UNIVERSAL LIQUID MIXTURE MODELS FOR VAPOR-LIQUID AND LIQUID- LIQUID EQUILIBRIA IN HEXANE-BUTANOL -WATER SYSTEM

by

Akand Wahid Islam

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Department: Chemical Engineering
Major: Chemical Engineering
Major Professor: Dr. Vinayak Kabadi

North Carolina A&T State University
Greensboro, North Carolina
2009

School of Graduate Studies
North Carolina Agricultural and Technical State University

This is to certify that the Master's Thesis of

Akand Wahid Islam

has met the thesis requirements of
North Carolina Agricultural and Technical State University

Greensboro, North Carolina
2009

Vinayak Kabadi
Dr. Vinayak N. Kabadi
Major Professor

L.C. Uitenham
Dr. Leonard C. Uitenham
Department Chairperson

Kenneth H Murray
Dr. Kenneth H. Murray
Dean of Graduate Studies

BIOGRAPHICAL SKETCH

Akand Wahid Islam was born on 26 October, 1980 in Madaripur, Bangladesh. He received his Bachelor of Science degree in Chemical Engineering from Bangladesh University of Engineering and Technology (BUET), Bangladesh, in 2005. He is a candidate for the Master of Science degree in Chemical Engineering.

ACKNOWLEDGMENTS

I wish to express my sincerest gratitude to the individuals who supported and encouraged me both professionally and personally in the completion of this work. Foremost, I would like to thank my direct supervisor, Dr. Vinayak Kabadi. Admittedly, without his continued support, encouragement, patience and valuable advice, this work would not have been possible. Despite the fact that I had no previous research experience, his enthusiasm, inspiration and effort drove me to conduct this research in a highly professional manner.

I would also like to thank my committee members**,** Dr. Shamsuddin Ilias and Dr. John Kizito, for their cooperation and suggestions. I would also like to thank the Department of Chemical Engineering for providing me the opportunity to pursue my M.S. degree.

I also wish to express my deepest appreciation to my parents and other family members for their lifelong sacrifices and belief in me. Their consistent mental support, love and concern have played a significant role in my life’s journey.

I would like to acknowledge Ferdaus Faruq for his cooperation and my friends in Yanceyville who made my stay very comfortable in Greensboro, North Carolina.

TABLE OF CONTENTS

LIST OF FIGURES

FIGURE **PAGE**

LIST OF TABLES

TABLE **PAGE**

LIST OF SYMBOLS

G^{IM}	Gibbs Energy of ideal mixture
G^{ex}	Excess Gibbs Energy
R	Universal gas constant
P	Total pressure
T	Temperature
x_i	Mole fraction of component *i* in liquid phase
y_i	Mole fraction of component *i* in vapor phase
γ_i	Activity coefficient of component *i*
μ_i^I	Chemical potential of component *i* in phase I
μ_i^{II}	Chemical potential of component *i* in phase II
a_i^I	Activity of component *i* in phase I
a_i^{II}	Activity of component *i* in phase II
p_i^{sat}	Saturated vapor pressure of component *i*
$\gamma_{i,j}^{\infty}$	Infinite dilution activity coefficient *i* in *j*
T_c	Critical temperature
Pc	Critical pressure
ω_i	Accentric factor of component *i*
Tr	Reduced temperature
P_{cij}	Cross critical pressure of components *i* and *j*
T_{cij}	Cross critical temperature of components *i* and *j*
γ_{iL}	Activity coefficient of component *i* in liquid phase
f_{iL}^0	Fugacity of pure liquid component *i* at temperature T, pressure P of mixture
f_{iV}^0	Fugacity of pure vapor component *i* at temperature T, pressure P of mixture

$\varphi_{P,T}$	Fugacity coefficient of component *i* at pressure P, temperature T
φ_i^s	Saturated fugacity coefficient

ABSTRACT

Islam, Akand Wahid. UNIVERSAL LIQUID MIXTURE MODELS FOR VAPOR-LIQUID AND LIQUID-LIQUID EQUILIBRIA IN HEXANE-BUTANOL-WATER SYSTEM. **(Advisor: Dr. Vinayak Kabadi)**, North Carolina Agricultural and Technical State University.

The research conducted here was an attempt to use the currently available activity coefficient methods with universal sets of parameters to simultaneously predict binary and ternary vapor-liquid and liquid-liquid equilibrium data. Literature studies available with such correlations based on two-parameter models (UNIQUAC and LSG) and three-parameter models (NRTL and GEM-RS) used different binary interaction parameters to represent vapor-liquid and liquid-liquid equilibrium data. The focus of this research was to calculate all kinds of phase equilibrium data within fair error using only a single set of parameters obtained from the above-mentioned models regardless of vapor-liquid or liquid-liquid equilibrium. This was proven by an investigation of the Hexane-Butanol-Water ternary system, in which Hexane-Butanol, Hexane-Water, and Water-Butanol binary LLE data, binary VLE data, and γ^{∞} (infinite dilution activity coefficient) data was used to analyze the ternary system. Ternary LLE data for the Hexane-Butanol-Water system was also analyzed. In each of the mentioned binary systems and the ternary system, the calculated and experimental data were compared.

The results of this analysis predicted binary mutual solubility data, binary VLE data, ternary LLE data, infinite dilution activity coefficient and infinite dilution distribution coefficient concurrently within reasonable error (not more than 15%).

