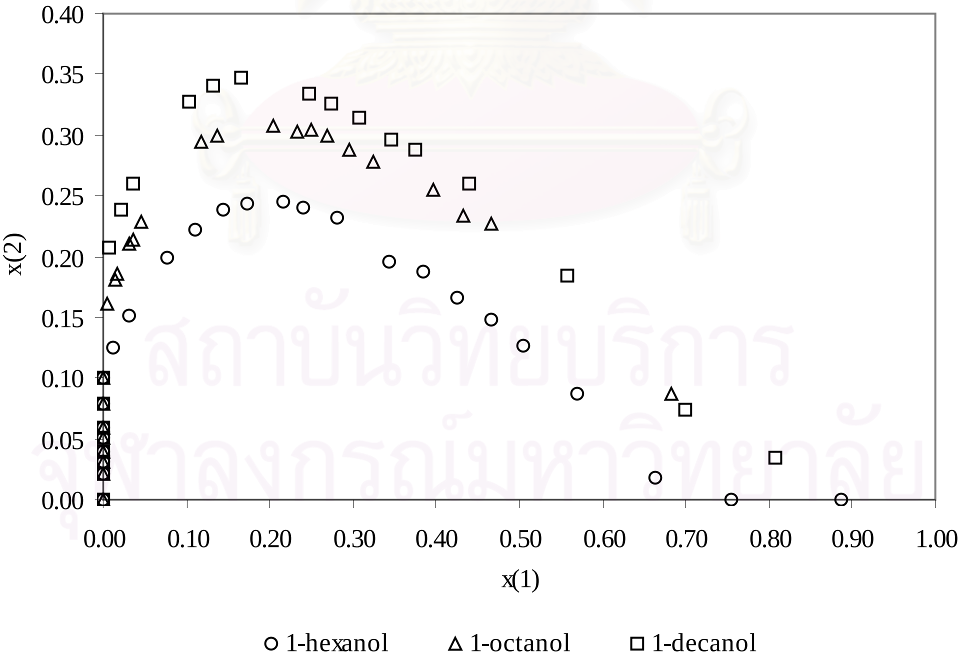


Figure 6.7 Experimental binodal curves of solvent(1)-ethanol(2)-water (3) at 40°C

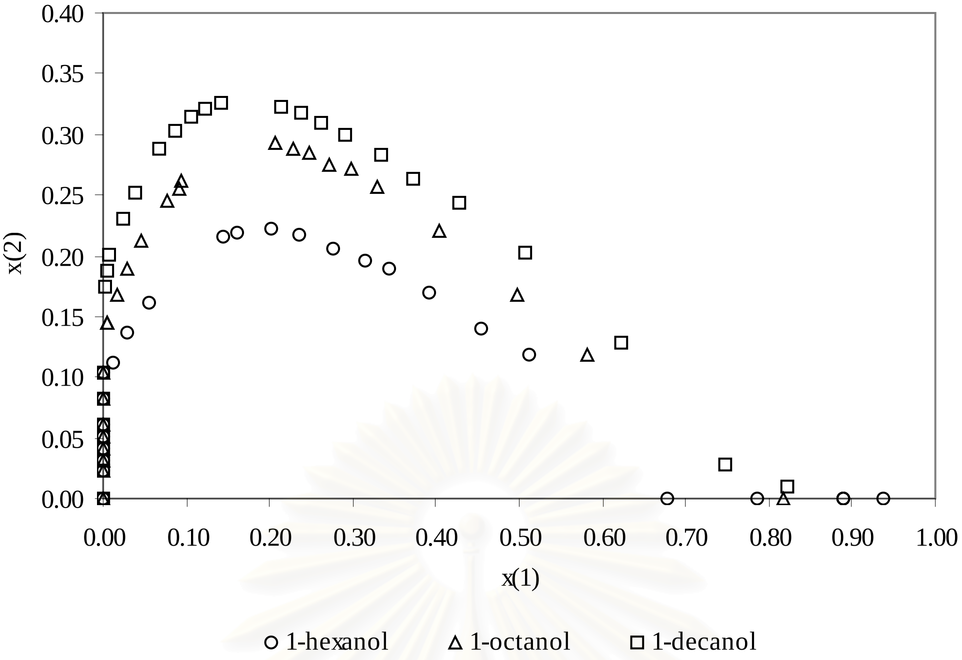


Figure 6.8 Experimental binodal curves of solvent(1)-ethanol(2)-water (3) at 50°C

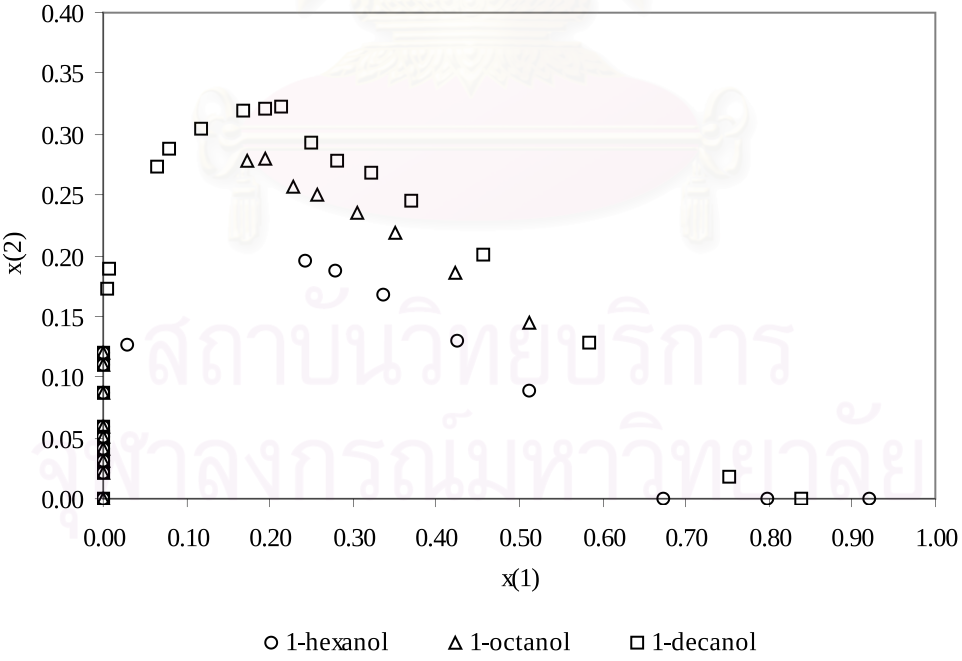


Figure 6.9 Experimental binodal curves of solvent(1)-ethanol(2)-water (3) at 60°C

6.3 Binary Interaction Parameters in Acitivity Coefficient Equation

6.3.1 Values of Binary Interaction Parameters in Activity Coefficient Equation

Based on the experimental data obtained in this work, binary interaction parameters (τ_{ij} or a_{ij}) of UNIQUAC were obtained by data reduction method described in Chapter V. The results are listed in Tables E.1 to E.6 and Figures 6.10 to 6.16.

6.3.2 Effect of Temperature on Binary Interaction Parameters

Figures 6.10 to 6.12 show the effect of temperature on binary interaction parameters (a_{ij}). All of parameters are linear function with temperature. In each system, the temperature dependence of the parameters a_{13}, a_{31}, a_{23}, and a_{32} over the temperature range from 30 to 60°C are relatively small. But for parameters a_{12}, a_{21} are highly dependent with temperature.

6.3.3 Dependence of Binary Interaction Parameters on Molecular Size of Solvents

Figures 6.13 to 6.16 show the effect of molecular size, represented by molecular weight, on binary interaction parameters (a_{ij}). As the molecular weight increases, the parameter a_{12} is increased but the parameter a_{21} is decreased. The parameter a_{13} increase when solvent molecular weight is increased but the parameter a_{31} decreased when solvent molecular weight is increased.

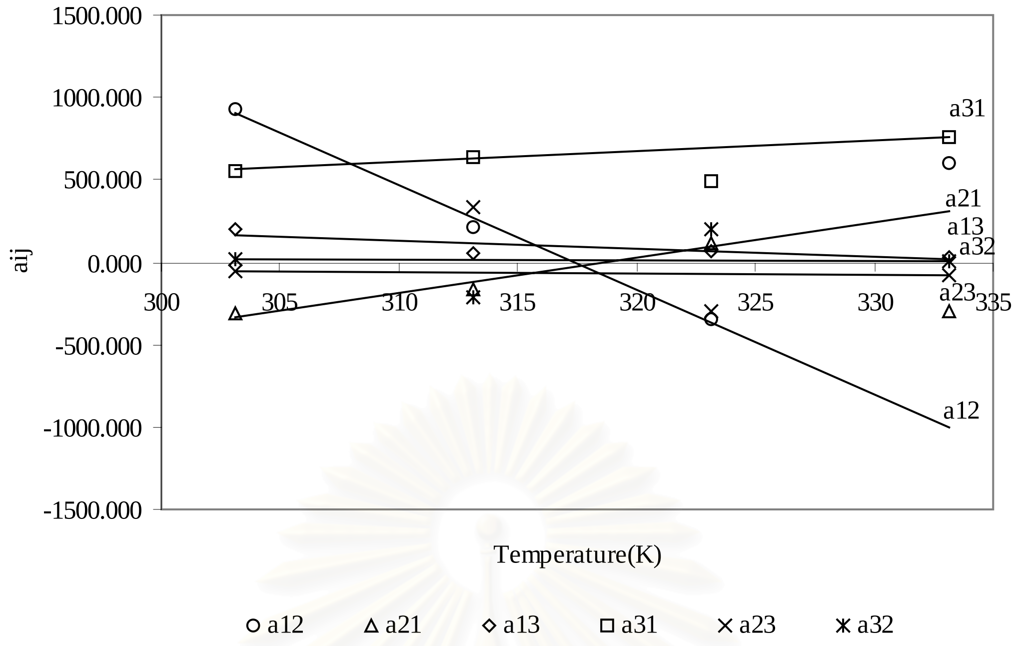


Figure 6.10 Binary Interaction Parameters (a_{ij}) of 1-hexanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

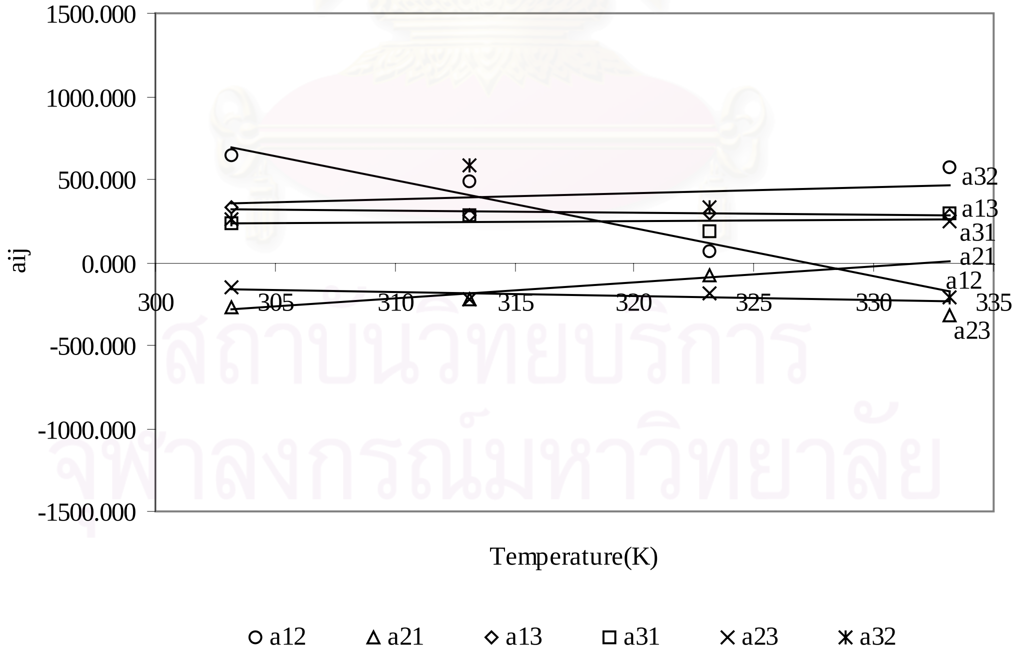


Figure 6.11 Binary Interaction Parameters (a_{ij}) of 1-octanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

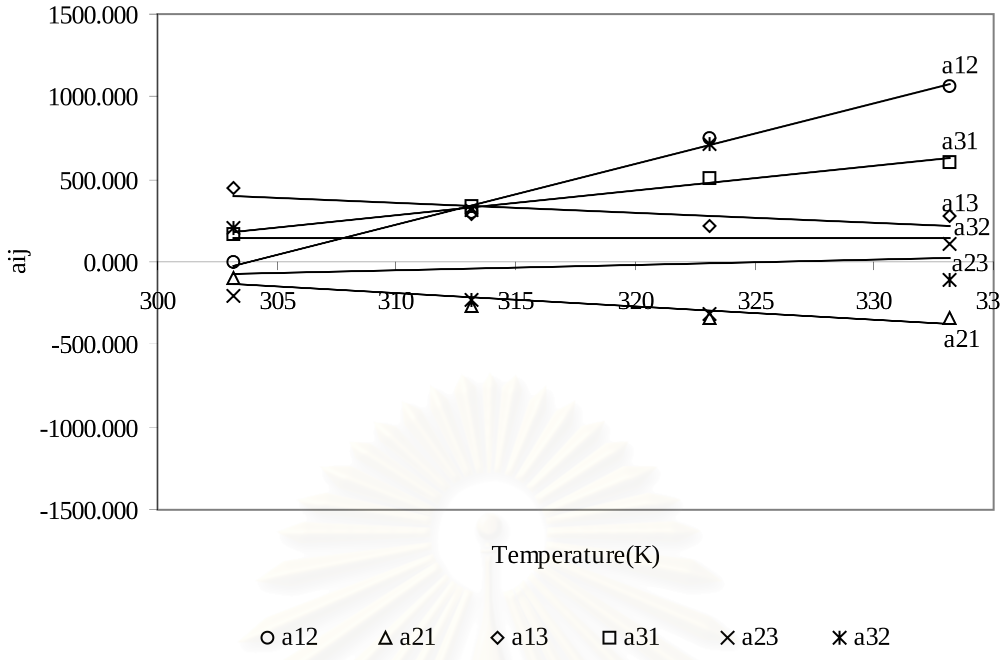


Figure 6.12 Binary Interaction Parameters (a_{ij}) of 1-decanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

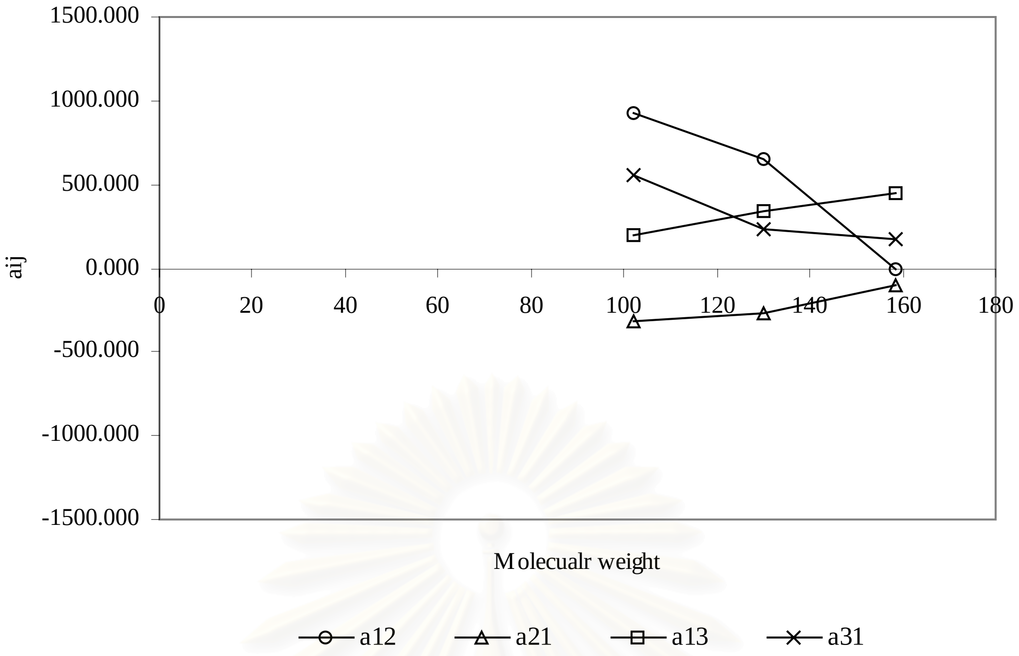


Figure 6.13 Binary Interaction Parameters (a_{ij}) for 1-hexanol, 1-octanol, and 1-decanol(1)-ethanol(2)-water(3) at 30°C

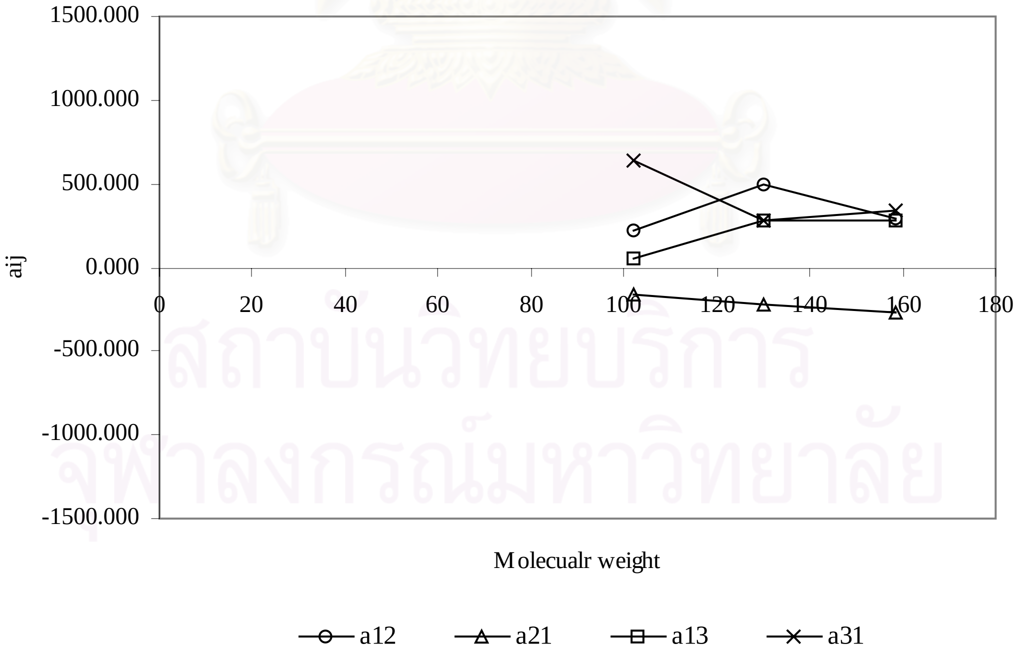


Figure 6.14 Binary Interaction Parameters (a_{ij}) for 1-hexanol, 1-octanol, and 1-decanol(1)-ethanol(2)-water(3) at 40°C

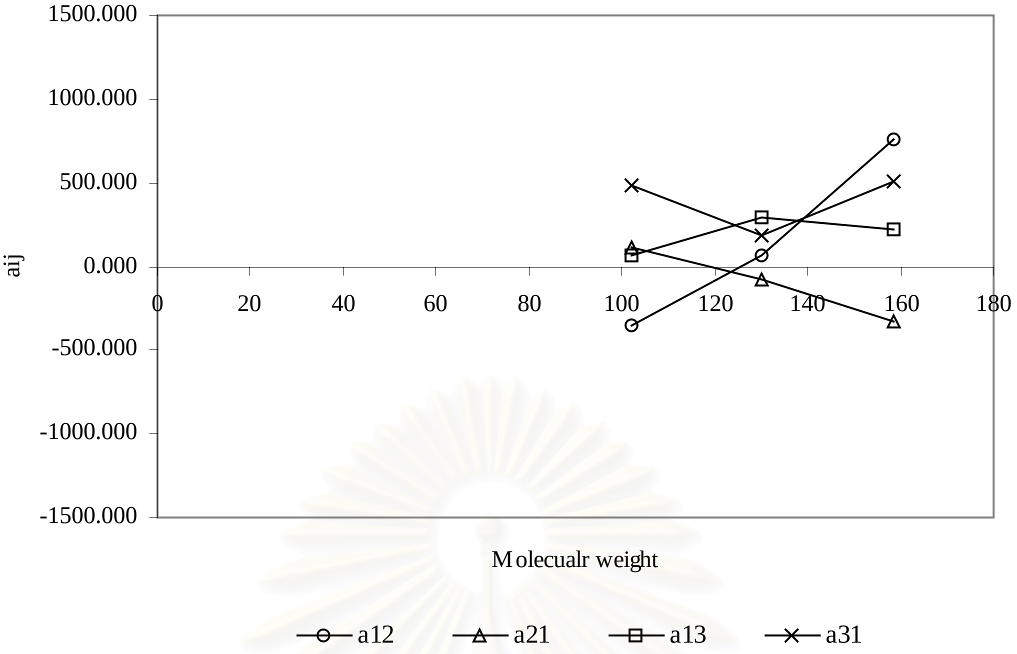


Figure 6.15 Binary Interaction Parameters (a_{ij}) for 1-hexanol, 1-octanol, and 1-decanol(1)-ethanol(2)-water(3) at 50°C

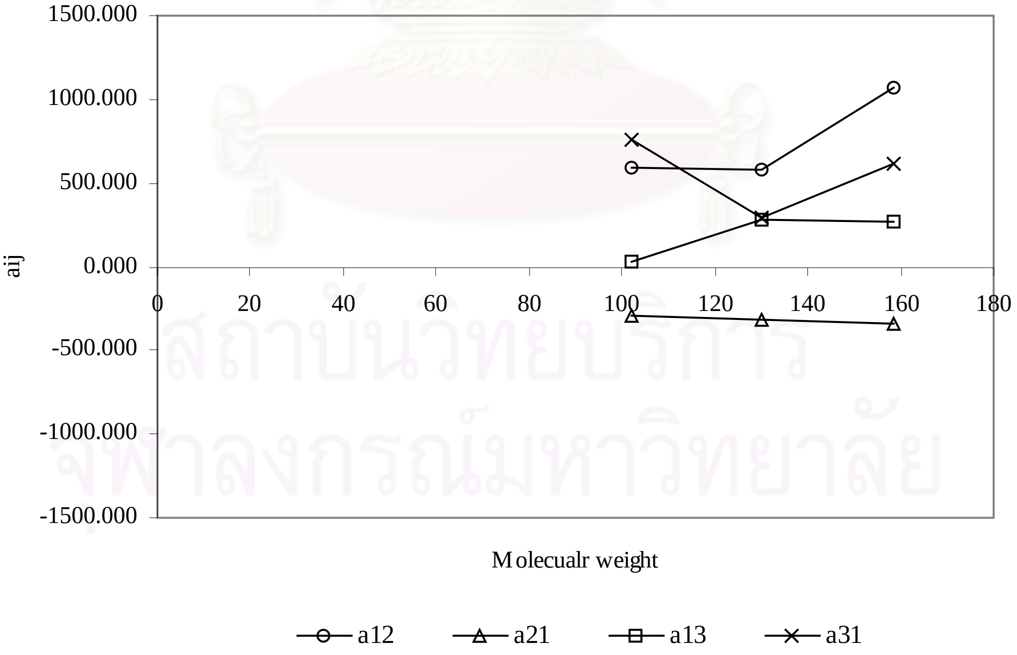


Figure 6.16 Binary Interaction Parameters (a_{ij}) for 1-hexanol, 1-octanol, and 1-decanol(1)-ethanol(2)-water(3) at 60°C

6.4 Liquid-Liquid Equilibrium by Activity Coefficient Models

The results of liquid-liquid equilibrium data obtained from the computer program of UNIQUAC and UNIFAC models were reported in the Tables F.1 to F.24 in the Appendix F. The comparison of two models with experimental data at one temperature for each interested system are shown in Figures 6.17 to 6.28. The quality of fit was calculated in terms of the percentage of the root mean square deviation (% rms) defined as follow.

$$\%\ \text{rms} = 100 \times \left(\sum_{k}^{M} \sum_{j}^{2} \sum_{i}^{3} \left(x_{ijk} - \hat{x}_{ijk} \right)^{2} / \ 6M \right)^{\frac{1}{2}}$$

The % rms are listed in Table 6.2 belows.

Table 6.2 Percentage root mean square deviation of UNIQUAC and UNIFAC models

Model	root mean square deviation (% rms) at several temperatures			
	30°C	40°C	50°C	60°C
	1-Hexanol-Ethanol-Water			
UNIQUAC	2.1203	1.0445	0.8828	1.1440
UNIFAC	3.9520	4.4247	4.3008	4.3152
	1-Octanol-Ethanol-Water			
UNIQUAC	2.0463	1.8243	0.5894	1.1829
UNIFAC	3.6840	3.0387	2.2683	4.5081
	1-Decanol-Ethanol-Water			
UNIQUAC	0.5628	0.5475	0.5371	0.7755
UNIFAC	4.2609	2.0126	4.1193	6.7655

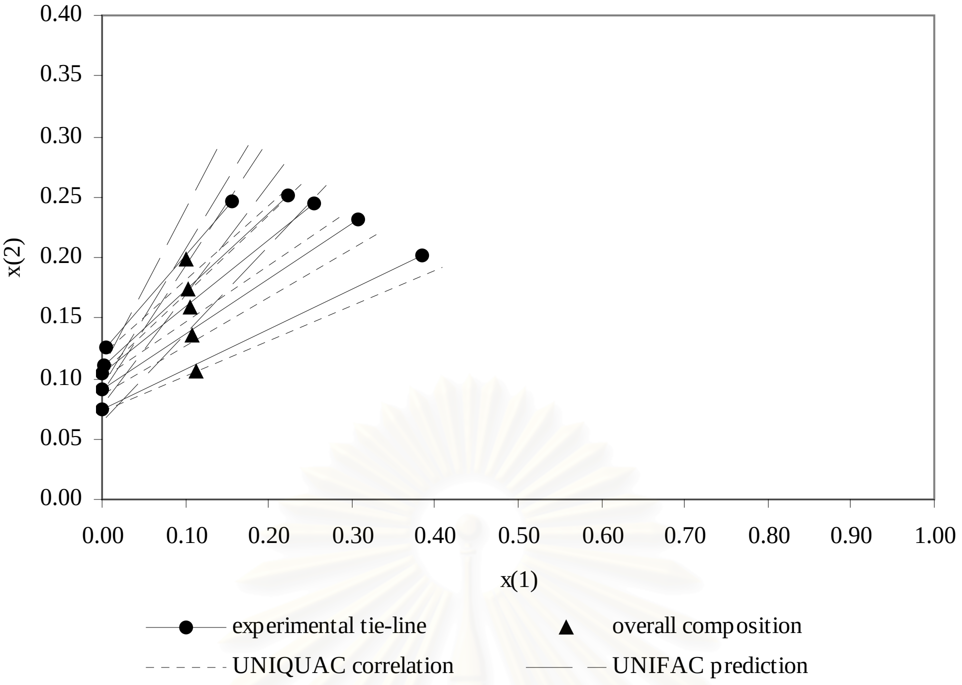


Figure 6.17 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-hexanol(1)-ethanol(2)-water(3) at 30°C

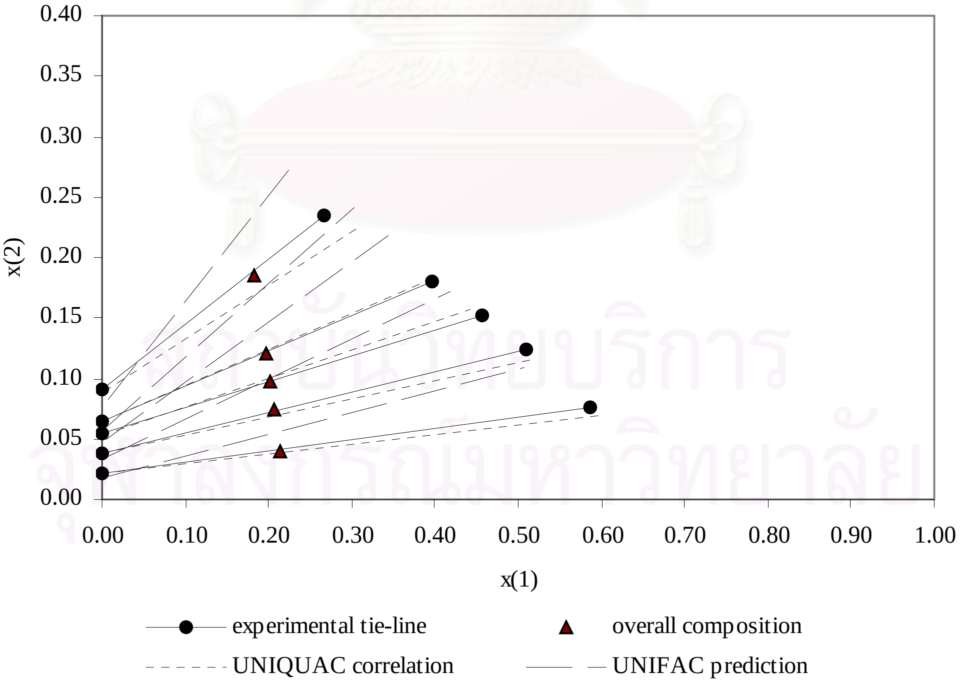


Figure 6.18 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-hexanol(1)-ethanol(2)-water(3) at 40°C

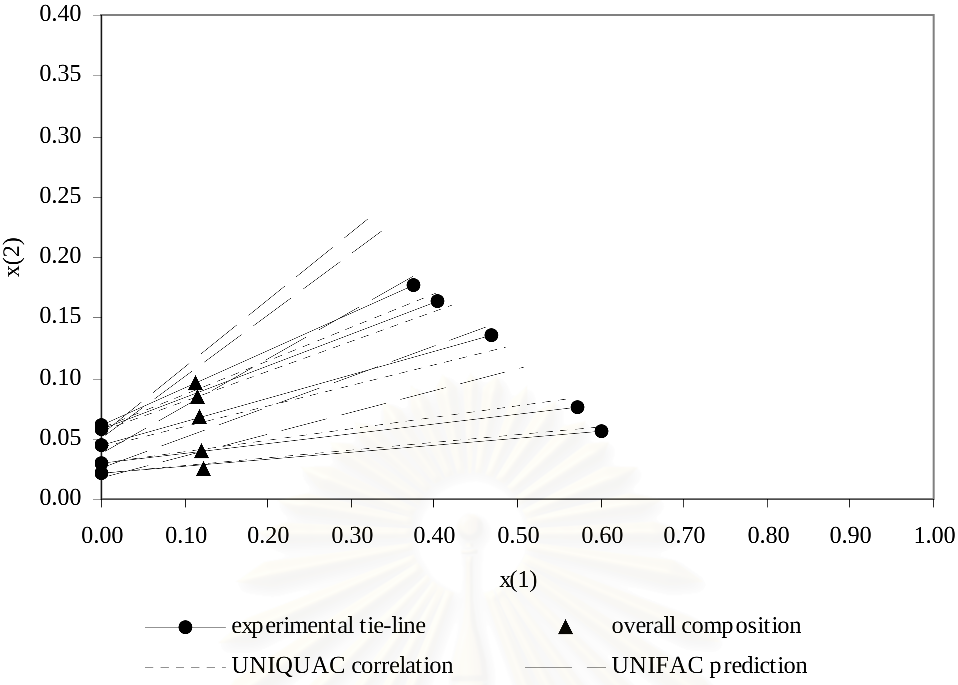


Figure 6.19 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-hexanol(1)-ethanol(2)-water(3) at 50°C

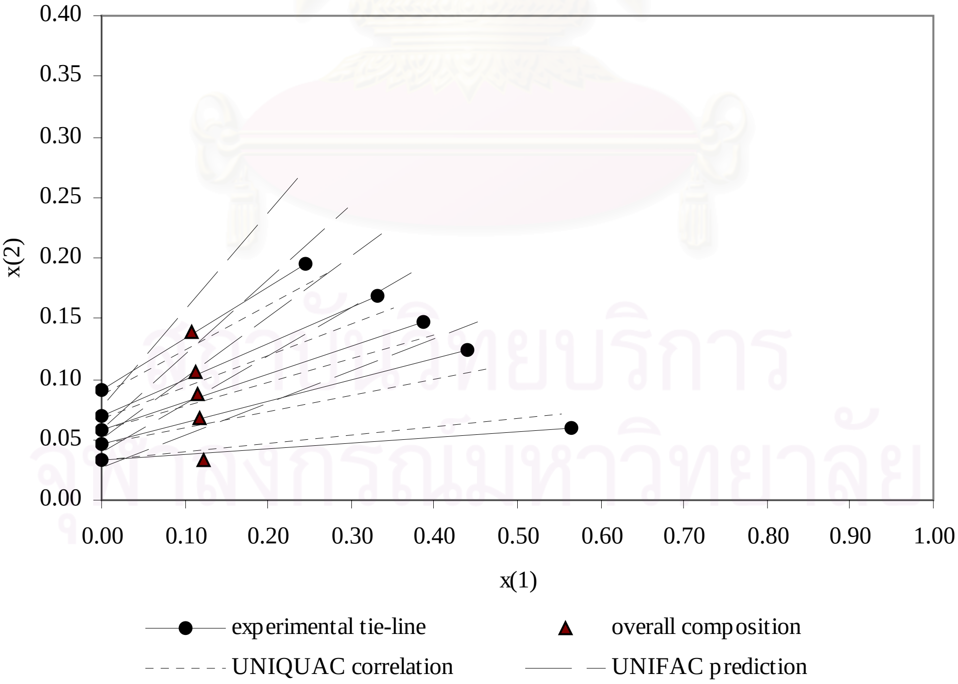


Figure 6.20 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-hexanol(1)-ethanol(2)-water(3) at 60°C

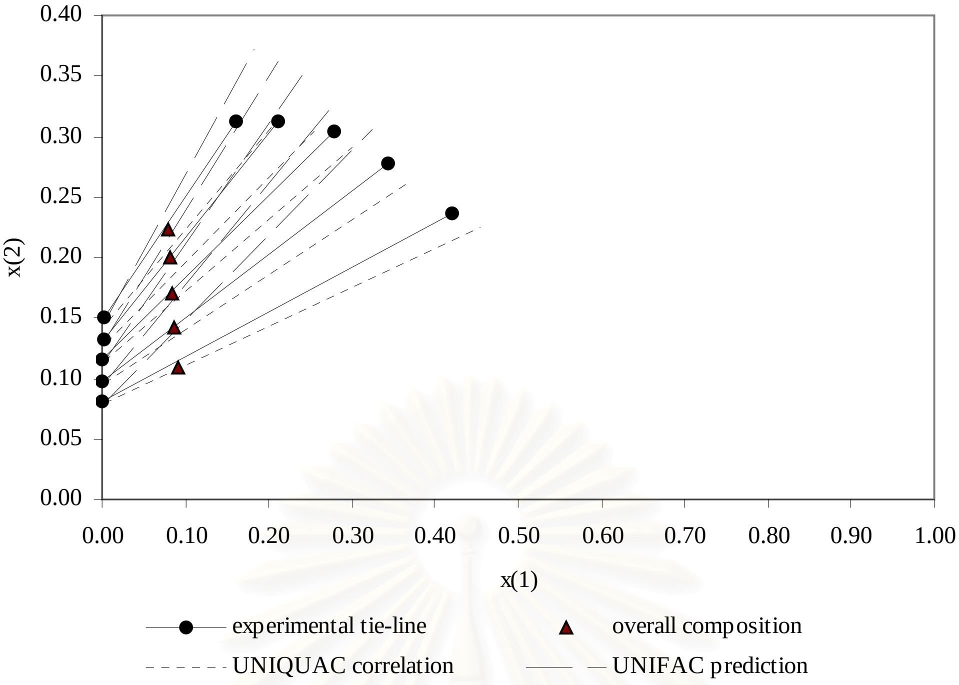


Figure 6.21 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-octanol(1)-ethanol(2)-water(3) at 30°C

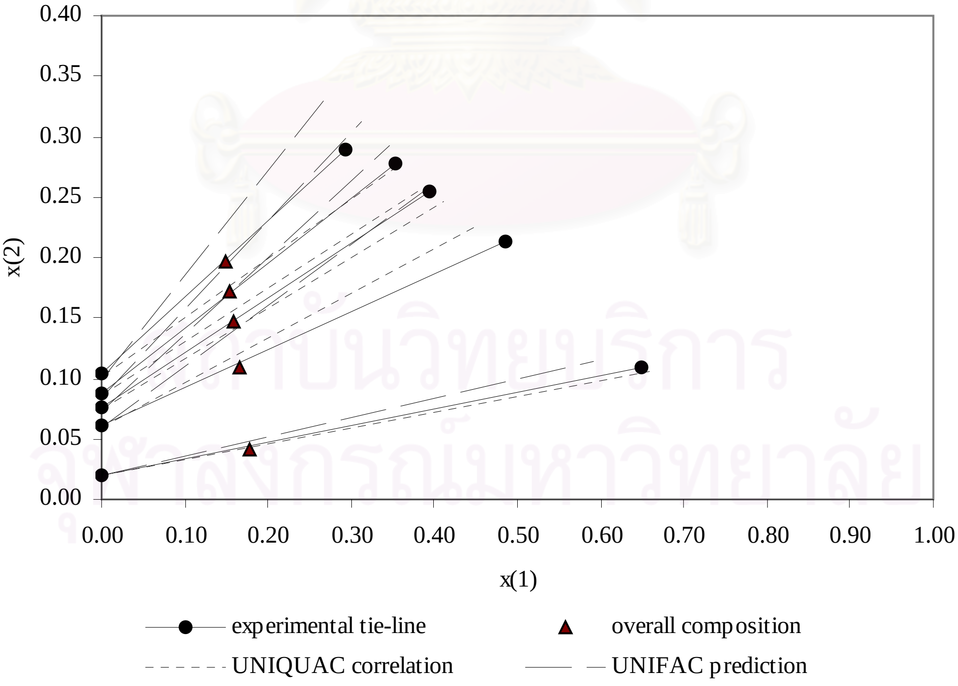


Figure 6.22 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-octanol(1)-ethanol(2)-water(3) at 40°C

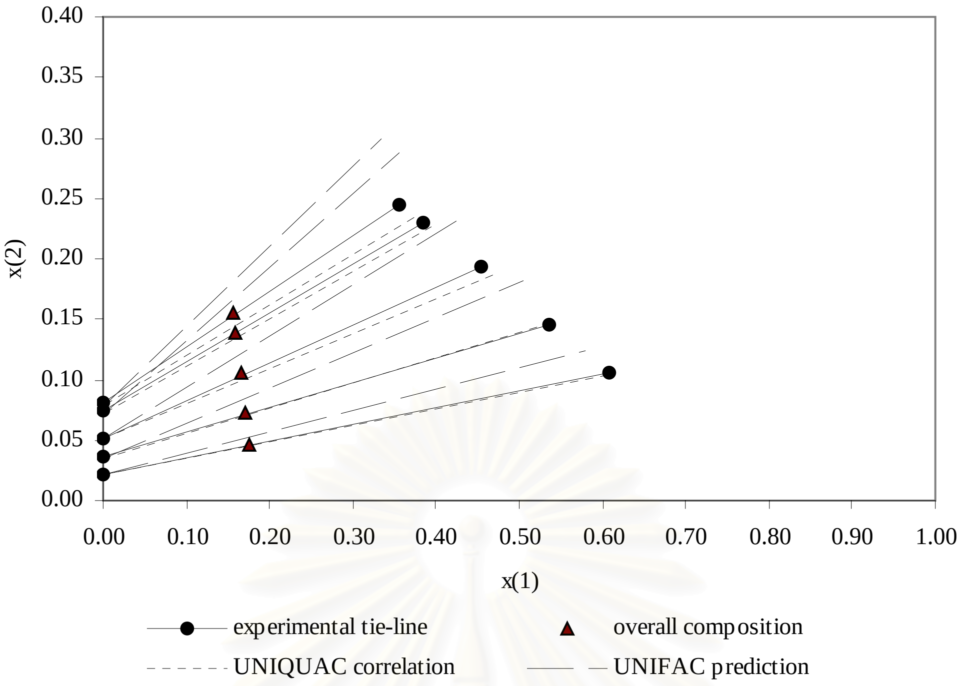


Figure 6.23 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-octanol(1)-ethanol(2)-water(3) at 50°C

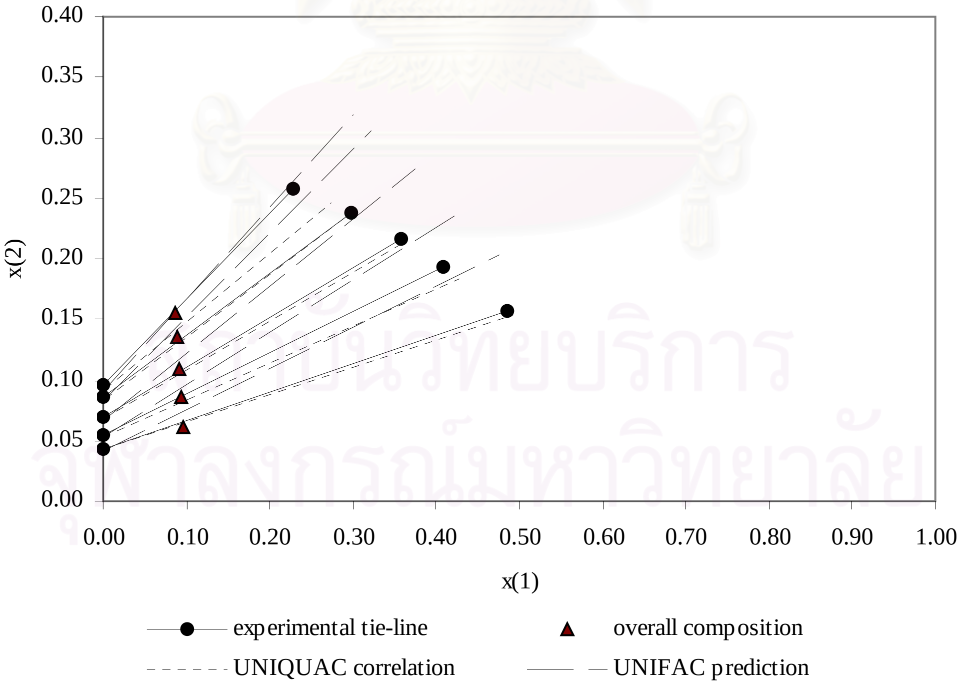


Figure 6.24 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-octanol(1)-ethanol(2)-water(3) at 60°C