CHAPTER 1

INTRODUCTION

This work is based on the hypothesis that liquid should exhibit the same physical behavior when it is in equilibrium with another substance whether or not said substance is in liquid phase or vapor phase. Hence, using only a single set of parameters of a universal model, all kinds of phase equilibrium data can be calculated with acceptable error and the use of different parameters to calculate different phase equilibrium data will not be required. To prove this hypothesis, an extensive analysis was carried out on the Hexane-Butanol-Water ternary system which is non-ideal. Experimental liquid-liquid equilibrium data of this system was measured by Javvadi [1] from very dilute regions to higher concentrations. Javvadi tried to fit his experimental data with currently available liquid state model UNIQUAC [2]. Javvadi found that experimental and calculated distribution coefficient of Butanol in Hexane-Water differs with an error of about 1000%. When Javvadi correctly fitted finite concentration data, he failed to predict dilute region data and vice versa. When trying to calculate other phase equilibrium data like γ^{∞}, mutual solubility data, and VLE data for each binary pairs using Javvadi's regressed parameters [1], it was found that the calculated data shows large errors in comparison with the experimental data. These results indicate that liquid behaves differently when it is in binary equilibrium with another liquid/vapor phase or in ternary equilibrium with two other liquids, a natural condition which is contradictory to our presumed hypothesis. Despite this contradiction, it had to be determined whether or not the hypothesis was acceptable. In order to determine this acceptability, a single set of binary parameters of a phase equilibrium model had to be obtained with which all types of phase equilibrium data could be calculated, and thus show that the hypothesis is reasonable.

During the course of this study, a number of ternary systems were investigated and both distribution coefficients as well as finite concentration data were attempted to fit. For some systems UNIQUAC showed very good fit, but for others, this model produced large errors between experimental and calculated *Dsw*. Also in some cases, parameters obtained from ternary data could not be used for binary calculations. Based on this investigation, it was found that Hexane-Water and Butanol-Water pairs could be fitted with ease. For these pairs both mutual solubility and infinite dilution activity coefficient data could be fitted. However, Hexane-Butanol presented a challenge as far as fitting the data was concerned. The data for this pair could not be fit throughout the concentration range. Hence, various models were used in order to obtain an acceptable fit for this pair.

There are different models available for correlating phase equilibrium. The simplest and most effective models among them are Margules, Van Laar, Redlich-Kister and Black equations [2]**.** These equations often give good results, but extrapolation to concentrations beyond the range of data or the prediction of ternary phase diagrams from only binary information cannot be carried out with these models due to large errors. Local composition models like LSG, LCG, GEM-RS, GEM-QC [3], NRTL [4] and UNIQUAC [5-12], have proven superior to the simple models, both for correlating binary and ternary liquid-liquid equilibria and for predicting ternary phase diagrams from binary data. The UNIQUAC model has only two adjustable parameters per binary. Abrams and Prausnitz [6] showed that UNIQUAC performs reasonably well, both in predicting ternary diagrams from binary information and correlating ternary diagrams. Anderson and Prausnitz [7] also showed UNIQUAC sufficiently predicts ternary diagrams from binary information when binary vapor-liquid and liquid-liquid equilibrium data are correlated simultaneously. Essentially, the UNIQUAC model is a two-parameter model and is of considerable use because of its wide applicability to various liquid solutions. In order to yield better results for systems containing water and alcohols, Anderson and Prausnitz [7] have empirically modified the UNIQUAC equation by using different values for the pure component area parameter q for water and alcohols in combinatorial and residual parts. Nagata and Katoh [11] have also proposed another modified UNIQUAC equation for a variety of systems containing alcohols and water. However, this model poses some problems in its extension to systems with more than three components.

For phase equilibrium calculations, all models require binary interaction parameters. These parameters can be obtained in several ways. If the two components are completely miscible, then parameters can be regressed by taking vapor-liquid equilibrium data only. But for partial miscible pairs, these can be obtained either by mutual solubility data or by vapor-liquid equilibrium data. Binary interaction parameters can also be fitted from specific ternary systems. These show good results for that particular ternary system; however, they cannot be used to calculate data like binary VLE (vapor-liquid equilibrium), binary LLE (liquid-liquid equilibrium), infinite dilution activity coefficient (γ^{∞}), and so on. These parameters cannot represent the data of both very dilute regions and finite concentrations. On the other hand, the parameters that are regressed from binary data cannot predict ternary data. Hence, a single set of parameters are unable to represent different types of phase equilibrium data. Here we will introduce new kinds of interaction parameters which we have termed universal parameters. Universal binary interaction parameters are the parameters which are able to predict binary mutual solubility data, binary VLE data, ternary LLE data, infinite dilution activity coefficient and infinite dilution distribution coefficient correctly with reasonable error. Universal parameters are fitted using all possible phase equilibrium data simultaneously. In this work, a process to obtain said universal parameters is devised.

CHAPTER 2

THEORY AND BACKGROUND

In the case of liquid-liquid equilibrium, one liquid phase is in equilibrium with another liquid phase, and in vapor-liquid equilibrium, one liquid phase is in equilibrium with another vapor phase. To be in equilibrium, three conditions must be fulfilled for a component. The conditions are

$$Ti^{I}=Ti^{II} \tag{2.1}$$

$$Pi^{I}=Pi^{II} \tag{2.2}$$

$$f_i^{I}=f_i^{II} \tag{2.3}$$

Here T is for temperature, P is for pressure, subscript i is for component and superscript I and II are for phase numbers. Here f_i represents fugacity of component i. In ternary liquid-liquid equilibrium, liquids are separated into two phases. The reasons behind these separations are discussed in the following section.