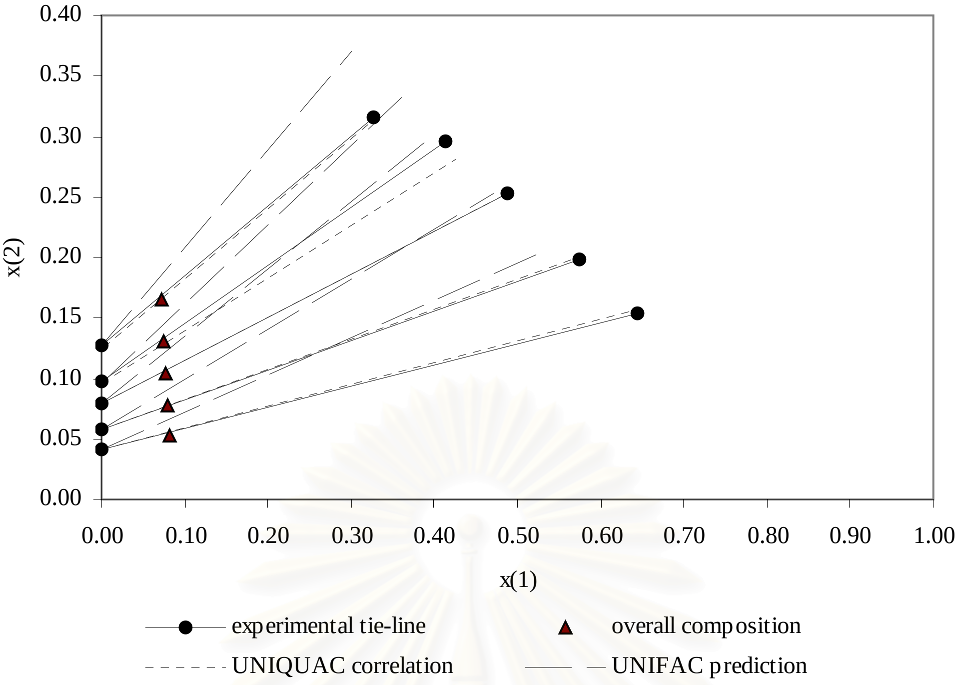


Figure 6.25 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-decanol(1)-ethanol(2)-water(3) at 30°C

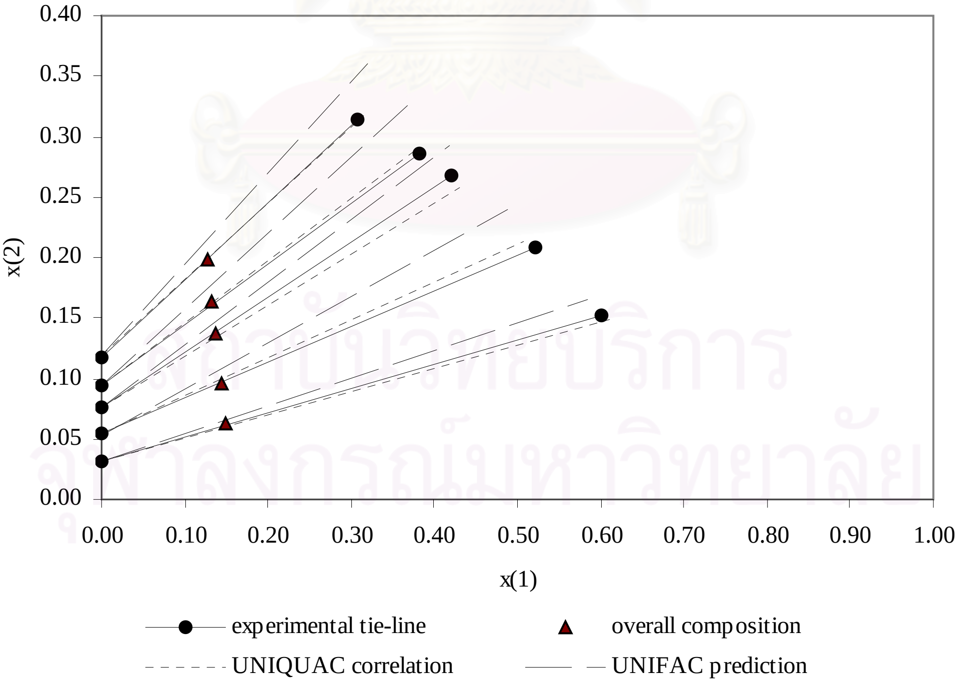


Figure 6.26 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-decanol(1)-ethanol(2)-water(3) at 40°C

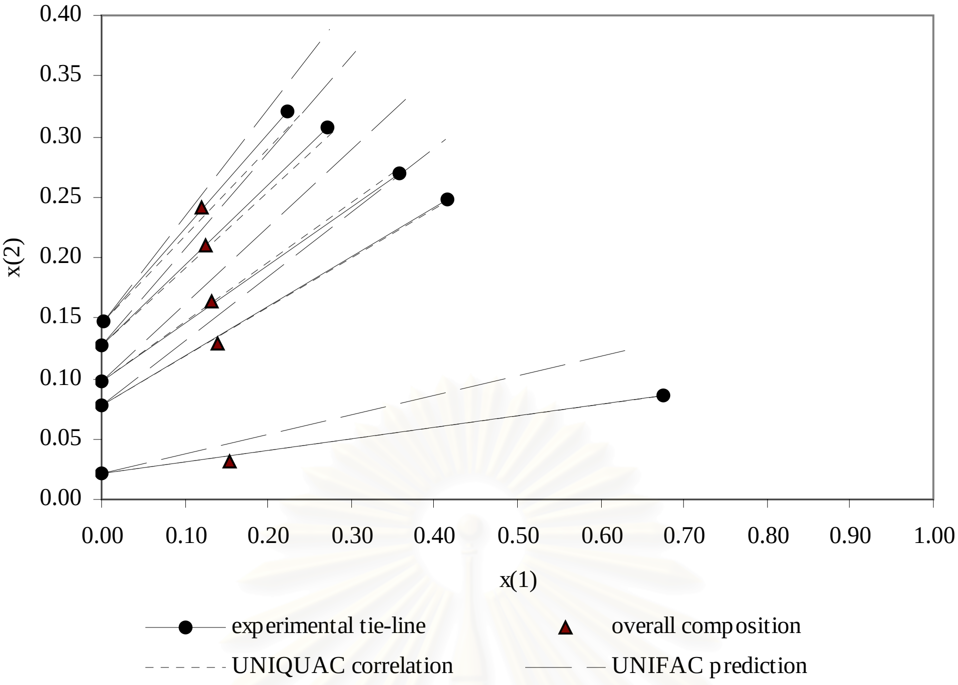


Figure 6.27 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-decanol(1)-ethanol(2)-water(3) at 50°C

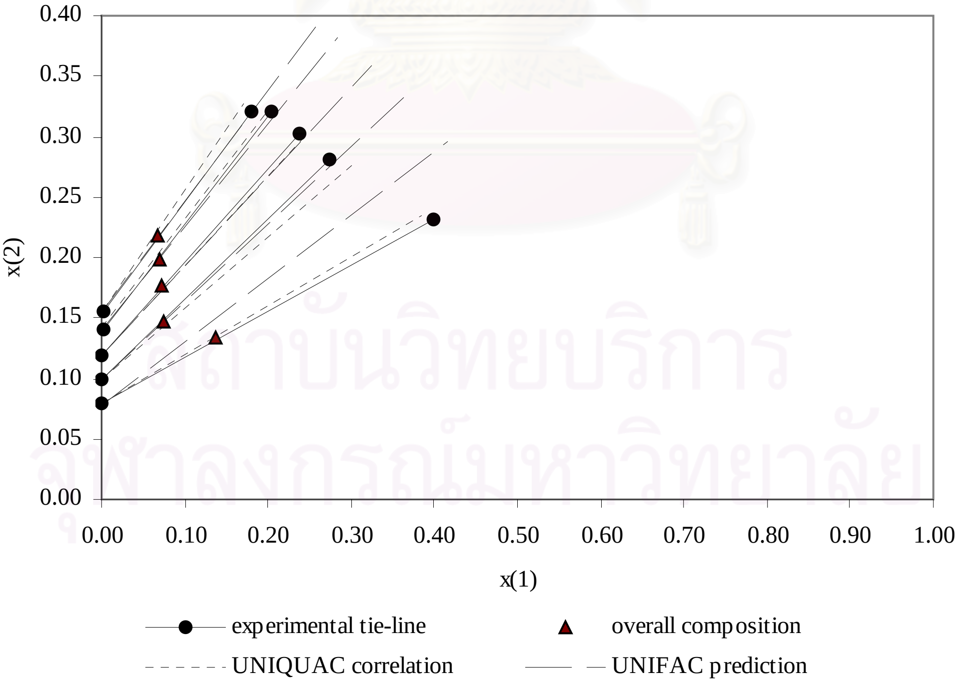


Figure 6.28 Comparison of UNIQUAC and UNIFAC models estimations of liquid-liquid Equilibrium for 1-decanol(1)-ethanol(2)-water(3) at 60°C

The results shows that the UNIQUAC can model represent the experimental data of our ternary systems well and gives much better fit than the UNIFAC model.

6.5 The UNIFAC Program

The computer program of Figure 5.4 is used to calculate liquid-liquid equilibrium data using UNIFAC model. Its accuracy is compared with the UNIFAC calculator of Bruce C.(1997) as presented in Table 6.3. Both computer programs give the same results.

Table 6.3 Comparing activity coefficient calculated from UNIFAC program in this work with activity coefficient calculated from UNIFAC calculator of Bruce C. (1997)

For the system 1-hexanol-ethanol-water			
Temperature (°C)	x	γ calculated from UNIFAC program in this work	γ calculated from UNIFAC calculator of Bruce C.
30	x(1) = 0.3	γ(1) = 1.4920	γ(1) = 1.4920
	x(2) = 0.23	γ(2) = 1.0042	γ(2) = 1.0042
	x(3) = 0.47	γ(3) = 2.0745	γ(3) = 2.0745
40	x(1) = 0.58	γ(1) = 1.1366	γ(1) = 1.1366
	x(2) = 0.08	γ(2) = 0.9976	γ(2) = 0.9976
	x(3) = 0.34	γ(3) = 2.7603	γ(3) = 2.7603

6.6 Distribution Coefficient and Relative Selectivity

All of the solvents used (1-hexanol, 1-octanol, and 1-decanol) are found to satisfy all criteria for a good solvent. Distribution coefficients for ethanol are greater than 1 as shown in Figures 6.29 to 6.32. It is also found that the distribution coefficient of 1-octanol is closed to 1-decanol, and both of them is higher than 1-hexanol at all of the tested temperature. Along with the low values of the distribution coefficients for water, lead to high values of the relative selectivity as in Figures 6.36 to 6.39. It is also presented that the relative selectivity of all solvents are more greater than 1. and the relative selectivity of 1-decanol is higher than 1-octanol and 1-hexanol, respectively.

In comparison with the distribution coefficients for ethanol and the relative selectivity of ethanol over water of all the solvents through all the range of temperature tested as illustrated by Figures 6.33 to 6.35 and Figures 6.40 to 6.42, it is found that the temperature has slightly effect on the value of the distribution coefficients and the relative selectivity.

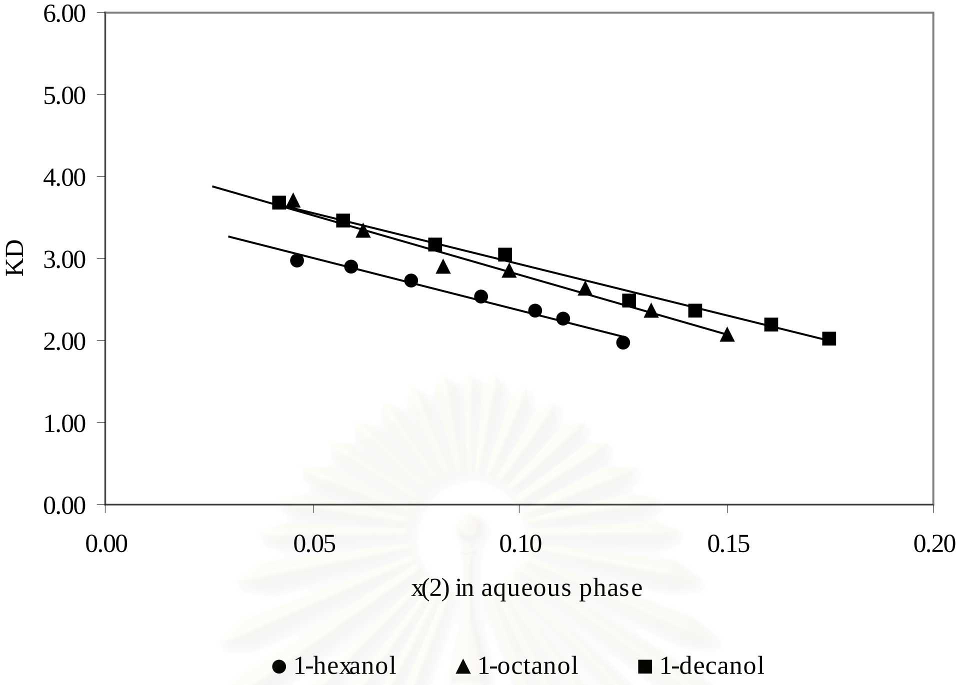


Figure 6.29 Distribution coefficient of ethanol for solvent(1)-ethanol(2)-water(3) at 30°C

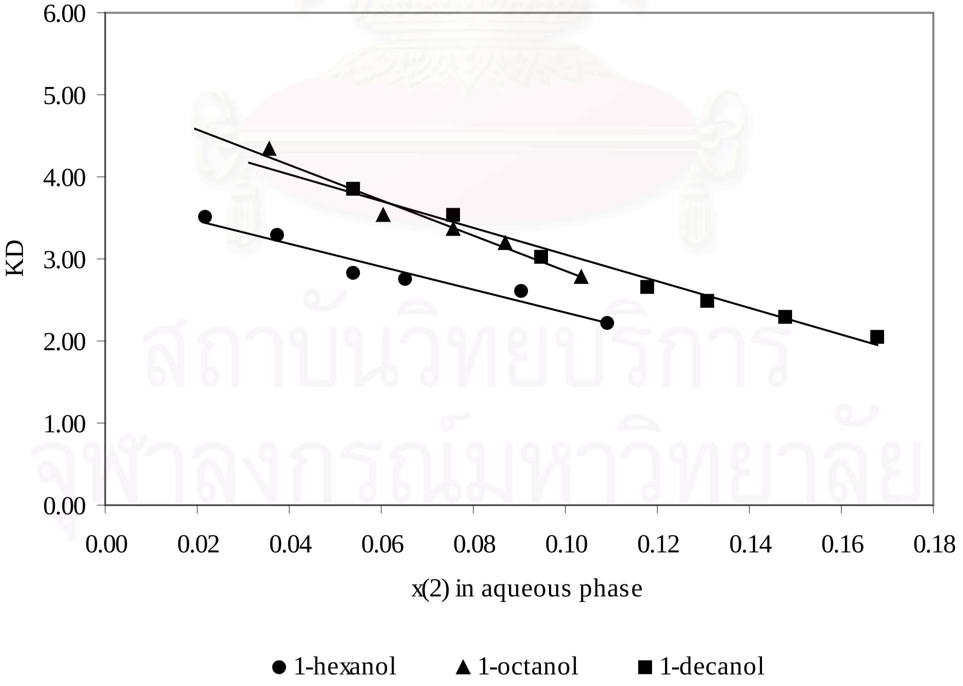


Figure 6.30 Distribution coefficient of ethanol for solvent(1)-ethanol(2)-water(3) at 40°C

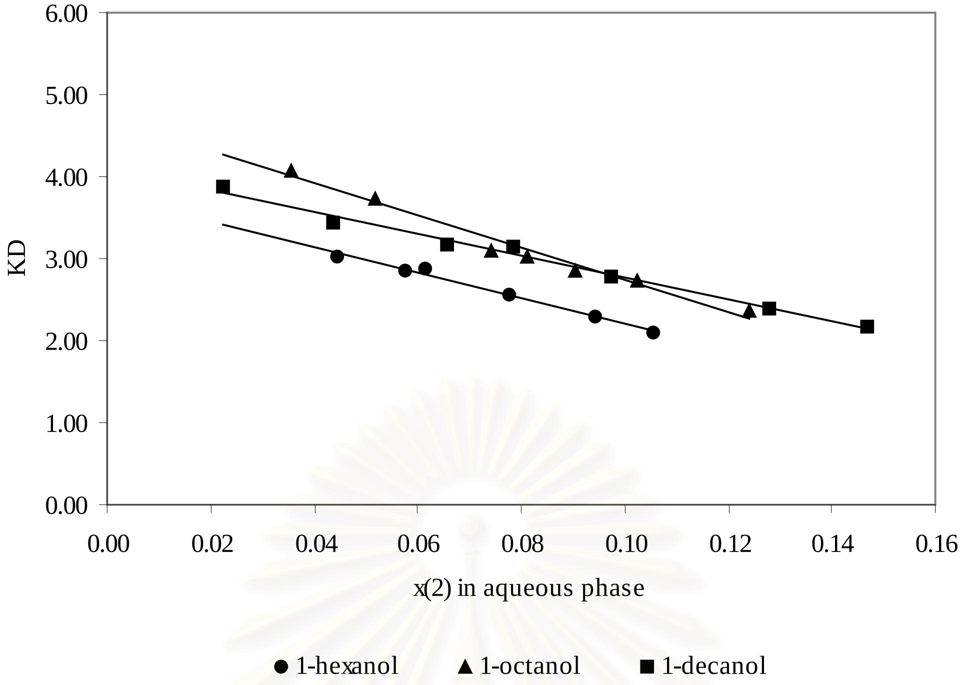


Figure 6.31 Distribution coefficient of ethanol for solvent(1)-ethanol(2)-water(3) at 50°C

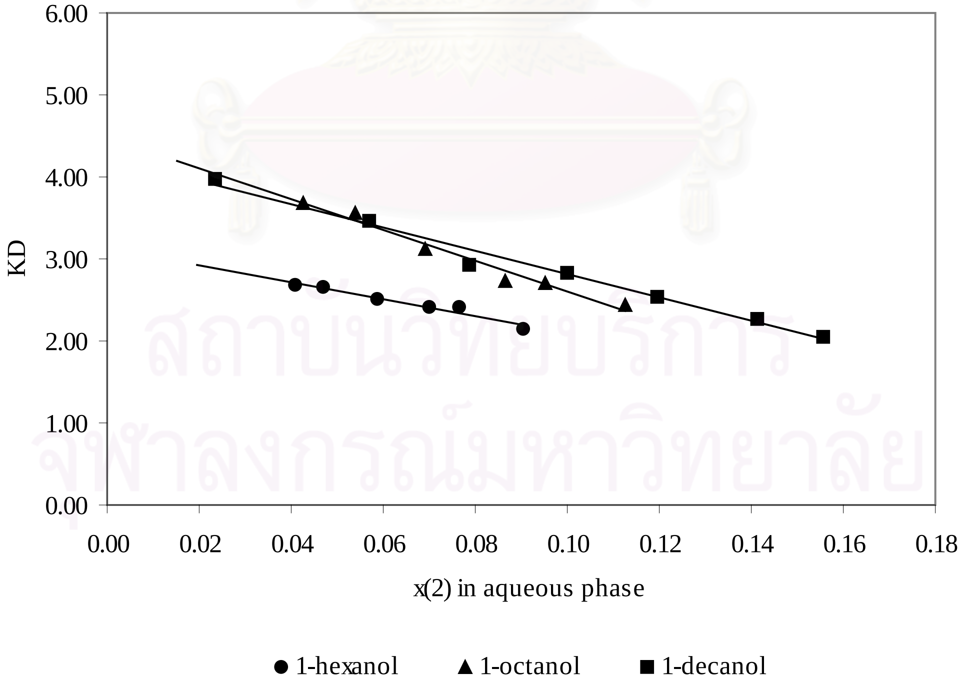


Figure 6.32 Distribution coefficient of ethanol for solvent(1)-ethanol(2)-water(3) at 60°C