2.1 Separation of Liquid Mixture into Two Phases

A stable state is defined as a state that has a minimum Gibbs free energy at a fixed temperature and pressure. For an ideal mixture, Gibbs free energy is given by

$$\underline{G}^{IM} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i \tag{2.4}$$

Here x_i 's are always less than unity, ln (x_i)≤ 0 and the last term in the above equation is negative. Therefore, Gibbs Free Energy of an ideal mixture is always less than the mole fraction weighted sum of the pure component Gibbs free energies. For a real mixture, we have

$$\underline{G} = \underline{G}^{IM} + \underline{G}^{ex} \tag{2.5}$$

Excess Gibbs free energy would be determined by experiment, or approximated by a liquid solution model. For a mixture with a Gibbs free energy curve shown in Figure 2.1, with an overall composition between $x_1^{'}$ and $x_1^{''}$, the lowest value of Gibbs free energy is obtained when the mixture separates into two phases, one of composition $x_1^{'}$ and the other of composition $x_1^{''}$. In this case Gibbs free energy of the mixture is a linear combination of the Gibbs free energies of the two coexisting equilibrium liquid phases. If the overall composition is less than $x_1{}'$ or greater than $x_1{}''$, only a single phase will exist.

2.2 Thermodynamic Conditions for Phase Equilibrium

The necessary and sufficient condition of equilibrium is that the Gibbs free energy of mixing for the mixture is minimum. Since the molar Gibbs free energy of mixing is minimum, a differential change of composition occurring at equilibrium at fixed pressure and temperature will not produce any change in ΔG and hence,

$$d(\Delta G)_{T,P} = 0 \tag{2.6}$$

This criterion is necessary but not sufficient, since ΔG can be either a maximum or a minimum. The usual equilibrium condition is:

$$\mu_i^I\left(T,P,x_i{}^I\right) = \mu_i^{II}\left(T,P,x_i{}^{II}\right) \tag{2.7}$$

Or more conveniently in terms of activities

$$a_i^I = a_i^{II} \tag{2.8}$$

Equations 2.3 and 2.5 are often used in liquid-liquid equilibrium calculations and in order to carry out these calculations, one must have

1. a model giving G^E or γ_I, as functions of compositions and temperature, and
2. a method for calculating liquid-liquid equilibrium compositions using the above model.

2.3 Phase Equilibrium Calculation

If an expression is available for relating molar excess Gibbs energy G^{ex} to composition, the activity coefficient of every component can be calculated. For a liquid-liquid equilibrium system containing *m* components, there are *m* equations of equilibrium. The standard-state fugacity for every component *i* in all phases should be the same.

If an appropriate expression for G^{ex} is available, it is not immediately obvious how to solve these *m* equations simultaneously when m>2. To fix ideas, consider a ternary system at a fixed temperature and pressure. We want to know coordinates $x_{1'}$ and $x_{2'}$ on the binodal curve that are in equilibrium with coordinates $x_{1''}$ and $x_{2''}$. Therefore, we have four unknowns. However, there are only three equations of equilibrium. To find the desired coordinates, therefore, it is not sufficient to consider only three equations of equilibrium indicated by Equation 2.1.

$$f(g_1^E)' x_1' = f(g_1^E)'' x_1'' \tag{2.9}$$

To obtain the coordinates, we must use a material balance by performing what is commonly known as an *isothermal flash calculation.*

One mole of a liquid stream with overall composition x_1, x_2 is introduced into a flash chamber where that stream isothermally separates into two liquid phases ' and ". The number of moles of phases between ' and " are designated by L' and L".

$$L' + L'' = 1 \tag{2.10}$$

$$x_1' L' + x_1'' L'' = x_1 \tag{2.11}$$

$$x_2' L' + x_2'' L'' = x_2 \tag{2.12}$$

There are six equations that must be solved simultaneously. Three equations of equilibrium and three material balances. We also have six unknowns: x_1', x_2', x_1'' x_2'', L', and L''. In principle, therefore, the problem is solved, although the numerical procedure for doing so efficiently is not necessarily easy. This flash calculation for a ternary system is readily generalized to systems containing any number of components. When m components are present, we have a total of $2m$ unknowns: $2(m-1)$ compositions and two mole numbers, L' and L''. These are found from m independent equations of equilibrium and m independent material balances.

To calculate ternary liquid-liquid equilibrium at a fixed temperature, we require an expression for the molar excess Gibbs Energy G^{ex} as a function of composition; this expression requires binary parameters characterizing 1-2, 1-3 and 2-3 interactions. Calculated ternary equilibrium is strongly sensitive to the choice of these parameters. The success of the calculation depends directly on the care exercised in choosing these binary parameters from data reduction.

To calculate phase equilibrium for a ternary mixture, it is necessary to estimate binary parameters for each of the three binaries; there is always some uncertainty in the three sets of binary parameters. To obtain reliable calculated ternary liquid-liquid equilibrium, the most important task is to choose the best set of binary parameters. This choice can only be made if a few ternary liquid-liquid data are available, for example, by Bender and Black, who used the NRTL equation, and by Anderson, who used the UNIQUAC equation. Procedures of VLE calculation are the same as LLE calculation. To calculate vapor phase fugacity virial equation or some equation of states are used like Peng-Robinson Equation of State, and so on.

2.4 Models for Activity Coefficients

As mentioned earlier there are different models available for correlating liquid-liquid equilibrium and the simplest and most effective models among them are Margules, Van Laar, Redlich-Kister and Black equations [2]. Local composition models, like NRTL [4] and UNIQUAC [5-12], have proven superior to the simple models, both for correlating binary and ternary liquid-liquid equilibrium and for predicting ternary phase diagrams from binary data. There are also some models which are particularly used for calculation of infinite dilution activity coefficient. These are described in Table 2.1.

2.4.1 UNIQUAC Model

The UNIQUAC model [5] is derived by phenomenological arguments based on a two-fluid theory and it allows local compositions to result from both size and energy differences between the molecules in the mixture.

$$\frac{G^{ex}}{RT} = \frac{G^{ex}(combinatorial)}{RT} + \frac{G^{ex}(residual)}{RT} \tag{2.13}$$

The first term in the above expression accounts for molecular size and shape differences and the second term accounts largely for energy differences.

$$\frac{G^{ex}(combinatorial)}{RT} = \sum_i x_i \ln\frac{\phi_i}{x_i} + \frac{z}{2}\sum_i x_i q_i \ln\frac{\theta_i}{\phi_i} \tag{2.14}$$

$$\frac{G^{ex}(residual)}{RT} = -\sum q_i x_i \ln\left(\sum \theta_i \phi\right) \tag{2.15}$$

where

r$_i$ =volume parameter for species *i*

q$_i$ = surface area parameter for species *i*

θ_i , area fraction of species *i*

$$\theta_i = x_i q_i / \sum x_j q_j \tag{2.16}$$

ϕ_i , volume fraction of species *i*

$$\varphi_i' = x_i r_i / \sum x_j r_j \tag{2.17}$$

$$\ln \tau_{ij} = \frac{\left(u_{ij} - u_{jj}\right)}{RT} \tag{2.18}$$

u_{ij} being the average interaction energy between *i-j* and *z* being the average coordination number, usually taken to be 10.

$$\ln \gamma_i (combinatorial) = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{\theta_i} \sum_j x_j l_j \tag{2.19}$$

$$\ln \gamma_i (residual) = q_i \left[1 - \ln\left(\sum_j \theta j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ji}}{\sum_k \theta_k \tau_{kj}} \right] \tag{2.20}$$

The UNIQUAC model is essentially a two-parameter model and is of considerable use because of its wide applicability to various liquid solutions.

2.4.2 Modified UNIQUAC Model

To yield better results for systems containing water and alcohols, Anderson and Prausnitz [7] have empirically modified the UNIQUAC equation by using different values for the pure component area parameter *q* for water and alcohols in combinatorial and residual parts. These are shown in Table 2.2.

$$\frac{G^{ex}(residual)}{RT} = -\sum q_i' x_i \ln\left(\sum \theta_i' \tau_{ji}\right) \tag{2.20}$$

$$\ln \gamma_i (residual) = q_i^{'} \left[1 - \ln\left(\sum_j \theta_j^{'} \tau_{ji} \right) - \sum_j \frac{\theta_j^{i} \tau_{ji}}{\sum_k \theta_k^{'} \tau_{kj}} \right] \tag{2.21}$$

where

$$\theta_i^{'} = \frac{x_i q_i^{'}}{\sum_j x_j q_j^{'}} \tag{2.22}$$

There is another modified UNIQUAC equation proposed by Nagata and Katoh [8] for a variety of systems containing alcohols and water but it can be extended to multi component systems only under additional assumptions that the third parameter C is the same for all the binaries, which comprise the multi component mixture.

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \left(\frac{Z}{2} \right) q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum x_j l_j$$

$$+ C \left[-\ln\left(\sum_j x_j G_{ji} \right) + 1 - \sum_k \frac{x_k G_{ik}}{\sum_j x_j G_{jk}} - \left(\ln \frac{\theta_i}{x_i} + 1 - \frac{\theta_i}{x_i} \right) \right] \tag{2.23}$$

where

$$l_i = (Z/2)(r_i - q_i) - (r_i - 1) \tag{2.24}$$

$$G_{ij} = (q_i / q_j) \exp\left(\frac{-\Delta u_{ij}}{CRT} \right) \tag{2.25}$$

In general UNIQUAC is a very useful two-parameter equation for excess Gibbs energy but the modified UNIQUAC is more effective. Introducing a third parameter in effective UNIQUAC eliminates the advantages of two-parameter model and also does relax any other assumptions.

2.4.3 Different Forms of UNIQUAC Models

Abrams and Prausnitz [5] first developed the UNIQUAC Model. Later on based on applicability on different systems and to get better results than the original, this model has been modified over the years. First Maurer and Prausnitz [6] modified this model introducing a constant ‘C’ with residual part. Weidlich and Gmehling [7] modified volume fraction. Larsen et al. [8] first introduced a temperature dependent function for this model to make more applicable over the temperature range. Different forms of the modified UNIQUAC model are shown as follows

Maurer and Prausnitz [6]:

$$\frac{G^{ex}(combinatorial)}{RT} = \sum_i x_i \ln\frac{\phi_i}{x_i} + \frac{z}{2}\sum_i x_i q_i \ln\frac{\theta_i}{\phi_i} \tag{2.26}$$

$$\frac{G^{ex}(residual)}{RT} = -C\sum q_i x_i \ln\left(\sum \theta_j \tau_{ji}\right) \tag{2.27}$$

$$\ln\gamma_i(combinatorial) = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i \ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{\theta_i}\sum_j x_j l_j \tag{2.28}$$

$$\ln\gamma_i(residual) = \left[Cq_i - q_i \ln\left(\sum_j \theta j\,\tau_{ji}\right) - Cq_i \sum_j \frac{\theta_j \tau_{ji}}{\sum_k \theta_k \tau_{kj}}\right] \tag{2.29}$$

Weidlich and Gmehling [10]:

$$\frac{G^{ex}(combinatorial)}{RT} = \sum_i x_i \ln\frac{\phi_i'}{x_i} + \frac{z}{2}\sum_i x_i q_i \ln\frac{\theta_i}{\phi_i} \tag{2.30}$$

$$\frac{G^{ex}(residual)}{RT} = -C\sum q_i x_i \ln\left(\sum \theta_i \tau_{ji}'\right) \tag{2.31}$$

$$\ln\gamma_i(combinatorial) = \ln\frac{\phi_i'}{x_i} + 1 - \frac{\phi_i'}{x_i} - \frac{Z}{2}q_i[\ln\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}] \tag{2.32}$$

$$\ln\gamma_i(residual) = \left[q_i' - q_i' \ln\left(\sum_j \theta j\,\tau_{ji}'\right) - q_i' \sum_j \frac{\theta_j \tau_{ji}'}{\sum_k \theta_k \tau_{kj}'}\right] \tag{2.33}$$