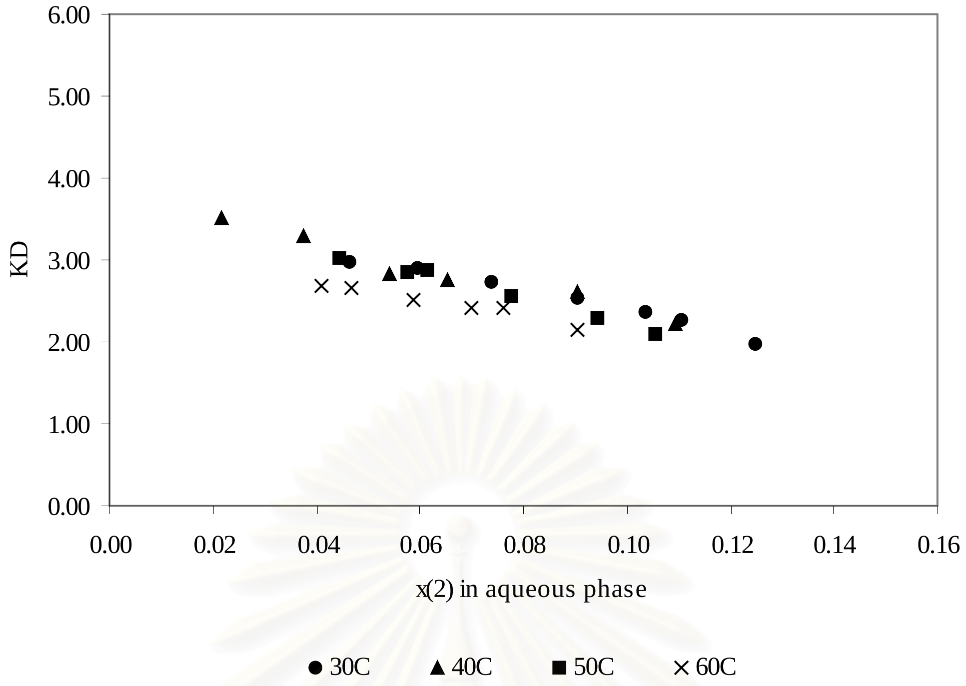


Figure 6.33 Distribution coefficient of ethanol for 1-hexanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

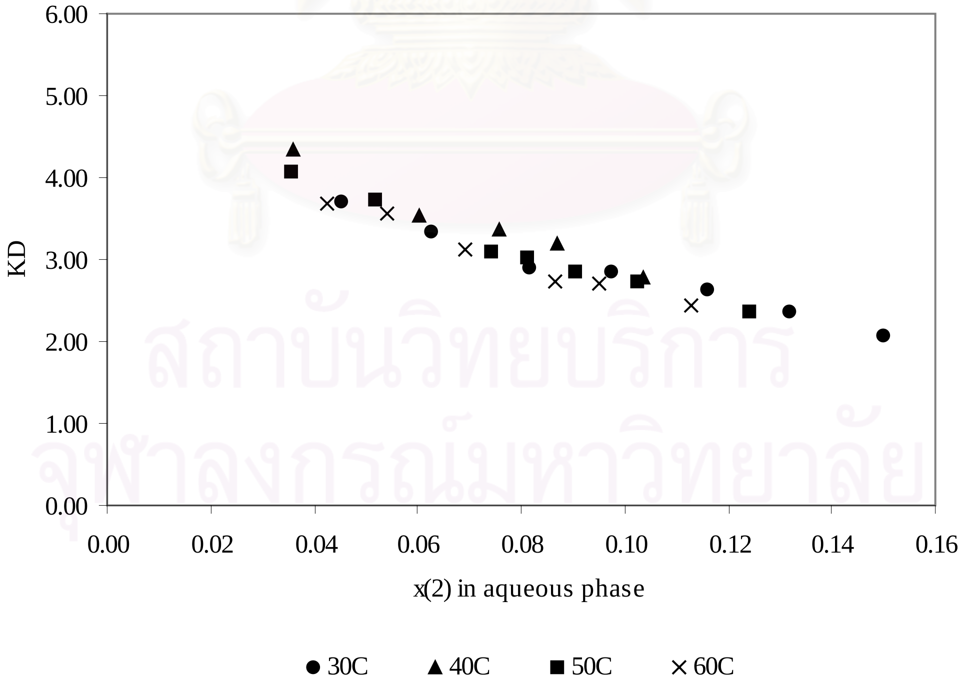


Figure 6.34 Distribution coefficient of ethanol for 1-octanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

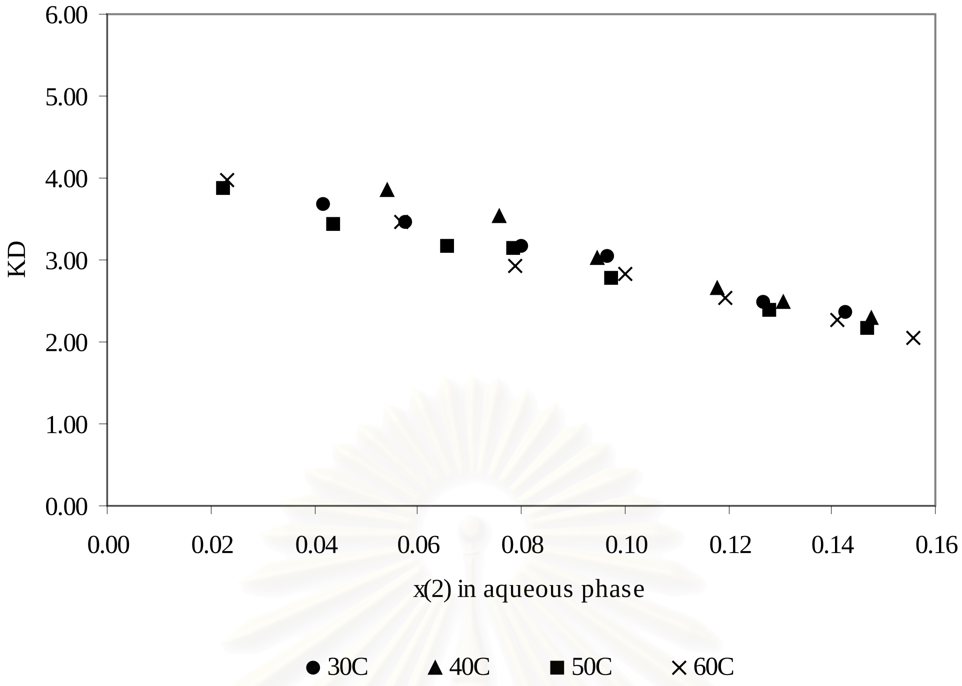


Figure 6.35 Distribution coefficient of ethanol for 1-decanol(1)-ethanol(2)-water(3) at 30, 40, 50, and 60°C

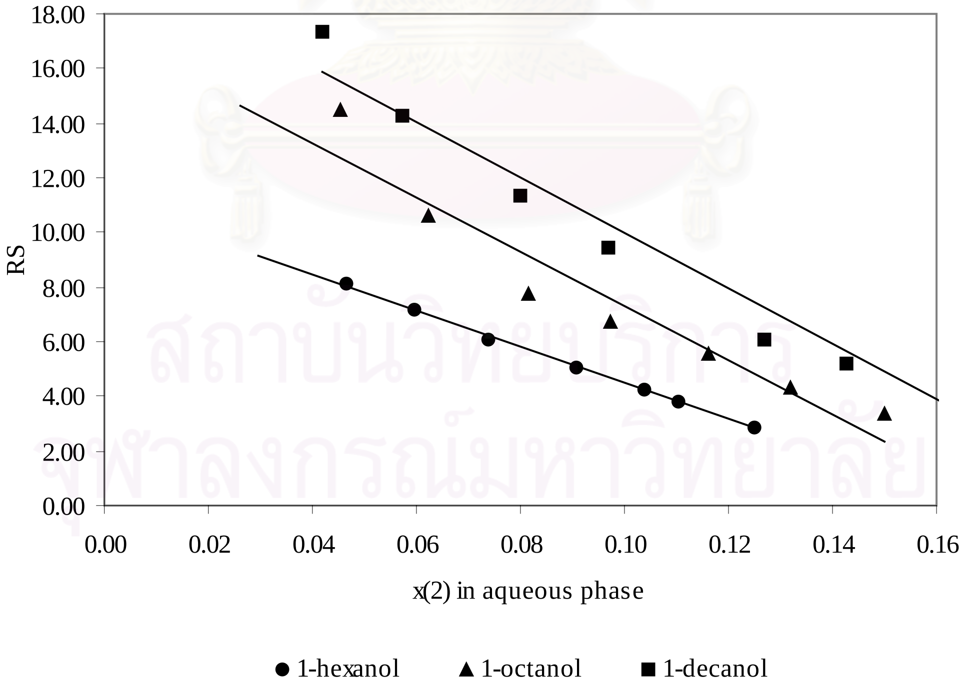


Figure 6.36 Relative selectivity for ethanol over water for solvent(1)-ethanol(2)-water(3) at 30°C

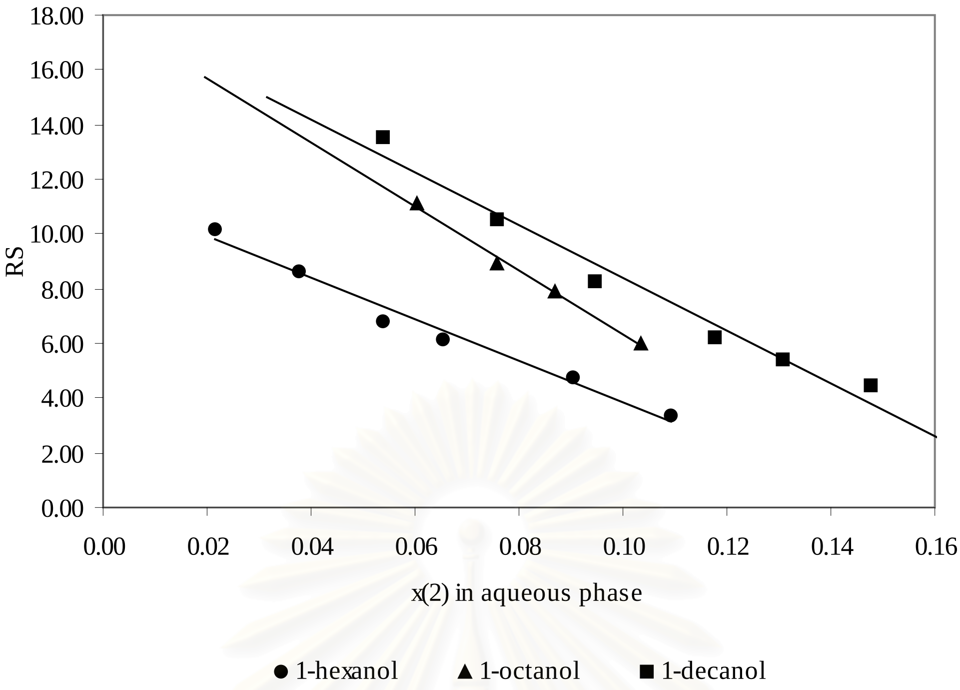


Figure 6.37 Relative selectivity for ethanol over water for solvent(1)-ethanol(2)-water(2) at 40°C

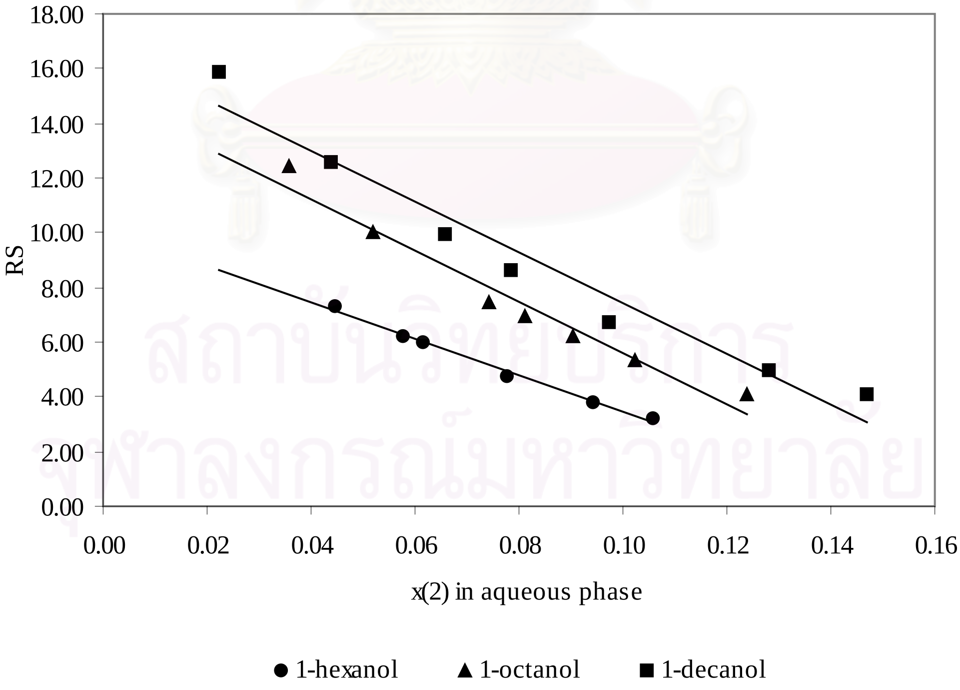


Figure 6.38 Relative selectivity for ethanol over water for solvent(1)-ethanol(2)-water(3) at 50°C

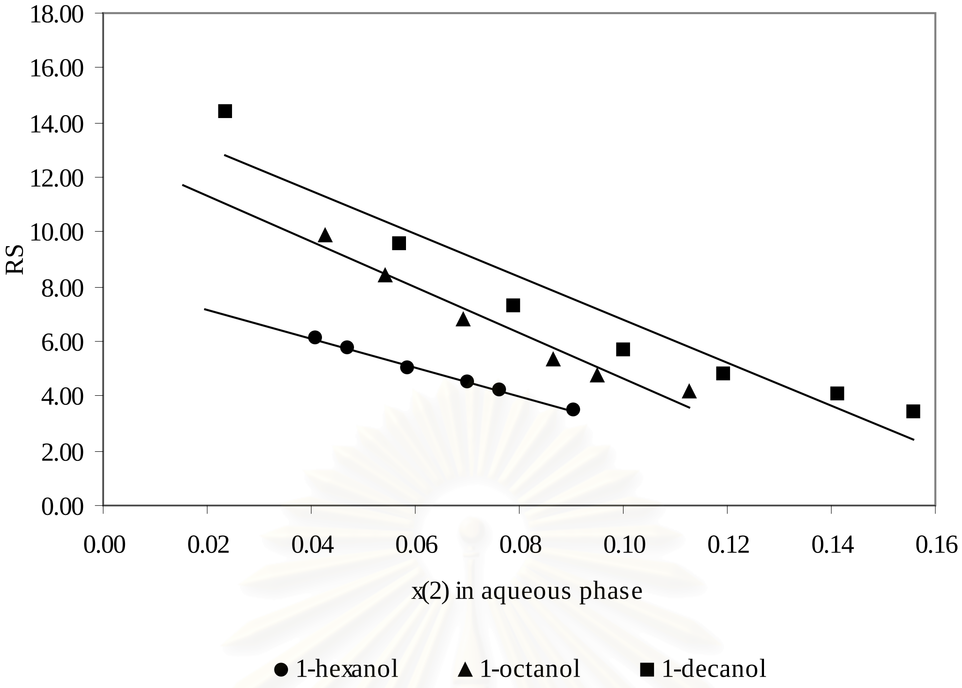


Figure 6.39 Relative selectivity for ethanol over water for solvent(1)-ethanol(2)-water(3) at 60°C Figure

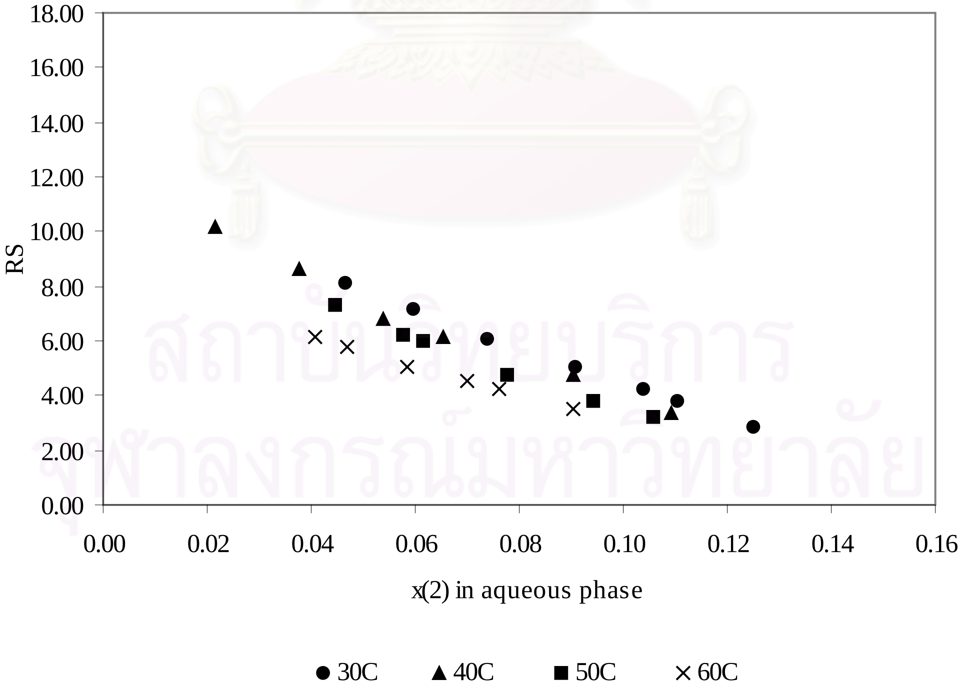


Figure 6.40 Relative selectivity for ethanol over water for 1-hexanol(1)-ethanol(2)-water (3) at 30, 40, 50, and 60°C

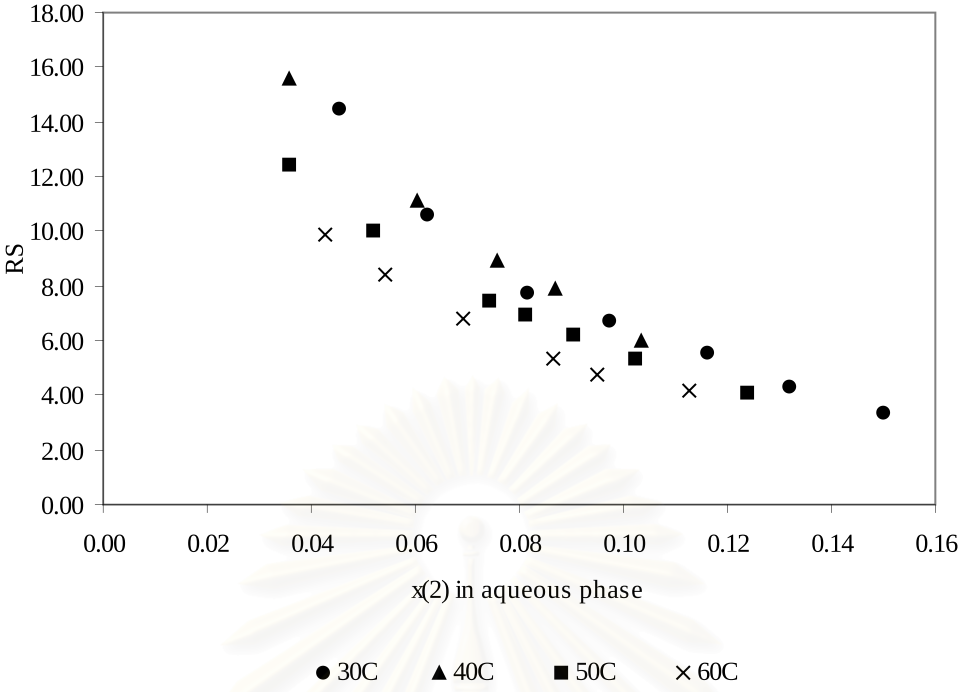


Figure 6.41 Relative selectivity for ethanol over water for 1-octanol(1)-ethanol(2)-water (3) at 30, 40, 50, and 60°C

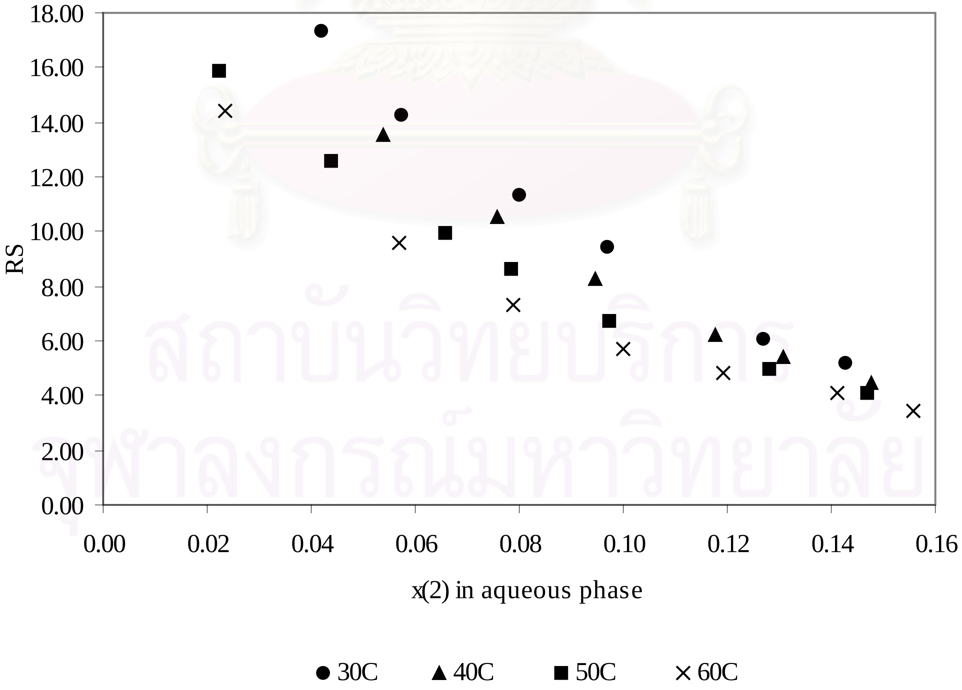


Figure 6.42 Relative selectivity for ethanol over water for 1-decanol(1)-ethanol(2)-water (3) at 30, 40, 50, and 60°C

CHAPTER VII

CONCLUSION AND RECOMMENDATION

7.1 Conclusion

1. The obtained three ternary liquid-liquid equilibria of (i) 1-hexanol-ethanol-water, (ii) 1-octanol-ethanol-water, and (iii) 1-decanol-ethanol-water at the temperatures range from 30 to 60°C in this research can be used for liquid-liquid extraction process calculation .
2. The solubility of solvent (1-hexanol, 1-octanol, and 1-decanol) in water is increased with the increasing temperature.
3. The solubility of solvent in water is decreased with the increasing molecular size of straight chain solvents.
4. The UNIQUAC model has been successfully applied to all liquid-liquid equilibria systems studied.
5. The binary interaction parameter (a_{ij}) of UNIQUAC model are linear function of temperature and dependent on molecular weight of solvent used. These parameters can be further used to predict liquid-liquid equilibria data for studied mixtures at other conditions of operation and to predict the equilibrium data for other straight chain alcohols as solvent in the extraction of ethanol solutions.