θ_i and ϕ_i are determined from equations. 2.16 and 2.17

$\phi_i^{/}$ is modified volume fraction of species *i*

$$\tau_{ji}^{/} = \exp\left[-\frac{a_{ij} + b_{ij}T + c_{ij}T^2}{T} \right] \tag{2.34}$$

$$\phi_i^{/} = x_i r_i^{3/4} / \sum x_j r_i^{3/4} \tag{2.35}$$

Larsen, Rasmussen and Fredenslund [9]:

$$\frac{G^{ex}(combinatorial)}{RT} = \sum_i x_i \ln \frac{\phi_i^{/}}{x_i} \tag{2.36}$$

$$\frac{G^{ex}(residual)}{RT} = -\sum q_i x_i \ln\left(\frac{\theta_{ii}}{\theta_i} \right) \tag{2.37}$$

θ_i and ϕ_i are determined from equations. 2.16 and 2.17

$$\theta_{ji} = \frac{\theta_j \tau_{ji}}{\sum \theta_j \tau_{ji}} \tag{2.38}$$

$$\tau_{ji} = \exp\left[-\frac{a_{ji}^{/}}{T} \right] \tag{2.39}$$

$$a_{ji}^{/} = a_{ji} + b_{ji}(T - T_0) + c_{ji}(T \ln \frac{T_0}{T} + T - T_0) \tag{2.40}$$

T_0=reference temp (like 298.15 K)

$$\ln \gamma_i(combinatorial) = \ln \frac{\phi_i^{/}}{x_i} + 1 - \frac{\phi_i^{/}}{x_i} - \frac{Z}{2} q_i [\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}] \tag{2.41}$$

$$\ln \gamma_i(residual) = \frac{Z}{2} q_i \left[-\left\{ \ln\left(\sum \theta_j \tau_{ji} \right) \right\} + 1 - \frac{\sum \theta_j \tau_{ij}}{\sum \theta_m \tau_{mj}} \right] \tag{2.42}$$

Nagata [11]:

$$\frac{G^{ex}(combinatorial)}{RT} = \sum_i x_i \ln \frac{\phi_i^{/}}{x_i} + \frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\phi_i} \tag{2.43}$$

$$\frac{G^{ex}(residual)}{RT} = -\sum q_i^{/} x_i \ln\left(\sum \theta_j \tau_{ji} + \sum_j \sum_{j<k} \theta_j \theta_k \tau_{jki} \right) \tag{2.44}$$

$$\ln \gamma_i(combinatorial) = \ln \frac{\phi_i^{/}}{x_i} + 1 - \frac{\phi_i^{/}}{x_i} - \frac{Z}{2} q_i [\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}] \tag{2.45}$$

$$\ln \gamma_i(residual) = -q_i^{/} \ln\left(\sum \theta_j \tau_{ji} + \theta_j \theta_k \tau_{jki} \right) + q_i \sum \left(\frac{q_j^{/}}{q_j} \right) \theta_j - \frac{q_i^{/} \theta_i \left(\tau_{ii} - \theta_j \theta_k \tau_{jkii} \right)}{\sum \theta_j \tau_{ji} + \theta_j \theta_k \tau_{jki}}$$

$$- \frac{q_i \left(\frac{q_j^{/}}{q_j} \right) \theta_j \left[\tau_{ji} + \left(1 - \theta_i \right) \theta_k \tau_{jki} \right]}{\sum \theta_j \tau_{jj} + \theta_i \theta_k \tau_{ikj}} - \frac{q_i \left(\frac{q_k^{/}}{q_k} \right) \theta_k \left[\tau_{ik} + \left(1 - \theta_i \right) \theta_j \tau_{ijk} \right]}{\sum \theta_j \tau_{jk} + \theta_i \theta_j \tau_{ijk}} \tag{2.46}$$

Tamura, Chen, Tada, Yama and Nagata [12]:

$$\frac{G^{ex}(combinatorial)}{RT} = \sum_i x_i \ln \frac{\phi_i^{/}}{x_i} + \frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\phi_i} \tag{2.47}$$

$$\frac{G^{ex}(residual)}{RT} = -\sum q_i^{/} x_i \ln\left(\sum \theta_j \tau_{ji} + \sum_j \sum_{j<k} \theta_j \theta_k \tau_{jki} \right) \tag{2.48}$$

$$\ln \gamma_i(combinatorial) = \ln \frac{\phi_i^{/}}{x_i} + 1 - \frac{\phi_i^{/}}{x_i} - \frac{Z}{2} q_i [\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}] \tag{2.49}$$

$$\ln \gamma_i(residual) = -q_i^{/} \ln\left(\sum \theta_j \tau_{ji} + \theta_j \theta_k \tau_{jki} \right) + C[q_i \sum \left(\frac{q_j^{/}}{q_j} \right) \theta_j - \frac{q_i^{/} \theta_i \left(\tau_{ii} - \theta_j \theta_k \tau_{jkii} \right)}{\sum \theta_j \tau_{ji} + \theta_j \theta_k \tau_{jki}}$$

$$- \frac{q_i \left(\frac{q_j^{/}}{q_j} \right) \theta_j \left[\tau_{ji} + \left(1 - \theta_i \right) \theta_k \tau_{jki} \right]}{\sum \theta_j \tau_{jj} + \theta_i \theta_k \tau_{ikj}} - \frac{q_i \left(\frac{q_k^{/}}{q_k} \right) \theta_k \left[\tau_{ik} + \left(1 - \theta_i \right) \theta_j \tau_{ijk} \right]}{\sum \theta_j \tau_{jk} + \theta_i \theta_j \tau_{ijk}}] \tag{2.50}$$

This model was used for our calculation. Values of r and q are reported in Chapter 4.