6. All of solvents used are found to satisfy all criteria for a good solvent because of the distribution coefficients of ethanol are greater than 1 and the relative selectivity are much greater than 1.
7. The temperature dependence of the distribution coefficients and the relative selectivity over the temperature range from 30 to 60°C are relatively small.

7.2 Recommendation

Further work to obtain liquid-liquid equilibrium of ternary system of alcohol solvent of larger molecular size is recommended.

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APPENDICES

APPENDIX A

PHYSICAL PROPERTIES OF PURE CHEMICALS

Table A.1 Physical properties of pure chemicals

Name	Formula	Formula weight	Form and color	Specific gravity	Melting point, °C	Boiling Point, °C	Solubility in 100 parts		
							Water	Alcohol	Ether
1-Hexanol	$CH_3(CH_2)_4CH_2OH$	102.17	col. lq.	$0.820^{20/20}$	-51.6	157.2	0.6^{20}	∞	∞
1-Octanol	$CH_3(CH_2)_6CH_2OH$	130.22	col. lq.	$0.827^{20/4}$	-16	194-5	0.054^{25}	∞	∞
1-Decanol	$CH_3(CH_2)_8CH_2OH$	158.28	col. oil	$0.830^{20/4}$	7	232.9	i.	s.	
1-Ethanol	CH_3CH_2OH	46.07	col. lq.	$0.789^{20/4}$	-112	78.4	∞	∞	∞
Water	H_2O	18.016	col. lq.	1.00	0	100		∞	sl. s.

Abbreviation:	col.	colorless
	i.	insoluble
	lq.	liquid
	s.	soluble
	sl.	slightly
	∞	infinitely

(Liley et al., 1997: 2-1 – 2-47)

APPENDIX B

UNIQUAC AND UNIFAC GROUP PARAMETERS

Table B.1 Group volume parameters (R_k) and group area parameters (Q_k)

Main group	Subgroup	k	R_k	Q_k	Examples of molecules and their constituent groups	
1 “CH_2”	CH_3	1	0.9011	0.848	n-Butane:	$2CH_3$, $2CH_2$
	CH_2	2	0.6744	0.540	Isobutane:	$3CH_3$, 1CH
	CH	3	0.4469	0.228	2,2-Dimethyl propane:	$4CH_3$, 1C
	C	4	0.2195	0.000		
3 “ACH” (AC = aromatic carbon)	ACH	10	0.5313	0.400	Benzene:	6ACH
4 “$ACCH_2$”	$ACCH_3$	12	1.2663	0.968	Toluene:	5ACH, $1ACCH_3$
	$ACCH_2$	13	1.0396	0.660	Ethylbenzene:	$1CH_3$, 5ACH, $1ACCH_2$
5 “OH”	OH	15	1.0000	1.200	Ethanol:	$1CH_3$, $1CH_2$, 1OH
7 “H_2O”	H_2O	17	0.9200	1.400	Water:	$1H_2O$
9 “CH_2CO”	CH_3CO	19	1.6724	1.488	Acetone:	$1CH_3CO$, $1CH_3$
	CH_2CO	20	1.4457	1.180	3-Pentanone:	$2CH_3$, $1CH_2CO$, $1CH_2$
13 “CH_2O”	CH_3O	25	1.1450	1.088	Dimethyl ether:	$1CH_3$, $1CH_3O$
	CH_2O	26	0.9183	0.780	Diethyl ether:	$2CH_3$, $1CH_2$, $1CH_2O$
	CH-O	27	0.6908	0.468	Diisopropyl ether:	$4CH_3$, 1CH, CH-O
15 “CNH”	CH_3NH	32	1.4337	1.244	Dimethylamine:	$1CH_3$, $1CH_3NH$
	CH_2NH	33	1.2070	0.936	Diethylamine:	$2CH_3$, $1CH_2$, $1CH_2NH$
	CHNH	34	0.9795	0.624	Diisopropyl amine:	$4CH_3$, 1CH, 1CHNH
19 “CCN”	CH_3CN	41	1.8701	1.724	Acetonitrile:	$1CH_3CN$
	CH_2CN	42	1.6434	1.416	Propionitrile:	$1CH_3$, $1CH_2CN$

(Smith, J. M., Van Ness, H. C., and Abbott, M. M, 1996: 742)

Table B.2 Group interaction parameters (a_{mn}) in kelvins

	1	3	4	5	7	9	13	15	19
1 CH_2	0.00	61.13	76.50	986.50	1,318.00	476.40	251.50	255.70	597.00
3 ACH	-11.12	0.00	167.00	636.10	903.80	25.77	32.14	122.80	212.50
4 $ACCH_2$	-69.70	- 146.80	0.00	803.20	5,695.00	- 52.10	213.10	-49.29	6,096.00
5 OH	156.40	89.60	25.82	0.00	353.50	84.00	28.06	42.70	6.712
7 H_2O	300.00	362.30	377.60	-229.10	0.00	-195.40	540.50	168.00	112.60
9 CH_2CO	26.76	140.10	365.80	164.50	472.50	0.00	-103.60	-174.20	481.70
13 CH_2O	83.36	52.13	65.69	237.70	-314.70	191.10	0.00	251.50	-18.51
15 CNH	65.33	-22.31	223.00	-150.00	-448.20	394.60	-56.08	0.00	147.10
19 CCN	24.82	-22.97	-138.40	185.40	242.80	-287.50	38.81	-108.50	0.00

(Smith et al., 1996: 744)

APPENDIX C

EXPERIMENTAL DATA

Table C.1 Experimental binodal curve data for the system 1-hexanol(1)-ethanol(2)-water(3) at 30°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3292	0.1415	0.2443	0.6142	1.3755
0.0000	0.0207	0.9793	1.3325	0.1863	0.2513	0.5625	1.3797
0.0000	0.0346	0.9654	1.3345	0.2314	0.2506	0.5180	1.3835
0.0000	0.0439	0.9561	1.3358	0.2884	0.2378	0.4738	1.3877
0.0000	0.0531	0.9469	1.3372	0.3527	0.2157	0.4316	1.3918
0.0000	0.0646	0.9354	1.3388	0.4314	0.1804	0.3881	1.3959
0.0000	0.0799	0.9201	1.3408	0.5139	0.1383	0.3478	1.3995
0.0000	0.0983	0.9017	1.3432	0.7300	0.0000	0.2700	1.4070
0.0000	0.1055	0.8945	1.3440	0.8358	0.0000	0.1642	1.4087
0.0070	0.1289	0.8641	1.3482	0.9021	0.0000	0.0979	1.4098
0.0217	0.1528	0.8255	1.3540				

Table C.2 Experimental tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 30°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0298	0.9702	1.3338	0.6003	0.0830	0.3167	1.4025
0.0000	0.0466	0.9534	1.3362	0.5139	0.1383	0.3478	1.3995
0.0000	0.0596	0.9404	1.3381	0.4452	0.1734	0.3814	1.3965
0.0000	0.0738	0.9262	1.3400	0.3854	0.2011	0.4136	1.3935
0.0000	0.0906	0.9094	1.3422	0.3088	0.2308	0.4604	1.3890
0.0000	0.1037	0.8963	1.3438	0.2558	0.2451	0.4991	1.3853
0.0015	0.1105	0.8880	1.3449	0.2231	0.2507	0.5262	1.3828
0.0058	0.1250	0.8692	1.3475	0.1553	0.2464	0.5982	1.3768

Table C.3 Experimental binodal curve data for the system 1-hexanol(1)-ethanol(2)-water(3) at 40°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3280	0.1725	0.2439	0.5837	1.3762
0.0000	0.0216	0.9784	1.3311	0.2166	0.2447	0.5387	1.3805
0.0000	0.0309	0.9691	1.3324	0.2408	0.2409	0.5183	1.3823
0.0000	0.0400	0.9600	1.3339	0.2812	0.2317	0.4870	1.3850
0.0000	0.0508	0.9492	1.3345	0.3438	0.1962	0.4600	1.3881
0.0000	0.0597	0.9403	1.3359	0.3842	0.1868	0.4289	1.3904
0.0000	0.0783	0.9217	1.3386	0.4264	0.1663	0.4072	1.3923
0.0000	0.0998	0.9002	1.3411	0.4667	0.1477	0.3856	1.3944
0.0111	0.1246	0.8643	1.3463	0.5049	0.1269	0.3681	1.3966
0.0300	0.1517	0.8183	1.3505	0.5704	0.0879	0.3417	1.3990
0.0779	0.1992	0.7228	1.3662	0.6630	0.0176	0.3194	1.4020
0.1103	0.2227	0.6669	1.3705	0.7552	0.0000	0.2448	1.4040
0.1446	0.2381	0.6173	1.3741	0.8866	0.0000	0.1134	1.4059

Table C.4 Experimental tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 40°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0216	0.9784	1.3311	0.5859	0.0761	0.3380	1.3995
0.0000	0.0376	0.9624	1.3335	0.5104	0.1236	0.3659	1.3968
0.0000	0.0539	0.9461	1.3350	0.4571	0.1522	0.3907	1.3939
0.0000	0.0652	0.9348	1.3367	0.3976	0.1804	0.4221	1.3910
0.0000	0.0903	0.9097	1.3400	0.2663	0.2351	0.4986	1.3840
0.0043	0.1093	0.8864	1.3431	0.1725	0.2439	0.5837	1.3762

Table C.5 Experimental binodal curve data for the system 1-hexanol(1)-ethanol(2)-water(3) at 50°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3260	0.2020	0.2223	0.5757	1.3751
0.0000	0.0222	0.9778	1.3291	0.2362	0.2170	0.5467	1.3789
0.0000	0.0314	0.9686	1.3305	0.2767	0.2059	0.5175	1.3812
0.0000	0.0408	0.9592	1.3318	0.3142	0.1966	0.4892	1.3833
0.0000	0.0511	0.9489	1.3332	0.3431	0.1894	0.4674	1.3848
0.0000	0.0615	0.9385	1.3345	0.3914	0.1702	0.4384	1.3874
0.0000	0.0827	0.9173	1.3370	0.4538	0.1400	0.4063	1.3905
0.0000	0.1032	0.8968	1.3391	0.5129	0.1187	0.3685	1.3926
0.0112	0.1111	0.8777	1.3420	0.6782	0.0000	0.3218	1.3990
0.0293	0.1360	0.8347	1.3441	0.7851	0.0000	0.2149	1.4005
0.0547	0.1617	0.7836	1.3464	0.8886	0.0000	0.1114	1.4020
0.1431	0.2161	0.6408	1.3700	0.8903	0.0000	0.1097	1.4021
0.1610	0.2188	0.6202	1.3714	0.9375	0.0000	0.0625	1.4025

Table C.6 Experimental tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 50°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0222	0.9778	1.3291	0.6007	0.0556	0.3437	1.3960
0.0000	0.0301	0.9699	1.3303	0.5723	0.0760	0.3517	1.3949
0.0000	0.0445	0.9555	1.3323	0.4678	0.1349	0.3973	1.3910
0.0000	0.0575	0.9425	1.3340	0.4035	0.1644	0.4322	1.3880
0.0000	0.0615	0.9385	1.3345	0.3747	0.1769	0.4484	1.3865
0.0000	0.0776	0.9224	1.3364	0.3088	0.1980	0.4932	1.3830
0.0000	0.0944	0.9056	1.3382	0.2380	0.2165	0.5455	1.3790
0.0035	0.1057	0.8909	1.3400	0.1987	0.2220	0.5793	1.3748

Table C.7 Experimental binodal curve data for the system 1-hexanol(1)-ethanol(2)-water(3) at 60°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3250	0.0300	0.1271	0.8429	1.3418
0.0000	0.0216	0.9784	1.3271	0.2422	0.1951	0.5627	1.3751
0.0000	0.0312	0.9688	1.3282	0.2785	0.1876	0.5338	1.3775
0.0000	0.0409	0.9591	1.3295	0.3369	0.1676	0.4955	1.3815
0.0000	0.0505	0.9495	1.3311	0.4263	0.1306	0.4431	1.3859
0.0000	0.0595	0.9405	1.3321	0.5114	0.0889	0.3998	1.3899
0.0000	0.0875	0.9125	1.3356	0.6726	0.0000	0.3274	1.3954
0.0000	0.1095	0.8905	1.3379	0.7976	0.0000	0.2024	1.3972
0.0000	0.1194	0.8806	1.3385	0.9205	0.0000	0.0795	1.3990

Table C.8 Experimental tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 60°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0195	0.9805	1.3269	0.6316	0.0226	0.3458	1.3940
0.0000	0.0327	0.9673	1.3284	0.5641	0.0598	0.3761	1.3917
0.0000	0.0409	0.9591	1.3295	0.4688	0.1097	0.4214	1.3879
0.0000	0.0469	0.9531	1.3305	0.4391	0.1243	0.4366	1.3865
0.0000	0.0586	0.9414	1.3320	0.3877	0.1466	0.4657	1.3840
0.0000	0.0699	0.9301	1.3334	0.3325	0.1691	0.4984	1.3812
0.0000	0.0763	0.9237	1.3342	0.2888	0.1841	0.5271	1.3782
0.0000	0.0904	0.9096	1.3359	0.2452	0.1945	0.5603	1.3753

Table C.9 Experimental binodal curve data for the system 1-octanol(1)-ethanol(2)-water(3) at 30°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3292	0.1584	0.3112	0.5304	1.3852
0.0000	0.0207	0.9793	1.3325	0.1749	0.3153	0.5097	1.3872
0.0000	0.0346	0.9654	1.3345	0.2058	0.3125	0.4818	1.3908
0.0000	0.0439	0.9561	1.3358	0.2489	0.3101	0.4410	1.3944
0.0000	0.0531	0.9469	1.3372	0.2817	0.3040	0.4143	1.3970
0.0000	0.0646	0.9354	1.3388	0.3013	0.2927	0.4060	1.3981
0.0000	0.0799	0.9201	1.3408	0.3727	0.2665	0.3608	1.4032
0.0000	0.0983	0.9017	1.3432	0.4574	0.2133	0.3293	1.4078
0.0000	0.1055	0.8945	1.3440	0.5103	0.2070	0.2827	1.4100
0.0029	0.1597	0.8374	1.3502	0.6645	0.1289	0.2066	1.4158
0.0168	0.1954	0.7878	1.3546	0.8728	0.0000	0.1272	1.4212
0.1471	0.3092	0.5436	1.3843				

Table C.10 Experimental tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 30°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0263	0.9737	1.3333	0.6566	0.1329	0.2105	1.4155
0.0000	0.0452	0.9548	1.3360	0.5874	0.1679	0.2447	1.4129
0.0000	0.0625	0.9375	1.3385	0.4959	0.2087	0.2954	1.4094
0.0000	0.0814	0.9186	1.3410	0.4206	0.2364	0.3430	1.4058
0.0000	0.0975	0.9025	1.3431	0.3433	0.2773	0.3794	1.4011
0.0006	0.1160	0.8834	1.3452	0.2779	0.3047	0.4174	1.3967
0.0014	0.1317	0.8669	1.3470	0.2105	0.3122	0.4772	1.3912
0.0024	0.1501	0.8475	1.3491	0.1601	0.3116	0.5283	1.3854

Table C.11 Experimental binodal curve data for the system 1-octanol(1)-ethanol(2)-water(3) at 40°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3280	0.1169	0.2940	0.5892	1.3758
0.0000	0.0216	0.9784	1.3311	0.1358	0.3003	0.5639	1.3792
0.0000	0.0309	0.9691	1.3324	0.2044	0.3077	0.4879	1.3876
0.0000	0.0400	0.9600	1.3339	0.2335	0.3029	0.4635	1.3906
0.0000	0.0508	0.9492	1.3345	0.2501	0.3041	0.4458	1.3918
0.0000	0.0597	0.9403	1.3359	0.2687	0.3000	0.4312	1.3940
0.0000	0.0783	0.9217	1.3386	0.2959	0.2879	0.4162	1.3955
0.0000	0.0998	0.9002	1.3411	0.3235	0.2783	0.3982	1.3971
0.0047	0.1608	0.8344	1.3478	0.3471	0.2804	0.3726	1.3986
0.0143	0.1814	0.8043	1.3505	0.3965	0.2545	0.3490	1.4021
0.0165	0.1865	0.7970	1.3517	0.4336	0.2341	0.3323	1.4032
0.0311	0.2101	0.7588	1.3530	0.4663	0.2267	0.3070	1.4056
0.0350	0.2146	0.7504	1.3532	0.6822	0.0870	0.2308	1.4132
0.0459	0.2290	0.7251	1.3545	0.7939	0.0514	0.1548	1.4159

Table C.12 Experimental tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 40°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0196	0.9804	1.3308	0.6481	0.1091	0.2428	1.4120
0.0000	0.0358	0.9642	1.3332	0.5771	0.1550	0.2679	1.4095
0.0000	0.0604	0.9396	1.3360	0.4862	0.2139	0.3000	1.4063
0.0000	0.0756	0.9244	1.3382	0.3951	0.2552	0.3497	1.4020
0.0000	0.0869	0.9131	1.3396	0.3527	0.2774	0.3699	1.3990
0.0003	0.1034	0.8963	1.3415	0.2941	0.2887	0.4172	1.3954

Table C.13 Experimental binodal curve data for the system 1-octanol(1)-ethanol(2)-water(3) at 50°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3260	0.0762	0.2451	0.6787	1.3695
0.0000	0.0222	0.9778	1.3291	0.0906	0.2556	0.6538	1.3708
0.0000	0.0314	0.9686	1.3305	0.0945	0.2615	0.6440	1.3713
0.0000	0.0408	0.9592	1.3318	0.2060	0.2926	0.5014	1.3855
0.0000	0.0511	0.9489	1.3332	0.2294	0.2878	0.4828	1.3876
0.0000	0.0615	0.9385	1.3345	0.2475	0.2841	0.4684	1.3894
0.0000	0.0827	0.9173	1.3370	0.2715	0.2753	0.4532	1.3920
0.0000	0.1032	0.8968	1.3391	0.2978	0.2709	0.4313	1.3932
0.0049	0.1446	0.8505	1.3429	0.3284	0.2573	0.4143	1.3954
0.0050	0.1451	0.8500	1.3435	0.4050	0.2207	0.3744	1.4000
0.0156	0.1683	0.8161	1.3460	0.4982	0.1681	0.3337	1.4050
0.0278	0.1899	0.7823	1.3472	0.5827	0.1192	0.2980	1.4083
0.0454	0.2129	0.7418	1.3490	0.8171	0.0000	0.1829	1.4149

Table C.14 Experimental tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 50°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0222	0.9778	1.3291	0.6076	0.1066	0.2858	1.4090
0.0000	0.0357	0.9643	1.3311	0.5366	0.1459	0.3175	1.4065
0.0000	0.0519	0.9481	1.3333	0.4535	0.1933	0.3532	1.4026
0.0000	0.0742	0.9258	1.3360	0.3850	0.2302	0.3848	1.3988
0.0000	0.0810	0.9190	1.3368	0.3550	0.2446	0.4004	1.3970
0.0000	0.0905	0.9095	1.3378	0.3256	0.2585	0.4158	1.3952
0.0000	0.1022	0.8978	1.3390	0.2605	0.2794	0.4602	1.3908
0.0025	0.1239	0.8736	1.3410	0.2060	0.2926	0.5014	1.3855

Table C.15 Experimental binodal curve data for the system 1-octanol(1)-ethanol(2)-water(3) at 60°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3250	0.1948	0.2795	0.5257	1.3800
0.0000	0.0216	0.9784	1.3271	0.2278	0.2575	0.5147	1.3860
0.0000	0.0312	0.9688	1.3282	0.2584	0.2500	0.4916	1.3870
0.0000	0.0409	0.9591	1.3295	0.3042	0.2352	0.4607	1.3905
0.0000	0.0505	0.9495	1.3311	0.3515	0.2186	0.4299	1.3930
0.0000	0.0595	0.9405	1.3321	0.4224	0.1861	0.3915	1.3990
0.0000	0.0875	0.9125	1.3356	0.5121	0.1454	0.3425	1.4011
0.0000	0.1095	0.8905	1.3379	0.5915	0.1105	0.2980	1.4040
0.0000	0.1194	0.8806	1.3385	0.7420	0.0142	0.2438	1.4089
0.1721	0.2784	0.5495	1.3782	0.8556	0.0000	0.1444	1.4107

Table C.16 Experimental tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 60°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0154	0.9846	1.3265	0.6222	0.0909	0.2869	1.4050
0.0000	0.0364	0.9636	1.3289	0.5641	0.1225	0.3133	1.4030
0.0000	0.0427	0.9573	1.3298	0.4865	0.1570	0.3565	1.4005
0.0000	0.0541	0.9459	1.3315	0.4082	0.1926	0.3992	1.3978
0.0000	0.0691	0.9309	1.3333	0.3574	0.2159	0.4267	1.3935
0.0000	0.0867	0.9133	1.3355	0.2976	0.2373	0.4651	1.3900
0.0000	0.0952	0.9048	1.3364	0.2278	0.2575	0.5147	1.3860
0.0000	0.1128	0.8872	1.3381	0.1997	0.2762	0.5241	1.3809

Table C.17 Experimental binodal curve data for the system 1-decanol(1)-ethanol(2)-water(3) at 30°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3292	0.0186	0.2453	0.7361	1.3595
0.0000	0.0207	0.9793	1.3325	0.1464	0.3536	0.5000	1.3902
0.0000	0.0346	0.9654	1.3345	0.1636	0.3550	0.4814	1.3928
0.0000	0.0439	0.9561	1.3358	0.1943	0.3556	0.4501	1.3964
0.0000	0.0531	0.9469	1.3372	0.2220	0.3521	0.4259	1.3992
0.0000	0.0646	0.9354	1.3388	0.2683	0.3395	0.3921	1.4037
0.0000	0.0799	0.9201	1.3408	0.3270	0.3163	0.3566	1.4080
0.0000	0.0983	0.9017	1.3432	0.3709	0.3081	0.3210	1.4108
0.0000	0.1055	0.8945	1.3440	0.4338	0.2890	0.2772	1.4146
0.0038	0.2066	0.7896	1.3535	0.6049	0.1783	0.2168	1.4218
0.0063	0.2175	0.7763	1.3555	0.8044	0.0502	0.1455	1.4280

Table C.18 Experimental tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 30°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0418	0.9582	1.3355	0.6435	0.1535	0.2030	1.4230
0.0000	0.0574	0.9426	1.3378	0.5740	0.1983	0.2277	1.4205
0.0000	0.0799	0.9201	1.3408	0.4885	0.2537	0.2579	1.4169
0.0000	0.0967	0.9033	1.3430	0.4123	0.2956	0.2922	1.4133
0.0008	0.1268	0.8724	1.3460	0.3270	0.3163	0.3566	1.4080
0.0014	0.1428	0.8558	1.3475	0.2724	0.3379	0.3897	1.4040
0.0021	0.1608	0.8371	1.3492	0.2191	0.3525	0.4285	1.3989
0.0026	0.1747	0.8227	1.3505	0.1747	0.3552	0.4701	1.3941

Table C.19 Experimental binodal curve data for the system 1-decanol(1)-ethanol(2)-water(3) at 40°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3280	0.1331	0.3400	0.5269	1.3853
0.0000	0.0216	0.9784	1.3311	0.1648	0.3467	0.4884	1.3898
0.0000	0.0309	0.9691	1.3324	0.2483	0.3346	0.4171	1.3984
0.0000	0.0400	0.9600	1.3339	0.2739	0.3254	0.4006	1.4012
0.0000	0.0508	0.9492	1.3345	0.3068	0.3140	0.3792	1.4042
0.0000	0.0597	0.9403	1.3359	0.3462	0.2960	0.3578	1.4065
0.0000	0.0783	0.9217	1.3386	0.3759	0.2888	0.3353	1.4090
0.0000	0.0998	0.9002	1.3411	0.4409	0.2593	0.2999	1.4148
0.0066	0.2074	0.7860	1.3512	0.5587	0.1847	0.2566	1.4180
0.0222	0.2387	0.7392	1.3550	0.6997	0.0737	0.2266	1.4230
0.0353	0.2596	0.7051	1.3568	0.8066	0.0350	0.1584	1.4249
0.1044	0.3274	0.5682	1.3810				

Table C.20 Experimental tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 40°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0315	0.9685	1.3325	0.6010	0.1514	0.2476	1.4195
0.0000	0.0539	0.9461	1.3350	0.5219	0.2080	0.2701	1.4170
0.0000	0.0756	0.9244	1.3382	0.4218	0.2679	0.3102	1.4131
0.0000	0.0946	0.9054	1.3405	0.3815	0.2862	0.3322	1.4095
0.0011	0.1179	0.8810	1.3428	0.3068	0.3140	0.3792	1.4042
0.0019	0.1307	0.8674	1.3440	0.2772	0.3243	0.3985	1.4015
0.0030	0.1477	0.8493	1.3456	0.2309	0.3371	0.4320	1.3966
0.0042	0.1680	0.8278	1.3475	0.1592	0.3455	0.4953	1.3890

Table C.21 Experimental binodal curve data for the system 1-decanol(1)-ethanol(2)-water(3) at 50°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3260	0.1066	0.3152	0.5782	1.3800
0.0000	0.0222	0.9778	1.3291	0.1217	0.3205	0.5579	1.3838
0.0000	0.0314	0.9686	1.3305	0.1416	0.3259	0.5325	1.3862
0.0000	0.0408	0.9592	1.3318	0.2144	0.3225	0.4631	1.3935
0.0000	0.0511	0.9489	1.3332	0.2373	0.3169	0.4458	1.3953
0.0000	0.0615	0.9385	1.3345	0.2622	0.3102	0.4276	1.3980
0.0000	0.0827	0.9173	1.3370	0.2917	0.3001	0.4082	1.4010
0.0000	0.1032	0.8968	1.3391	0.3335	0.2830	0.3836	1.4029
0.0024	0.1742	0.8235	1.3451	0.3728	0.2628	0.3644	1.4055
0.0044	0.1874	0.8082	1.3464	0.4288	0.2432	0.3280	1.4085
0.0080	0.2015	0.7905	1.3482	0.5061	0.2018	0.2921	1.4121
0.0233	0.2300	0.7466	1.3503	0.6231	0.1286	0.2483	1.4162
0.0376	0.2516	0.7108	1.3512	0.7474	0.0276	0.2250	1.4205
0.0676	0.2883	0.6441	1.3733	0.8219	0.0096	0.1684	1.4218
0.0857	0.3034	0.6109	1.3770				

Table C.22 Experimental tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 50°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0222	0.9778	1.3291	0.6751	0.0863	0.2386	1.4180
0.0000	0.0438	0.9562	1.3322	0.5889	0.1500	0.2611	1.4150
0.0000	0.0658	0.9342	1.3350	0.4932	0.2087	0.2981	1.4115
0.0000	0.0785	0.9215	1.3365	0.4157	0.2478	0.3365	1.4078
0.0000	0.0973	0.9027	1.3385	0.3592	0.2698	0.3710	1.4046
0.0008	0.1280	0.8711	1.3412	0.2720	0.3068	0.4212	1.3990
0.0015	0.1470	0.8516	1.3428	0.2233	0.3203	0.4564	1.3942

Table C.23 Experimental binodal curve data for the system 1-decanol(1)-ethanol(2)-water(3) at 60°C

x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0000	1.0000	1.3250	0.1180	0.3050	0.5769	1.3792
0.0000	0.0216	0.9784	1.3271	0.1687	0.3198	0.5114	1.3840
0.0000	0.0312	0.9688	1.3282	0.1950	0.3210	0.4840	1.3872
0.0000	0.0409	0.9591	1.3295	0.2150	0.3219	0.4631	1.3890
0.0000	0.0505	0.9495	1.3311	0.2504	0.2924	0.4572	1.3941
0.0000	0.0595	0.9405	1.3321	0.2811	0.2790	0.4399	1.3965
0.0000	0.0875	0.9125	1.3356	0.3219	0.2675	0.4106	1.4005
0.0000	0.1095	0.8905	1.3379	0.3708	0.2457	0.3836	1.4020
0.0000	0.1194	0.8806	1.3385	0.4557	0.2001	0.3442	1.4066
0.0041	0.1733	0.8227	1.3424	0.5835	0.1284	0.2880	1.4121
0.0082	0.1898	0.8019	1.3438	0.7531	0.0186	0.2283	1.4170
0.0639	0.2729	0.6632	1.3702	0.8396	0.0000	0.1604	1.4182
0.0799	0.2883	0.6318	1.3727				

Table C.24 Experimental tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 60°C

aqueous phase				organic phase			
x(1)	x(2)	x(3)	n_D	x(1)	x(2)	x(3)	n_D
0.0000	0.0233	0.9767	1.3273	0.6389	0.0926	0.2685	1.4137
0.0000	0.0451	0.9549	1.3302	0.5580	0.1428	0.2992	1.4110
0.0000	0.0568	0.9432	1.3318	0.4627	0.1962	0.3411	1.4069
0.0000	0.0787	0.9213	1.3345	0.3985	0.2308	0.3707	1.4035
0.0000	0.0999	0.9001	1.3369	0.2747	0.2818	0.4435	1.3960
0.0000	0.1194	0.8806	1.3385	0.2386	0.3022	0.4592	1.3924
0.0016	0.1413	0.8571	1.3400	0.2039	0.3214	0.4747	1.3880
0.0027	0.1558	0.8415	1.3410	0.1810	0.3204	0.4986	1.3855

APPENDIX D

COMPUTER PROGRAMS

D.1 Computer Program for Evaluation of Binary Interaction Parameters

```
#include <iostream.h>
#include <math.h>
void UNIQUAC();
float ObjectiveFunction(int);
float Rconst(int);
float Qconst(int);
int ntieline;
const int nphase = 2, ncomponent = 3, maxgroup = 10;
int totalgroup[ncomponent+1], numgroup[ncomponent+1][maxgroup+1],
     group[ncomponent+1][maxgroup+1];
float x[nphase+1][ncomponent+1],gramma[nphase+1][ncomponent+1],
        town[ncomponent+1][ncomponent+1],Xexperiment[20][nphase+1][ncomponent+1];

void main()
 {
 // System Selection
 float Utown[ncomponent+1][ncomponent+1],Ltown[ncomponent+1][ncomponent+1],
        Obj,minObj=1000, DiffTown, Optimumtown[ncomponent+1][ncomponent+1],
         DiffUtownLtown;
 int SystemSelection, ntieline, grid, i, j, k;
 do
    {
   cout << "================================================== \n";
   cout << "   CALCULATING PARAMETERS OF UNIQUAC MODEL \n";
   cout << "================================================== \n";
   cout << "               SYSTEM SELECTION \n";
   cout << "choose 1 for system...1-Hexanol-Ethanol-Water \n";
   cout << "choose 2 for system...1-Octanol-Ethanol-Water \n";
   cout << "choose 3 for system...1-Decanol-Ethanol-Water \n";
   cout << "Select 1...3 :";
   cin  >> SystemSelection;
    }
 while((SystemSelection<1)||(SystemSelection>3));

 //Set value for the first component (Solvent)
 switch(SystemSelection)
    {
```

```
case 1:
        totalgroup[1] = 3;
         group[1][1]   = '1A' ;
         numgroup[1][1]= 1;
         group[1][2]   = '1B';
         numgroup[1][2]= 5;
         group[1][3]   = '5';
         numgroup[1][3]= 1; break;
case 2:
        totalgroup[1] = 3;
         group[1][1]   = '1A';
         numgroup[1][1]= 1;
         group[1][2]   = '1B';
         numgroup[1][2]= 7;
         group[1][3]   = '5';
         numgroup[1][3]= 1; break;
case 3:
        totalgroup[1] = 3;
         group[1][1]   = '1A';
         numgroup[1][1]= 1;
         group[1][2]   = '1B';
         numgroup[1][2]= 9;
         group[1][3]   = '5';
         numgroup[1][3]= 1; break;
  }

//Set Value for the second component (Ethanol)
        {
        totalgroup[2] = 3;
         group[2][1]   = '1A';
         numgroup[2][1]= 1;
         group[2][2]   = '1B';
         numgroup[2][2]= 1;
         group[2][3]   = '5';
         numgroup[2][3]= 1;
        }

//Set Value for the third component (Water)
        {
         totalgroup[3] = 1;
```

```
        group[3][1]   = '7';
        numgroup[3][1]= 1;
       }

//Input Total Number of Tie-Line
cout << "Total ntieline";
cin >> ntieline;

//Input Xexperiment
for(i=1;i<=ntieline;i++)
   {
       for(j=1;j<=nphase;j++)
           {
               for(k=1;k<=ncomponent-1;k++)
                  {
                  cout << "Enter Xexperiment" << i << "," << j << "," << k << " = " ;
                  cin >> Xexperiment[i][j][k];
                   }
           }
   cout << "----------------------" << endl;
    }

//Calculate Xexperiment[i][j][3]
for(i=1;i<=ntieline;i++)
   {
       for(j=1;j<=nphase;j++)
           {
           Xexperiment[i][j][3] = 1-Xexperiment[i][j][1]-Xexperiment[i][j][2];
           }
   }
for(i=1;i<=ntieline;i++)
   {
       for(j=1;j<=nphase;j++)
           {
              for(k=1;k<=ncomponent;k++)
                  {
                  if(Xexperiment[i][j][k] <= 0) Xexperiment[i][j][k] = 0.000001;
                  }
           }
   }
```

```
 //Define town & Input Uppertown[i][j] and Lowertown[i][j]
 cout << "Enter Ltown" << 1 << "," << 2 << " = " ;
 cin >> Ltown[1][2];
 cout << "Enter Utown" << 1 << "," << 2 << " = " ;
 cin >> Utown[1][2];
  for(i=1;i<=ncomponent;i++)
     {
           for(j=1;j<=ncomponent;j++)
               {
               if(i==j) town[i][j] = 1;
               else
                    {
                    Ltown[i][j] = Ltown[1][2];
                    Utown[i][j] = Utown[1][2];
                    }
                }
     }

  //Define Number of Grid
  cout << "Enter Number of grid" << " = " ;
  cin >> grid;
  for(i=1;i<=ncomponent;i++)
     {
     town[i][i] = 1;
     }
int i12, i21, i13, i31, i23, i32;
do
{
     for(i12=0;i12<=grid;i12++)
          {
          town[1][2]=Ltown[1][2]+ i12*((Utown[1][2]-Ltown[1][2])/grid);
          for(i21=0;i21<=grid;i21++)
                    {
                    town[2][1]=Ltown[2][1]+ i21*((Utown[2][1]-Ltown[2][1])/grid);
                    for(i13=0;i13<=grid;i13++)
                         {
                         town[1][3]=Ltown[1][3]+ i13*((Utown[1][3]-Ltown[1][3])/grid);
                         for(i31=0;i31<=grid;i31++)
                              {
                              town[3][1]=Ltown[3][1]+ i31*((Utown[3][1]-Ltown[3][1])/grid);
```

```
                    for(i23=0;i23<=grid;i23++)
                        {
                        town[2][3]=Ltown[2][3]+ i23*((Utown[2][3]-Ltown[2][3])/grid);
                        for(i32=0;i32<=grid;i32++)
                            {
                            town[3][2]=Ltown[3][2]+ i32*((Utown[3][2]-Ltown[3][2])/grid);
  Obj = 0;
  for(i=1;i<=ntieline;i++)
    {
        for(j=1;j<=nphase;j++)
            {
                for(k=1;k<=ncomponent;k++)
                    {
                    x[j][k] = Xexperiment[i][j][k];
                    }
            }
        UNIQUAC();
        Obj += ObjectiveFunction(i);
    }
        Obj = sqrt(Obj);
        if (Obj<=minObj)
            {
            minObj = Obj;
            Optimumtown[1][2] = town[1][2];
            Optimumtown[2][1] = town[2][1];
            Optimumtown[1][3] = town[1][3];
            Optimumtown[3][1] = town[3][1];
            Optimumtown[2][3] = town[2][3];
            Optimumtown[3][2] = town[3][2];
                            }
                        }
                    }
                }
            }
        }
    }
DiffUtownLtown = 0;
for(i=1;i<=ncomponent;i++)
  {
    for(j=1;j<=ncomponent;j++)
```

```
        {
        if(i!=j)
            {
            DiffTown = (Utown[i][j]-Ltown[i][j])/grid;
            Utown[i][j] = Optimumtown[i][j]+DiffTown;
            Ltown[i][j] = Optimumtown[i][j]-DiffTown;
            if(Ltown[i][j] < 0) Ltown[i][j] = 0;
            DiffUtownLtown += Utown[i][j]-Ltown[i][j];
            }
        }
    }
}
while(DiffUtownLtown >= 0.00001);

cout << "NewTown" << 1 << " , " << 2 << " = " << Optimumtown[1][2] << endl;
cout << endl;
cout << "NewTown" << 2 << " , " << 1 << " = " << Optimumtown[2][1] << endl;
cout << endl;
cout << "NewTown" << 1 << " , " << 3 << " = " << Optimumtown[1][3] << endl;
cout << endl;
cout << "NewTown" << 3 << " , " << 1 << " = " << Optimumtown[3][1] << endl;
cout << endl;
cout << "NewTown" << 2 << " , " << 3 << " = " << Optimumtown[2][3] << endl;
cout << endl;
cout << "NewTown" << 3 << " , " << 2 << " = " << Optimumtown[3][2] << endl;
cout << endl;
cin >> i;
}

void UNIQUAC()
 {
 // Calculate r, q, l
 float r[ncomponent+1], q[ncomponent+1], l[ncomponent+1],
        Totalrx[nphase+1], Totalqx[nphase+1], Totalxl[nphase+1],
        fee[nphase+1][ncomponent+1], seta[nphase+1][ncomponent+1],
        GrammaC[nphase+1][ncomponent+1],
        GrammaR[nphase+1][ncomponent+1], TotalSetaTown[nphase+1][ncomponent+1],
        FractionSetaTown[nphase+1][ncomponent+1];
 int i, j, k;
 const int Z=10;
```

```
for(i=1;i<=ncomponent;i++)
    {
    r[i] = 0;
    q[i] = 0;
         for(j=1;j<=totalgroup[i];j++)
              {
              r[i] += numgroup[i][j]*Rconst(group[i][j]);
              q[i] += numgroup[i][j]*Qconst(group[i][j]);
              }
    }
for(i=1;i<=ncomponent;i++)
    {
    l[i] = Z/2*(r[i]-q[i])-(r[i]-1);
    }
for(i=1;i<=nphase;i++)
    {
    Totalrx[i] = 0;
    Totalqx[i] = 0;
         for(j=1;j<=ncomponent;j++)
         {
         Totalrx[i] += r[j]*x[i][j];
         Totalqx[i] += q[j]*x[i][j];
         }
    }
for(i=1;i<=nphase;i++)
    {
         for(j=1;j<=ncomponent;j++)
              {
              fee[i][j]  = (r[j]*x[i][j])/Totalrx[i];
              seta[i][j] = (q[j]*x[i][j])/Totalqx[i];
              }
    }

//Find combinatorial part (GrammaC)
for(i=1;i<=nphase;i++)
    {
    Totalxl[i] = 0;
         for(j=1;j<=ncomponent;j++)
              {
              Totalxl[i] += x[i][j]*l[j];
```

```
            }
    }
for(i=1;i<=nphase;i++)
    {
        for(j=1;j<=ncomponent;j++)
            {
            GrammaC[i][j] = log(fee[i][j]/x[i][j]) + Z/2*q[j]*log(seta[i][j]/fee[i][j])
                                + l[j] - ((fee[i][j]/x[i][j])*Totalxl[i]);
            }
    }

//Find residual part (GrammaR)
for(i=1;i<=nphase;i++)
    {
        for(j=1;j<=ncomponent;j++)
            {
            TotalSetaTown[i][j] = 0;
                for(k=1;k<=ncomponent;k++)
                    {
                    TotalSetaTown[i][j] += seta[i][k] * town[k][j];
                    }
            }
    }
for(i=1;i<=nphase;i++)
    {
        for(j=1;j<=ncomponent;j++)
            {
            FractionSetaTown[i][j] = 0;
                for(k=1;k<=ncomponent;k++)
                    {
                    FractionSetaTown[i][j] += (seta[i][k] * town[j][k])/TotalSetaTown[i][k];
                    }
            }
    }
for(i=1;i<=nphase;i++)
    {
        for(j=1;j<=ncomponent;j++)
            {
            GrammaR[i][j] = q[j]*(1-log(TotalSetaTown[i][j])-FractionSetaTown[i][j]);
            }
```

```
    }

 //Finally Calculate gramma
 for(i=1;i<=nphase;i++)
    {
         for(j=1;j<=ncomponent;j++)
              {
              gramma[i][j] = exp(GrammaC[i][j] + GrammaR[i][j]);
              }
    }
}

float Rconst(int m)
    {
    float rconst;
    switch(m)
         {
         case '1A': rconst = 0.9011; break;
         case '1B': rconst = 0.6744; break;
         case '5' : rconst = 1.0000; break;
         case '7' : rconst = 0.9200; break;
         }
    return rconst;
    }

 float Qconst(int n)
    {
    float qconst;
    switch(n)
         {
         case '1A': qconst = 0.8480; break;
         case '1B': qconst = 0.5400; break;
         case '5' : qconst = 1.2000; break;
         case '7' : qconst = 1.4000; break;
         }
    return qconst;
    }
```

```
float ObjectiveFunction(int i)
    {
    int j,k;
    float DiffXGramma=0;
    float X[3][ncomponent+1],sumX=0,sumXb,sumX1;
    for(j=1;j<=ncomponent;j++)
        {
        X[1][j] = Xexperiment[i][1][j];
        }
    do
        {
        sumXb = sumX;
        sumX1 = X[1][1]+X[1][2];
        X[1][1] = (1-X[1][3])*X[1][1]/(sumX1);
        X[1][2] = (1-X[1][3])*X[1][2]/(sumX1);
            for(j=1;j<=ncomponent;j++)
                {
                X[2][j] =  X[1][j]*gramma[1][j]/gramma[2][j];
                }
            sumX = 0;
            for(j=1;j<=ncomponent;j++)
                {
                sumX += X[2][j];
                }
            for(j=1;j<=ncomponent;j++)
                {
                X[2][j] =X[2][j]/sumX;
                }
            X[1][1] = X[2][1]*gramma[2][1]/gramma[1][1];
        }
   while(fabs(sumX-sumXb)>=0.000001);
      for(k=1;k<=nphase;k++)
        {
            for(j=1;j<=ncomponent;j++)
                {
                DiffXGramma += pow((X[k][j] - Xexperiment[i][k][j]),2);
                }
        }
   return DiffXGramma;
    }
```