2.5 NRTL Model

This model was developed by Renon and Prausnitz [4] based on two-liquid theories. This is different from the UNIQAC and his two-parameter model. This model does not contain combinatorial and residual parts separately. For a solution of *m* components, the NRTL equation is

$$\frac{g^E}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} \tag{2.51}$$

where

$$\tau_{ji} = \frac{g_{ji}}{RT} \tag{2.52}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{2.53}$$

$$\alpha_{ji} = \alpha_{ij} \tag{2.54}$$

The activity coefficient for any component *i* is given by

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right) \tag{2.55}$$

Here, g_{ij}, g_{ji} and $\alpha_{ij}(\alpha_{ij}= \alpha_{ji})$ are regressed.

2.6 LSG Model

This model is based on Guggenheim's quasi-lattice model and Wilson's local composition concept proposed by Vera [2]. Like UNIQUAC this has also combinatorial and residual parts, although the equation is similar but not identical to UNIQUAC.

$$\ln\gamma_i = 1 - \frac{\varphi_i}{x_i} + \ln\frac{\varphi_i}{x_i} + \frac{zq_i}{2}\left[\frac{\varphi_i}{\theta_i} - \sum_k \frac{\theta_k\tau_{ki}}{\sum_j \theta_j\tau_{kj}} + \ln\frac{\theta_i/\varphi_i}{\sum_k \theta_k\tau_{ik}}\right] \tag{2.56}$$

where

r_i = volume parameter for species i

q_i = surface area parameter for species i

θ_i and ϕ_i are determined from eq. 2.16 and 2.17

$$\ln\tau_{ij} = \frac{u_{ij}}{RT} \tag{2.57}$$

Here, like UNIQUAC, u_{ij} and u_{ji} are regressed.

2.7 GEM-RS Model

This is the same as the LSG model but contains the third interaction parameters like the NRTL model. The method of obtaining *r* and *q* values is the same for the LSG and GEM-RS model. Methods of obtaining these volume and surface parameters are discussed in Chapter 4.

$$\ln\gamma_i = 1 - \frac{\varphi_i}{x_i} + \ln\frac{\varphi_i}{x_i} + \frac{zq_i}{2}\left[\frac{\varphi_i}{\theta_i} - \sum_k \frac{\theta_k\tau_{ki}}{\sum_j \theta_j\tau_{kj}} + \ln\frac{\theta_i/\varphi_i}{\sum_k \theta_k\tau_{ik}}\right]$$
$$\frac{zq_i}{2}\sum_{k\neq i}\pi_{ik}\theta_k - \frac{zq_i}{2}\sum_{k=1}\sum_{l>k}\pi_{kl}\theta_k\theta_l \tag{2.58}$$

where

r_i = volume parameter for species i

q_i = surface area parameter for species i

θ_i and ϕ_i are determined from eq. 2.16 and 2.17

$$\ln\tau_{ij} = \frac{u_{ij}}{RT} \tag{2.59}$$

$$\pi_{ij} = \frac{\lambda_{ij}}{RT} \tag{2.60}$$

Here, u_{ij} , u_{ij} and $\lambda_{ij}(\lambda_{ij}= \lambda_{ji})$ are regressed.

2.8 Computation of Binodal Curves for Ternary Systems

Using a given set of binary interaction parameters, a binodal curve for a ternary system can be constructed by establishing a series of tie lines using either the isoactivity method or minimization of Gibbs free energy methods. If these tie lines are spaced throughout the two-phase region, the entire binodal curve can be readily drawn. The first step in this computation is to establish the tie line with no solute, that is, on the base line of the triangular diagram. The next step is to predict a tie line a little above the base line and specifying the concentration of one of the components in one of the phases can do this. A more general method, which is also applicable for multi component systems, is to specify the amounts of each of the components in the feed, in other words, the overall composition is known.

Although the procedure looks straightforward, there is in reality an additional difficulty, which occurs frequently for both UNIQUAC and NRTL and for both correlation of ternary data sets and their predictions from binary data. Sometimes we obtain three liquid phases in equilibrium but in reality there exists only two phases. In correlating ternary data sets, it is important to ensure that the obtained parameters cannot yield extra two- and three-phase regions where these do not exist.