D.2 Computer Program for Calculation of Liquid-Liquid Equilibria Phase Compositions

```
#include <iostream.h>
#include <math.h>
void UNIFAC(float);
float Rconst(int);
float Qconst(int);
float amn(int,int);
const int nphase = 2, ncomponent = 3, maxgroup = 10;
int totalgroup[ncomponent+1], numgroup[ncomponent+1][maxgroup+1],
     group[ncomponent+1][maxgroup+1];
float x[nphase+1][ncomponent+1], gramma[nphase+1][ncomponent+1];

void main()
 {
 // System Selection
 float T;
 int Temp, SystemSelection, i, j;
 do
   {
   cout << "=============================================== \n";
   cout << "   CALCULATING X EQUILIBRIUM BY UNIFAC MODEL \n";
   cout << "=============================================== \n";
   cout << "               SYSTEM SELECTION \n";
   cout << "choose 1 for system...1-Hexanol-Ethanol-Water \n";
   cout << "choose 2 for system...1-Octanol-Ethanol-Water \n";
   cout << "choose 3 for system...1-Decanol-Ethanol-Water \n";
   cout << "Select 1...3 :";
   cin  >> SystemSelection;
   }
 while((SystemSelection<1)||(SystemSelection>3));

 //Set value for the first component (Solvent)
 switch(SystemSelection)
   {
   case 1:
          totalgroup[1] = 3;
          group[1][1]   = '1A' ;
          numgroup[1][1]= 1;
```

```
            group[1][2]   = '1B';
            numgroup[1][2]= 5;
            group[1][3]   = '5';
            numgroup[1][3]= 1; break;
   case 2:
            totalgroup[1] = 3;
            group[1][1]   = '1A';
            numgroup[1][1]= 1;
            group[1][2]   = '1B';
            numgroup[1][2]= 7;
            group[1][3]   = '5';
            numgroup[1][3]= 1; break;
case 3:
            totalgroup[1] = 3;
            group[1][1]   = '1A';
            numgroup[1][1]= 1;
            group[1][2]   = '1B';
            numgroup[1][2]= 9;
            group[1][3]   = '5';
            numgroup[1][3]= 1; break;
   }

   //Set Value for the second component (Ethanol)
           {
           totalgroup[2] = 3;
            group[2][1]   = '1A';
            numgroup[2][1]= 1;
            group[2][2]   = '1B';
            numgroup[2][2]= 1;
            group[2][3]   = '5';
            numgroup[2][3]= 1;
           }

  //Set Value for the third component (Water)
           {
            totalgroup[3] = 1;
            group[3][1]   = '7';
            numgroup[3][1]= 1;
           }
```

```
 //Temperature Selection
do
 {
  cout << "            TEMPERATURE SELECTION \n";
  cout << "choose 1 for temperature at...303.15K \n";
  cout << "choose 2 for temperature at...313.15K \n";
  cout << "choose 3 for temperature at...323.15K \n";
  cout << "choose 4 for temperature at...333.15K \n";
  cout << "Select 1...4 :";
  cin >> Temp;
  }
 while((Temp<1)||(Temp>4));
 switch(Temp)
  {
  case 1: T = 303.15; break;
  case 2: T = 313.15; break;
  case 3: T = 323.15; break;
  case 4: T = 333.15; break;
  }

 //Input x and Set Initial Condition of x
  {
  cout << "Enter x" << 1 << "," << 3 << " = " ;
  cin >> x[1][3]; cout << endl;
  }

    float sumX1;
    float sumX2;

 //The Loop for calculate x until end
    x[1][1] = x[1][2] = (1-x[1][3])/2;
    x[2][3] = 0.001;
    x[2][1] = x[2][2] = (1-x[2][3])/2;
do
  {
  sumX1 = 0;
  for(j=1;j<=ncomponent;j++)
     {
     sumX1 += x[1][j];
     }
```

```
    x[1][1] = (1-x[1][3])*x[1][1]/(x[1][2] + x[1][1]);
    x[1][2] = (1-x[1][3])*x[1][2]/(x[1][2] + x[1][1]);

    UNIFAC(T);

    {
    x[2][2] = x[1][2]*gramma[1][2]/gramma[2][2];
    x[2][3] = x[1][3]*gramma[1][3]/gramma[2][3];
    }
  sumX2 = 0;
  for(j=1;j<=ncomponent;j++)
    {
    sumX2 += x[2][j];
    }
        for(j=1;j<=ncomponent;j++)
            {
            x[2][j] = x[2][j]/sumX2;
            }
  x[1][1] = x[2][1]*gramma[2][1]/gramma[1][1];
}
while((fabs(1-sumX1)>=0.0000001) || (fabs(1-sumX2)>=0.0000001));

for(i=1;i<=nphase;i++)
    {
        for(j=1;j<=ncomponent;j++)
        {
        cout << "Xnew  " << i << "," << j << " = " << x[i][j] << endl;
        cout << endl;
        }
    }

  cin >>T;
}

void UNIFAC(float T)
{
// Calculate r, q, l
float r[ncomponent+1], q[ncomponent+1], l[ncomponent+1],
     groupmn[ncomponent+1][maxgroup+1][maxgroup+1],
     Totalrx[nphase+1], Totalqx[nphase+1], Totalxl[nphase+1],
```

```
     totalQXpure[ncomponent+1],
     totalQXmix[nphase+1], fee[nphase+1][ncomponent+1],
     seta[nphase+1][ncomponent+1],
     GrammaC[nphase+1][ncomponent+1], totalnumgroup[ncomponent+1],
     SumtotalnumgroupX, totalnumgroupX, Hpure[ncomponent+1][maxgroup+1],
     TotalHpuregroupmn[ncomponent+1][maxgroup+1],
     FractionHpuregroupmn[ncomponent+1][maxgroup+1],
     groupik[ncomponent+1][maxgroup+1],TotalHmixgroupmn[nphase+1][maxgroup+1],
     Xmix[nphase+1][maxgroup+1], FractionHmixgroupmn[nphase+1][maxgroup+1],
     groupre[nphase+1][maxgroup+1], GrammaR[nphase+1][ncomponent+1],
     Hmix[nphase+1][maxgroup+1], Xpure[ncomponent+1][maxgroup+1];
const int Z=10;
int i, j, k, a, m;
for(i=1;i<=ncomponent;i++)
    {
    r[i] = 0;
     q[i] = 0;
         for(j=1;j<=totalgroup[i];j++)
              {
              r[i] += numgroup[i][j]*Rconst(group[i][j]);
              q[i] += numgroup[i][j]*Qconst(group[i][j]);
              }
    }
for(i=1;i<=ncomponent;i++)
    {
    l[i] = Z/2*(r[i]-q[i])-(r[i]-1);
    }
for(i=1;i<=nphase;i++)
    {
    Totalrx[i] = 0;
    Totalqx[i] = 0;
         for(j=1;j<=ncomponent;j++)
              {
              Totalrx[i] += r[j]*x[i][j];
              Totalqx[i] += q[j]*x[i][j];
              }
    }
for(i=1;i<=nphase;i++)
    {
         for(j=1;j<=ncomponent;j++)
```

```
            {
            fee[i][j]  = (r[j]*x[i][j])/Totalrx[i];
            seta[i][j] = (q[j]*x[i][j])/Totalqx[i];
            }
    }

//Find combinatorial part (GrammaC)
for(i=1;i<=nphase;i++)
    {
    Totalxl[i] = 0;
        for(j=1;j<=ncomponent;j++)
            {
            Totalxl[i] += x[i][j]*l[j];
            }
    }
for(i=1;i<=nphase;i++)
    {
        for(j=1;j<=ncomponent;j++)
            {
            GrammaC[i][j] = log(fee[i][j]/x[i][j]) + Z/2*q[j]*log(seta[i][j]/fee[i][j]) +
                                l[j] - ((fee[i][j]/x[i][j])*Totalxl[i]);
            }
    }

// Calculate the group interaction parameter (group mn)
totalgroup[0] = totalgroup[1];
for(i=1;i<=totalgroup[1];i++)
    {
    group[0][i] = group[1][i];
    numgroup[0][i] = numgroup[1][i];
    }
for(i=2;i<=ncomponent;i++)
    {
        for(j=1;j<=totalgroup[i];j++)
            {
            a = 1;
                for(k=1;k<=totalgroup[0];k++)
                    {
                    if(group[i][j]==group[0][k])
                        {
```

```
                          numgroup[0][k] += numgroup[i][j];
                          a = a*0;
                          }
                      else
                          {
                          a = a*1;
                          }
                      }
              if(a==1)
                  {
                  totalgroup[0] = totalgroup[0]+1;
                  group[0][totalgroup[0]] = group[i][j];
                  numgroup[0][totalgroup[0]] = numgroup[i][j];
                  }
              }
    }
for(i=0;i<=ncomponent;i++)
    {
        for(j=1;j<=totalgroup[i];j++)
            {
                for(k=1;k<=totalgroup[i];k++)
                    {
                    groupmn[i][j][k] = exp(-amn(group[i][j],group[i][k])/T);
                    }
            }
    }

// Calculate H of pure substance(Hpure)
for(i=1;i<=ncomponent;i++)
    {
     totalnumgroup[i] = 0;
        for(j=1;j<=totalgroup[i];j++)
            {
            totalnumgroup[i] += numgroup[i][j];
            }
    }
for(i=1;i<=ncomponent;i++)
    {
        for(j=1;j<=totalgroup[i];j++)
        {
```

```
        Xpure[i][j] = numgroup[i][j]/totalnumgroup[i];
        }
    }
for(i=1;i<=ncomponent;i++)
    {
    totalQXpure[i] = 0;
        for(j=1;j<=totalgroup[i];j++)
            {
            totalQXpure[i] += Qconst(group[i][j])*Xpure[i][j];
            }
    }
for(i=1;i<=ncomponent;i++)
    {
        for(j=1;j<=totalgroup[i];j++)
            {
            Hpure[i][j] = (Qconst(group[i][j])*Xpure[i][j])/totalQXpure[i];
            }
    }

// Calculate  H mix is the H in the mixture  (Hmix)
for(i=1;i<=nphase;i++)
    {
    SumtotalnumgroupX = 0;
        for(k=1;k<=ncomponent;k++)
            {
            SumtotalnumgroupX += x[i][k]*totalnumgroup[k];
            }
        for(j=1;j<=totalgroup[0];j++)
            {
            totalnumgroupX = 0 ;
                for(k=1;k<=ncomponent;k++)
                    {
                        for(m=1;m<=totalgroup[k];m++)
                            {
                            if(group[0][j]==group[k][m])
                            totalnumgroupX += x[i][k]*numgroup[k][m] ;
                            }
                    }
            Xmix[i][j] = totalnumgroupX/SumtotalnumgroupX;
            }
```

```
    }
for(i=1;i<=nphase;i++)
    {
    totalQXmix[i] = 0;
        for(j=1;j<=totalgroup[0];j++)
            {
            totalQXmix[i] += Qconst(group[0][j])*Xmix[i][j];
            }
        for(j=1;j<=totalgroup[0];j++)
            {
            Hmix[i][j] = (Qconst(group[0][j])*Xmix[i][j])/totalQXmix[i];
            }
    }

/* Calculate the residual activity coefficient of group k in
a reference solution containing molecules of type i */
for(i=1;i<=ncomponent;i++)
    {
        for(j=1;j<=totalgroup[i];j++)
            {
            TotalHpuregroupmn[i][j] = 0;
                for(k=1;k<=totalgroup[i];k++)
                    {
                    TotalHpuregroupmn[i][j] += Hpure[i][k]*groupmn[i][k][j];
                    }
            }
    }
for(i=1;i<=ncomponent;i++)
    {
        for(j=1;j<=totalgroup[i];j++)
            {
            FractionHpuregroupmn[i][j] = 0;
                for(k=1;k<=totalgroup[i];k++)
                    {
                    FractionHpuregroupmn[i][j] += (Hpure[i][k]*groupmn[i][j][k])/
                                                        TotalHpuregroupmn[i][k];
                    }
            }
    }
```

```
for(i=1;i<=ncomponent;i++)
   {
        for(j=1;j<=totalgroup[i];j++)
             {
             groupik[i][j] = Qconst(group[i][j])*(1-log(TotalHpuregroupmn[i][j])-
                                  FractionHpuregroupmn[i][j]);
             }
   }

 // calculate the group residual activity coefficient
for(i=1;i<=nphase;i++)
   {
        for(j=1;j<=totalgroup[0];j++)
             {
             TotalHmixgroupmn[i][j] = 0;
                  for(k=1;k<=totalgroup[0];k++)
                       {
                       TotalHmixgroupmn[i][j] += Hmix[i][k]*groupmn[0][k][j];
                       }
             }
   }
for(i=1;i<=nphase;i++)
   {
        for(j=1;j<=totalgroup[0];j++)
             {
             FractionHmixgroupmn[i][j] = 0;
                  for(k=1;k<=totalgroup[0];k++)
                       {
                       FractionHmixgroupmn[i][j] += (Hmix[i][k]*groupmn[0][j][k])/
                                                             TotalHmixgroupmn[i][k];
                       }
             }
   }
for(i=1;i<=nphase;i++)
   {
        for(j=1;j<=totalgroup[0];j++)
             {
             groupre[i][j] = Qconst(group[0][j])*(1-log(TotalHmixgroupmn[i][j])
                                 - FractionHmixgroupmn[i][j]);
             }
```

```
    }
//Find residual part (GrammaR)
for(i=1;i<=nphase;i++)
    {
         for(j=1;j<=ncomponent;j++)
              {
              GrammaR[i][j] = 0;
                   for(k=1;k<=totalgroup[j];k++)
                        {
                             for(m=1;m<=totalgroup[0];m++)
                                  {
                                  if(group[j][k] == group[0][m])
                                  GrammaR[i][j] += numgroup[j][k]*(groupre[i][m]-groupik[j][k]);
                                  }
                        }
              }
    }

//Finally Calculate gramma
for(i=1;i<=nphase;i++)
    {
         for(j=1;j<=ncomponent;j++)
         {
         gramma[i][j] = exp(GrammaC[i][j] + GrammaR[i][j]);
         }
    }
}

float Rconst(int group)
    {
    float rconst;
    switch(group)
         {
         case '1A': rconst = 0.9011; break;
         case '1B': rconst = 0.6744; break;
         case '5'   : rconst = 1.0000; break;
         case '7'   : rconst = 0.9200; break;
         }
    return rconst;
    }
```

```
float Qconst(int group)
   {
    float qconst;
   switch(group)
       {
       case '1A': qconst = 0.8480; break;
       case '1B': qconst = 0.5400; break;
       case '5'   : qconst = 1.2000; break;
       case '7'   : qconst = 1.4000; break;
       }
   return qconst;
   }

float amn(int m,int n)
   {
   float amn[maxgroup][maxgroup];
   switch(m)
       {
       case '1A' :m = 1;break;
       case '1B' :m = 1;break;
       case '5'    :m = 5;break;
       case '7'    :m = 7;break;
       }
   switch(n)
       {
       case '1A' :n = 1;break;
       case '1B' :n = 1;break;
       case '5'    :n = 5;break;
       case '7'    :n = 7;break;
       }
   amn[1][1] = 0;
   amn[1][5] = 986.50;
   amn[1][7] = 1318.00;
   amn[5][1] = 156.40;
   amn[5][5] = 0;
   amn[5][7] = 353.50;
   amn[7][1] = 300.00;
   amn[7][5] = -229.10;
   amn[7][7] = 0;
```

```
return amn[m][n];
}
```

APPENDIX E

EVALUATED DATA OF INTERACTION BINARY PARAMETERS

Table E.1 Set of optimized UNIQUAC binary interaction parameters (τ_{ij}) for the system 1-hexanol(1)-ethanol(2)-water(3) at different temperatures

Temperature (°C)	τ_{12}	τ_{21}	τ_{13}	τ_{31}	τ_{23}	τ_{32}
30	0.0475755	2.8135100	0.5177330	0.1594800	1.2051200	0.9346820
40	0.5012850	1.6802500	0.8457540	0.1286760	0.3407180	2.0057800
50	2.9348000	0.6988610	0.8046100	0.2220510	2.5215900	0.5449860
60	0.1670730	2.4134400	0.9037090	0.1033550	1.2509600	0.9680210

Table E.2 Set of optimized UNIQUAC binary interaction parameters (τ_{ij}) for the system 1-octanol(1)-ethanol(2)-water(3) at different temperatures

Temperature (°C)	τ_{12}	τ_{21}	τ_{13}	τ_{31}	τ_{23}	τ_{32}
30	0.1179530	2.4572800	0.3295300	0.4662130	1.6427600	0.4228610
40	0.2080020	2.0000000	0.4015110	0.4087710	2.0500900	0.1552010
50	0.8053700	1.2543100	0.4003700	0.5534090	1.8141600	0.3548440
60	0.1769820	2.5760500	0.4229440	0.4177840	0.4689820	1.9082500

Table E.3 Set of optimized UNIQUAC binary interaction parameters (τ_{ij}) for the system 1-decanol(1)-ethanol(2)-water(3) at different temperatures

Temperature (°C)	τ_{12}	τ_{21}	τ_{13}	τ_{31}	τ_{23}	τ_{32}
30	1.0160400	1.3760000	0.2251580	0.5703830	1.9399100	0.5146610
40	0.3876480	2.3259100	0.4005360	0.3382320	0.3682220	2.1162000
50	0.0969414	2.8041800	0.5088970	0.2057530	2.6596000	0.1109700
60	0.0409905	2.7935400	0.4408290	0.1599950	0.7093050	1.4000100

Table E.4 Set of optimized UNIQUAC binary interaction parameters in terms of a_{ij} for the system 1-hexanol(1)-ethanol(2)-water(3) at different temperatures

Temperature (°C)	a_{12}	a_{21}	a_{13}	a_{31}	a_{23}	a_{32}
30	923.224	-313.588	199.562	556.534	-56.561	20.477
40	216.255	-162.507	52.461	642.101	337.169	-217.963
50	-347.916	115.786	70.252	486.292	-298.878	196.150
60	596.113	-293.523	33.731	756.112	-74.596	10.828