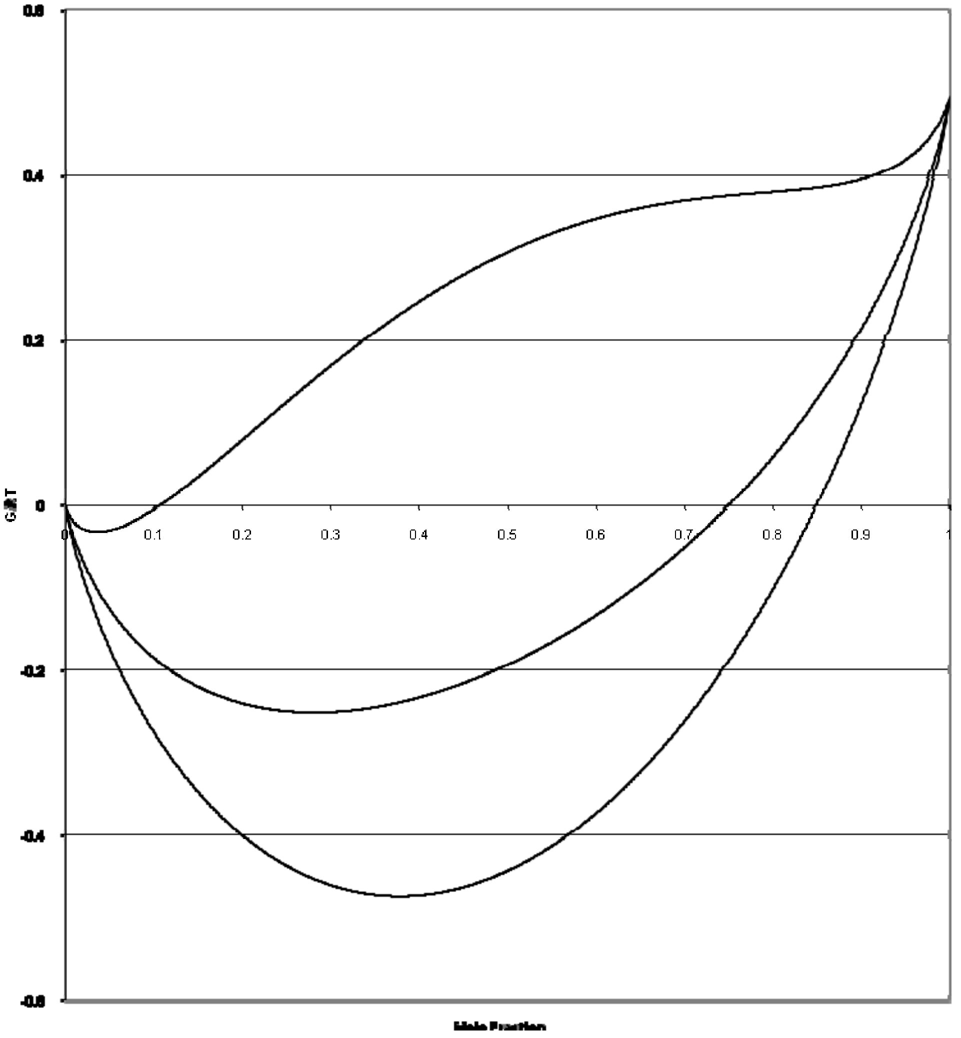

Figure 2.1. Molar Gibbs free energy for ideal and non-ideal binary mixtures

Table 2.1. List of activity coefficient models and their applicability

Model Name	Type of model	Application and Accuracy	Recommendation	Reference
ASOG	Group contribution method similar to UNIFAC but based on the Wilson equation.	Good to calculate LLE data mainly at finite concentration.	Not can be used for both finite and dilute region.	[63]
SPACE	Based on solvatochromic parameters for activity coefficient estimation.	Superior predictive method for γ^{∞} calculation in nonaqueous systems.	Not can be used for both finite and dilute region.	[64]
LSG	Based on Guggenheim's quasi-lattice model.	Good at LLE calculation.	Not can be used for both finite and dilute region.	[2]
LCG	Based on Wilson's local composition concept.	Good at LLE calculation.	Not can be used for both finite and dilute region.	[2]
GEM-QC	Based on Guggenheim's renormalized canonical partition function proposed by Wang and Vera.	Quasi-chemical model is good at LLE calculation for ternary systems containing water/organic solvents.	Includes non randomness, we can check this model for our purpose to get consistency between dilute region and finite concentration.	[3]

Table 2.1. (Continued)

Model Name	Type of model	Application and accuracy	Recommendation	Reference
GCSKOW	Based on group contribution salvation octanol-water partition coefficient.	Good at calculating γ^{∞} for organic compounds in water.	Not can be used for both finite and dilute region.	[61]
COSMO-SAC	Based on conductor like screening model for segment activity co-efficient.	Good at calculating γ^{∞} for organic compounds in water. This model is also good at VLE calculation.	Not can be used for both finite and dilute region.	[62]
COSMO-RS	Based on conductor like screening model for real solvent.	Good at calculating γ^{∞} for organic compounds in water. This model is also good at VLE calculation.	Not can be used for both finite and dilute region.	[62]
GCS	Infinite dilution activity coefficient model developed from group contribution salvation energy.	Applied only to calculate γ^{∞} for organic compounds in water.	Not can be used for both finite and dilute region.	[62]

Table 2.2. Size parameter q' for water and alcohols

Component	q'	Component	q'
Water	1.00	C_4 alcohols	0.88
CH_3OH	0.96	C_5 alcohols	1.15
C_2H_5OH	0.92	C_6 alcohols	1.78
C_3 alcohols	0.89	C_7 alcohols	2.71

CHAPTER 3
EXPERIMENTAL METHODS OF MEASURING γ^{∞}, VLE AND LLE DATA

The activity coefficient at infinite dilution (limiting activity coefficient, γ^{∞}) is an important parameter, particularly for the reliable design of thermal separation processes. Thus, the synthesis, simulation, and optimization of such processes requires exact values of the separation factors (α_{ij}) which, depending on pressure, temperature, and the composition of the mixture, can be calculated across the complete concentration range using the following simplified equation:

$$\alpha_{ij} = \frac{\gamma_i P_i^{sat}}{\gamma_j P_j^{sat}} \tag{3.1}$$

where, i is the low-boiling component and j is the high boiling component. Thus, the separation of the final traces of a component requires the greatest effort because the least favorable values of the separation factor occur at high dilution. In the case of positive deviations from Raoult's Law ($\gamma_i > 1$), the greatest separation effort is required at the top of the column ($x_i \rightarrow 1$). In such cases the separation factor is given by the relation

$$\alpha_{ij}^{\alpha} = \frac{P_i^{sat}}{\gamma_j^{\alpha} P_j^{sat}} \tag{3.2}$$

At the bottom of the column ($xj \rightarrow 1$) the effort involved in the separation is largest for negative deviations from Raoult's Law ($\gamma_i < 1$). In such cases the relation applies.

$$\alpha_{ij}^{\alpha} = \frac{\gamma_i^{\alpha} P_i^{sat}}{P_j^{sat}} \tag{3.3}$$

The effort necessary for the separation is determined by the value $\alpha - 1$. To avoid an overdesign of the distillation column and to minimize the investment and operating costs, reliable knowledge of the separation factor at high dilution (α_{ij}^{∞}) is important. The values of the limiting activity coefficients can be used for the reliable design of distillation columns; at the same time the type and the extent of the influence of selective additives on unfavorable separation factors ($0.9 \leq \alpha_{ij} \leq 1.1$) can be determined directly**.**

Thus, for example, in extractive distillation the addition of a selective solvent influences the limiting activity coefficients to differing extents to achieve separation factors very different from unity. This has been applied in a software package for the selection of selective solvents. Gmehling and Mollmann [66] have presented a detailed discussion of the selection of selective solvents for extractive distillation with the help of γ^{∞} data (taken from factual databases or calculated using thermodynamic models).