Table E.5 Set of optimized UNIQUAC binary interaction parameters in terms of a_{ij} for the system 1-octanol(1)-ethanol(2)-water(3) at different temperatures

Temperature (°C)	a_{12}	a_{21}	a_{13}	a_{31}	a_{23}	a_{32}
30	647.974	-272.549	336.523	231.338	-150.477	260.925
40	491.711	-217.059	285.756	280.144	-224.805	583.409
50	69.947	-73.221	295.801	191.194	-192.475	334.808
60	576.918	-315.246	286.681	290.770	252.258	-215.277

Table E.6 Set of optimized UNIQUAC binary interaction parameters in terms of a_{ij} for the system 1-decanol(1)-ethanol(2)-water(3) at different temperatures

Temperature (°C)	a_{12}	a_{21}	a_{13}	a_{31}	a_{23}	a_{32}
30	-4.824	-96.760	451.982	170.203	-200.880	201.366
40	296.759	-264.333	286.517	339.462	312.859	-234.744
50	754.119	-333.204	218.291	510.926	-316.097	710.444
60	1064.219	-342.248	272.883	610.535	114.427	-112.098

APPENDIX F

PROGRAM ESTIMATED DATA

Table F.1 Calculated tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 30°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0012	0.0726	0.9262	0.4095	0.1912	0.3992
0.0022	0.0884	0.9094	0.3329	0.2205	0.4466
0.0032	0.1005	0.8963	0.2875	0.2354	0.4770
0.0040	0.1080	0.8880	0.2424	0.2632	0.4944
0.0062	0.1246	0.8692	0.2171	0.2532	0.5297

Table F.2 Calculated tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 40°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0001	0.0215	0.9784	0.5980	0.0698	0.3322
0.0001	0.0375	0.9624	0.5174	0.1164	0.3662
0.0003	0.0536	0.9461	0.4422	0.1576	0.4002
0.0005	0.0647	0.9348	0.3951	0.1820	0.4229
0.0013	0.0890	0.9097	0.3065	0.2242	0.4693

Table F.3 Calculated tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 50°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0003	0.0219	0.9778	0.5956	0.0591	0.3453
0.0004	0.0297	0.9699	0.5575	0.0826	0.3598
0.0007	0.0438	0.9555	0.4850	0.1251	0.3899
0.0011	0.0564	0.9425	0.4200	0.1599	0.4201
0.0013	0.0602	0.9385	0.4007	0.1695	0.4298

Table F.4 Calculated tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 60°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0002	0.0325	0.9673	0.5517	0.0711	0.3772
0.0005	0.0465	0.9531	0.4688	0.1092	0.4220
0.0008	0.0578	0.9414	0.4050	0.1372	0.4578
0.0014	0.0685	0.9301	0.3513	0.1594	0.4894
0.0029	0.0875	0.9096	0.2735	0.1880	0.5385

Table F.5 Calculated tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 30°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0014	0.0800	0.9186	0.4549	0.2245	0.3206
0.0021	0.0954	0.9025	0.3701	0.2631	0.3668
0.0031	0.1135	0.8834	0.2996	0.2903	0.4101
0.0043	0.1288	0.8669	0.2540	0.3044	0.4415
0.0061	0.1464	0.8475	0.2118	0.3142	0.4740

Table F.6 Calculated tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 40°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0001	0.0195	0.9804	0.6591	0.1051	0.2358
0.0005	0.0599	0.9396	0.4514	0.2263	0.3223
0.0008	0.0748	0.9244	0.4116	0.2466	0.3419
0.0011	0.0858	0.9131	0.3869	0.2585	0.3547
0.0017	0.1020	0.8963	0.3537	0.2736	0.3727

Table F.7 Calculated tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 50°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0005	0.0217	0.9778	0.6089	0.1039	0.2873
0.0008	0.0349	0.9643	0.5375	0.1472	0.3153
0.0011	0.0508	0.9481	0.4685	0.1866	0.3449
0.0019	0.0723	0.9258	0.3936	0.2257	0.3806
0.0022	0.0788	0.9190	0.3742	0.2352	0.3907

Table F.8 Calculated tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 60°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0005	0.0422	0.9573	0.4919	0.1536	0.3544
0.0007	0.0534	0.9459	0.4272	0.1837	0.3891
0.0011	0.0680	0.9309	0.3598	0.2133	0.4269
0.0018	0.0849	0.9133	0.2989	0.2377	0.4634
0.0023	0.0929	0.9048	0.2744	0.2466	0.4789

Table F.9 Calculated tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 30°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0001	0.0417	0.9582	0.6440	0.1577	0.1983
0.0002	0.0572	0.9426	0.5723	0.2007	0.2270
0.0005	0.0794	0.9201	0.4831	0.2507	0.2662
0.0007	0.0960	0.9033	0.4259	0.2803	0.2938
0.0015	0.1261	0.8724	0.3379	0.3208	0.3414

Table F.10 Calculated tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 40°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0000	0.0315	0.9685	0.6104	0.1487	0.2409
0.0001	0.0538	0.9461	0.5078	0.2132	0.2790
0.0002	0.0755	0.9244	0.4303	0.2583	0.3114
0.0003	0.0943	0.9054	0.3746	0.2883	0.3371
0.0006	0.1184	0.8810	0.3148	0.3176	0.3676

Table F.11 Calculated tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 50°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0000	0.0222	0.9778	0.6771	0.0861	0.2368
0.0001	0.0784	0.9215	0.4106	0.2448	0.3446
0.0003	0.0970	0.9027	0.3559	0.2722	0.3719
0.0009	0.1280	0.8711	0.2802	0.3055	0.4144
0.0016	0.1468	0.8516	0.2413	0.3197	0.4390

Table F.12 Calculated tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 60°C by UNIQUAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0001	0.0786	0.9213	0.3841	0.2345	0.3815
0.0002	0.0997	0.9001	0.2998	0.2763	0.4238
0.0005	0.1189	0.8806	0.2458	0.3005	0.4537
0.0011	0.1418	0.8571	0.1965	0.3193	0.4843
0.0017	0.1568	0.8415	0.1701	0.3273	0.5026

Table F.13 Calculated tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 30°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0055	0.0683	0.9262	0.2685	0.2601	0.4714
0.0067	0.0839	0.9094	0.2221	0.2797	0.4982
0.0078	0.0959	0.8963	0.1923	0.2891	0.5186
0.0085	0.1035	0.8880	0.1758	0.2930	0.5312
0.0104	0.1204	0.8692	0.1441	0.2969	0.5590

Table F.14 Calculated tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 40°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0030	0.0186	0.9784	0.5079	0.1090	0.3831
0.0037	0.0339	0.9624	0.4175	0.1722	0.4103
0.0046	0.0493	0.9461	0.3443	0.2183	0.4374
0.0053	0.0599	0.9348	0.3023	0.2418	0.4559
0.0071	0.0832	0.9097	0.2286	0.2756	0.4958

Table F.15 Calculated tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 50°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0033	0.0189	0.9778	0.5077	0.1084	0.3838
0.0036	0.0265	0.9699	0.4614	0.1414	0.3971
0.0044	0.0401	0.9555	0.3893	0.1896	0.4211
0.0051	0.0524	0.9425	0.3354	0.2222	0.4424
0.0054	0.0561	0.9385	0.3206	0.2306	0.4489

Table F.16 Calculated tie-lines for the system 1-hexanol(1)-ethanol(2)-water(3) at 60°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0040	0.0287	0.9673	0.4512	0.1475	0.4013
0.0048	0.0421	0.9531	0.3831	0.1923	0.4246
0.0056	0.0530	0.9414	0.3360	0.2205	0.4435
0.0063	0.0636	0.9301	0.2968	0.2418	0.4615
0.0080	0.0824	0.9096	0.2386	0.2682	0.4932

Table F.17 Calculated tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 30°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0013	0.0801	0.9186	0.3241	0.3057	0.3702
0.0018	0.0957	0.9025	0.2822	0.3295	0.3883
0.0024	0.1142	0.8834	0.2409	0.3499	0.4091
0.0030	0.1301	0.8669	0.2112	0.3622	0.4266
0.0040	0.1485	0.8475	0.1816	0.3718	0.4466

Table F.18 Calculated tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 40°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0005	0.0191	0.9804	0.5918	0.1141	0.2941
0.0010	0.0594	0.9396	0.3966	0.2595	0.3439
0.0013	0.0743	0.9244	0.3460	0.2924	0.3616
0.0016	0.0853	0.9131	0.3137	0.3119	0.3744
0.0021	0.1016	0.8963	0.2724	0.3346	0.3930

Table F.19 Calculated tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 50°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0005	0.0217	0.9778	0.5791	0.1247	0.2962
0.0007	0.0350	0.9643	0.5059	0.1812	0.3129
0.0009	0.0510	0.9481	0.4335	0.2341	0.3324
0.0014	0.0728	0.9258	0.3546	0.2870	0.3584
0.0015	0.0795	0.9190	0.3344	0.2996	0.3661

Table F.20 Calculated tie-lines for the system 1-octanol(1)-ethanol(2)-water(3) at 60°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0009	0.0418	0.9573	0.4764	0.2033	0.3203
0.0011	0.0530	0.9459	0.4286	0.2376	0.3338
0.0014	0.0677	0.9309	0.3748	0.2739	0.3512
0.0018	0.0849	0.9133	0.3224	0.3065	0.3711
0.0021	0.0931	0.9048	0.3004	0.3190	0.3805

Table F.21 Calculated tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 30°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0001	0.0417	0.9582	0.5319	0.2050	0.2631
0.0002	0.0572	0.9426	0.4714	0.2521	0.2765
0.0003	0.0796	0.9201	0.4021	0.3033	0.2946
0.0004	0.0963	0.9033	0.3608	0.3321	0.3071
0.0008	0.1268	0.8724	0.3008	0.3707	0.3285

Table F.22 Calculated tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 40°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0001	0.0314	0.9685	0.5834	0.1649	0.2517
0.0002	0.0537	0.9461	0.4882	0.2404	0.2714
0.0003	0.0753	0.9244	0.4181	0.2928	0.2890
0.0004	0.0942	0.9054	0.3693	0.3272	0.3034
0.0007	0.1183	0.8810	0.3190	0.3603	0.3207

Table F.23 Calculated tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 50°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0001	0.0221	0.9778	0.6351	0.1233	0.2416
0.0003	0.0782	0.9215	0.4137	0.2969	0.2895
0.0005	0.0968	0.9027	0.3665	0.3299	0.3036
0.0009	0.1280	0.8711	0.3042	0.3700	0.3258
0.0013	0.1471	0.8516	0.2734	0.3880	0.3386

Table F.24 Calculated tie-lines for the system 1-decanol(1)-ethanol(2)-water(3) at 60°C by UNIFAC model

aqueous phase			organic phase		
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)
0.0004	0.0783	0.9213	0.4163	0.2955	0.2882
0.0006	0.0993	0.9001	0.3635	0.3324	0.3041
0.0008	0.1186	0.8806	0.3236	0.3584	0.3180
0.0013	0.1417	0.8571	0.2837	0.3825	0.3338
0.0016	0.1569	0.8415	0.2609	0.3951	0.3440

APPENDIX G

DATA OF DISTRIBUTION COEFFICIENTS AND RELATIVE SELECTIVITY

Table G.1 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-hexanol(1)-ethanol(2)-water(3) at 30°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0298	0.9702	0.6003	0.0830	0.3167	2.7885	8.5433
0.0000	0.0466	0.9534	0.5139	0.1383	0.3478	2.9702	8.1422
0.0000	0.0596	0.9404	0.4452	0.1734	0.3814	2.9102	7.1756
0.0000	0.0738	0.9262	0.3854	0.2011	0.4136	2.7255	6.1036
0.0000	0.0906	0.9094	0.3088	0.2308	0.4604	2.5469	5.0305
0.0000	0.1037	0.8963	0.2558	0.2451	0.4991	2.3632	4.2442
0.0015	0.1105	0.8880	0.2231	0.2507	0.5262	2.2681	3.8274
0.0058	0.1250	0.8692	0.1553	0.2464	0.5982	1.9717	2.8648

Table G.2 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-hexanol(1)-ethanol(2)-water(3) at 40°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0216	0.9784	0.5859	0.0761	0.3380	3.5172	10.1812
0.0000	0.0376	0.9624	0.5104	0.1236	0.3659	3.2902	8.6530
0.0000	0.0539	0.9461	0.4571	0.1522	0.3907	2.8210	6.8303
0.0000	0.0652	0.9348	0.3976	0.1804	0.4221	2.7658	6.1256
0.0000	0.0903	0.9097	0.2663	0.2351	0.4986	2.6027	4.7485
0.0043	0.1093	0.8864	0.1725	0.2439	0.5837	2.2308	3.3880

Table G.3 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-hexanol(1)-ethanol(2)-water(3) at 50°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0222	0.9778	0.6007	0.0556	0.3437	2.5021	7.1183
0.0000	0.0301	0.9699	0.5723	0.0760	0.3517	2.5286	6.9732
0.0000	0.0445	0.9555	0.4678	0.1349	0.3973	3.0319	7.2925
0.0000	0.0575	0.9425	0.4035	0.1644	0.4322	2.8569	6.2303
0.0000	0.0615	0.9385	0.3747	0.1769	0.4484	2.8742	6.0150
0.0000	0.0776	0.9224	0.3088	0.1980	0.4932	2.5507	4.7701
0.0000	0.0944	0.9056	0.2380	0.2165	0.5455	2.2934	3.8075
0.0035	0.1057	0.8909	0.1987	0.2220	0.5793	2.1009	3.2309

Table G.4 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-hexanol(1)-ethanol(2)-water(3) at 60°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0195	0.9805	0.6316	0.0226	0.3458	1.1588	3.2856
0.0000	0.0327	0.9673	0.5641	0.0598	0.3761	1.8294	4.7054
0.0000	0.0409	0.9591	0.4688	0.1097	0.4214	2.6847	6.1101
0.0000	0.0469	0.9531	0.4391	0.1243	0.4366	2.6528	5.7914
0.0000	0.0586	0.9414	0.3877	0.1466	0.4657	2.5020	5.0575
0.0000	0.0699	0.9301	0.3325	0.1691	0.4984	2.4188	4.5138
0.0000	0.0763	0.9237	0.2888	0.1841	0.5271	2.4129	4.2284
0.0000	0.0904	0.9096	0.2452	0.1945	0.5603	2.1519	3.4935

Table G.5 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-octanol(1)-ethanol(2)-water(3) at 30°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0263	0.9737	0.6566	0.1329	0.2105	5.0604	23.4082
0.0000	0.0452	0.9548	0.5874	0.1679	0.2447	3.7116	14.4843
0.0000	0.0625	0.9375	0.4959	0.2087	0.2954	3.3420	10.6058
0.0000	0.0814	0.9186	0.4206	0.2364	0.3430	2.9035	7.7762
0.0000	0.0975	0.9025	0.3433	0.2773	0.3794	2.8440	6.7648
0.0006	0.1160	0.8834	0.2779	0.3047	0.4174	2.6266	5.5592
0.0014	0.1317	0.8669	0.2105	0.3122	0.4772	2.3700	4.3050
0.0024	0.1501	0.8475	0.1601	0.3116	0.5283	2.0758	3.3300

Table G.6 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-octanol(1)-ethanol(2)-water(3) at 40°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0196	0.9804	0.6481	0.1091	0.2428	5.5783	22.5214
0.0000	0.0358	0.9642	0.5771	0.1550	0.2679	4.3361	15.6073
0.0000	0.0604	0.9396	0.4862	0.2139	0.3000	3.5423	11.0964
0.0000	0.0756	0.9244	0.3951	0.2552	0.3497	3.3771	8.9270
0.0000	0.0869	0.9131	0.3527	0.2774	0.3699	3.1922	7.8805
0.0003	0.1034	0.8963	0.2941	0.2887	0.4172	2.7918	5.9979

Table G.7 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-octanol(1)-ethanol(2)-water(3) at 50°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0222	0.9778	0.6076	0.1066	0.2858	4.7955	16.4054
0.0000	0.0357	0.9643	0.5366	0.1459	0.3175	4.0837	12.4040
0.0000	0.0519	0.9481	0.4535	0.1933	0.3532	3.7230	9.9935
0.0000	0.0742	0.9258	0.3850	0.2302	0.3848	3.1019	7.4631
0.0000	0.0810	0.9190	0.3550	0.2446	0.4004	3.0195	6.9303
0.0000	0.0905	0.9095	0.3256	0.2585	0.4158	2.8565	6.2475
0.0000	0.1022	0.8978	0.2605	0.2794	0.4602	2.7327	5.3313
0.0025	0.1239	0.8736	0.2060	0.2926	0.5014	2.3614	4.1142

Table G.8 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-octanol(1)-ethanol(2)-water(3) at 60°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0154	0.9846	0.6222	0.0909	0.2869	5.8965	20.2350
0.0000	0.0364	0.9636	0.5641	0.1225	0.3133	3.3660	10.3515
0.0000	0.0427	0.9573	0.4865	0.1570	0.3565	3.6795	9.8803
0.0000	0.0541	0.9459	0.4082	0.1926	0.3992	3.5621	8.4412
0.0000	0.0691	0.9309	0.3574	0.2159	0.4267	3.1246	6.8166
0.0000	0.0867	0.9133	0.2976	0.2373	0.4651	2.7359	5.3724
0.0000	0.0952	0.9048	0.2278	0.2575	0.5147	2.7056	4.7561
0.0000	0.1128	0.8872	0.1997	0.2762	0.5241	2.4483	4.1445

Table G.9 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-decanol(1)-ethanol(2)-water(3) at 30°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0418	0.9582	0.6435	0.1535	0.2030	3.6729	17.3399
0.0000	0.0574	0.9426	0.5740	0.1983	0.2277	3.4525	14.2930
0.0000	0.0799	0.9201	0.4885	0.2537	0.2579	3.1744	11.3258
0.0000	0.0967	0.9033	0.4123	0.2956	0.2922	3.0555	9.4460
0.0008	0.1268	0.8724	0.3270	0.3163	0.3566	2.4945	6.1019
0.0014	0.1428	0.8558	0.2724	0.3379	0.3897	2.3672	5.1992
0.0021	0.1608	0.8371	0.2191	0.3525	0.4285	2.1915	4.2814
0.0026	0.1747	0.8227	0.1747	0.3552	0.4701	2.0337	3.5591

Table G.10 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-decanol(1)-ethanol(2)-water(3) at 40°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0315	0.9685	0.6010	0.1514	0.2476	4.8078	18.8054
0.0000	0.0539	0.9461	0.5219	0.2080	0.2701	3.8561	13.5052
0.0000	0.0756	0.9244	0.4218	0.2679	0.3102	3.5449	10.5628
0.0000	0.0946	0.9054	0.3815	0.2862	0.3322	3.0250	8.2434
0.0011	0.1179	0.8810	0.3068	0.3140	0.3792	2.6642	6.1897
0.0019	0.1307	0.8674	0.2772	0.3243	0.3985	2.4820	5.4030
0.0030	0.1477	0.8493	0.2309	0.3371	0.4320	2.2821	4.4864
0.0042	0.1680	0.8278	0.1592	0.3455	0.4953	2.0571	3.4384

Table G.11 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-decanol(1)-ethanol(2)-water(3) at 50°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0222	0.9778	0.6751	0.0863	0.2386	3.8826	15.9139
0.0000	0.0438	0.9562	0.5889	0.1500	0.2611	3.4276	12.5518
0.0000	0.0658	0.9342	0.4932	0.2087	0.2981	3.1730	9.9440
0.0000	0.0785	0.9215	0.4157	0.2478	0.3365	3.1582	8.6485
0.0000	0.0973	0.9027	0.3592	0.2698	0.3710	2.7715	6.7422
0.0008	0.1280	0.8711	0.2720	0.3068	0.4212	2.3961	4.9561
0.0015	0.1470	0.8516	0.2233	0.3203	0.4564	2.1795	4.0669

Table G.12 Distribution coefficients of ethanol (K_D) and relative selectivity (RS) of ethanol over water for 1-decanol(1)-ethanol(2)-water(3) at 60°C

aqueous phase			organic phase			K_D	RS
x(1)	x(2)	x(3)	x(1)	x(2)	x(3)		
0.0000	0.0233	0.9767	0.6389	0.0926	0.2685	3.9686	14.4343
0.0000	0.0451	0.9549	0.5580	0.1428	0.2992	3.1678	10.1087
0.0000	0.0568	0.9432	0.4627	0.1962	0.3411	3.4560	9.5561
0.0000	0.0787	0.9213	0.3985	0.2308	0.3707	2.9326	7.2881
0.0000	0.0999	0.9001	0.2747	0.2818	0.4435	2.8194	5.7220
0.0000	0.1194	0.8806	0.2386	0.3022	0.4592	2.5307	4.8533
0.0016	0.1413	0.8571	0.2039	0.3214	0.4747	2.2754	4.1082
0.0027	0.1558	0.8415	0.1810	0.3204	0.4986	2.0562	3.4701

VITA

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