Taking into account limiting activity coefficients also improves the reliability of the description in the dilute range when reliable G^E model parameters are to be fitted or in the development and improvement of group contribution methods. In addition, it is possible to obtain reliable values for Henry constants and partition coefficients and to forecast the occurrence of azeotropic points.

3.1 Experimental Methods of Measuring Infinite Dilution Activity Coefficients

A large number of methods can be used for the measurement of activity coefficients, the most important being the retention time method (GLC), non steady state gas-liquid chromatography, differential ebulliometry, static methods, and the dilutor technique. All these techniques can only be used to determine the limiting activity coefficient in pure solvents, with the exception of the dilutor technique, which is also applicable to the measurement of γ^{∞} in solvent mixtures. The measurement of γ^{∞} values for high-boiling solutes can be carried out using the dew point method. Table 3.1 shows the range of applicability and comments about several measurement techniques. Since the ebulliometry method is used to measure γ^{∞} of Butanol in Hexane, Water systems, this technique is discussed here very elaborately.

3.1.1 Differential Ebulliometry Method

The principles of differential ebulliometry have been described and applied in many publications. In differential ebulliometry the boiling temperature of a liquid binary mixture (of a solute in a solvent) is compared to that of the pure solvent under the same pressure.

The application of that method to the determination of the infinite dilution activity coefficient of a solute in a solvent at the boiling point temperature of that solvent was first given by Gautreaux and Coates. The condition of phase equilibrium applied to the vapor-liquid equilibrium of the binary mixture gives the following relation, when the vapor phase is assumed to behave like an ideal gas and the influence of pressure on the properties of the liquid are neglected

$$\gamma_{1,2}^{\alpha} = \frac{p_2^{sat} - (dp_2^{sat}/dT)(\partial T/\partial x_1)_p^{\alpha}}{p_1^{sat}} \tag{3.3}$$

where, $\gamma_{1,2}{}^{\infty}$ is the activity coefficient of solute *1* infinitely diluted in solvent *2*, p_i^{sat} is the saturation pressure of pure component *i*, and $(\partial T/\partial x_1)^{\infty}$ is the change of the boiling temperature *T* with the liquid phase mole fraction of the solute, x_1, at constant pressure *p* extrapolated to zero solute concentration. That slope is determined in differential ebulliometry, where the difference $\Delta T=(T^{s}{}_{\text{pure solvent 2}}-T^{s}{}_{\text{mix of 1 and 2}})_p$ is calculated from a plot of ΔT versus the mole fraction of the solute x_1 at constant pressure. The ebulliometric method is typically restricted to mixtures of components with similar volatilities, i.e., when the ratio $\alpha_{1,2} = (y_1/x_1)/(y_2/x_2)$ and $0.1<\alpha_{12}<10$

Approximating the fugacity of a gaseous component by its partial pressure and replacing the fugacity of a pure liquid by its saturation pressure gives (at very small solute mole fractions):

$$\alpha_{1,2} = \left(\frac{p_1^{sat}\gamma_{1,2}^{\alpha}}{p_2^{sat}} \right) \tag{3.4}$$

Equations (2) and (3) represent that the ebulliometric method is appropriate as long as

$$\gamma_{1,2}^{\alpha} \approx (.1-10)p_2^{sat} \tag{3.5}$$

The ebulliometric method was used for the determination of infinite dilution activity coefficient by many researchers. Details are described in Dobrjakov et al. [65].

3.1.2 Description of Apparatus

The equipment used in this work is shown in Figure 3.1 (scheme of the complete experimental arrangement) and Figure 3.2 (scheme of the differential ebulliometer). Two ebulliometers of the Swietoslawskitype (cf. Malanowski [79]) are connected to a common pressostat. One ebulliometer contains about 80–100 cm^3 of the pure solvent, the other about the same amount of a binary solute/solvent mixture. The ebulliometers are heated separately and electrically so that both liquids boil at the same and constant pressure. The heaters are filled with Raschig-rings to reduce bumping. A Cotrell pump delivers the two-phase mixture into an equilibrium chamber where the vapor is separated from the liquid by gravitational force. The temperature in that equilibrium chamber is measured by quartz thermometers (Model 2804A with HP18111A type sensor, Hewlett-Packard, Rockville, MD, USA). The resolution of the thermometers corresponds to a temperature difference of 10−4 K. However, the fluctuations of the temperature amount up to about ±0.003 K. The vapor is condensed by cooling with thermo stated liquids.

The condensation is achieved in a two-step process. In the first step, the cooling agent is water of about 10 °C, in the second step; the temperature is reduced to about 4 °C by means of an ethylene glycol/water mixture. The heating and cooling powers are chosen so that some fluctuation of those powers has no influence on the final experimental results. These ranges were determined in preliminary experiments. Nitrogen is used for transferring the pressure in the condensers from the pressostat to the ebulliometers.

The pressostat consists of a large container (volume of about 250 dm3) charged with a certain amount of nitrogen. That amount can be adjusted (to result in a desired pressure) by means of a vacuum pump and by charging nitrogen from a high pressure bottle (for pressures below and above the atmospheric pressure, respectively). To keep the pressure constant the container is kept at a nearly constant temperature, as it is buried in the ground at a depth of about 1 m below the surface. The pressure is measured by a pressure transducer (type 891.10.500, range 0–0.25MPa, WIKA Alexander Wiegand GmbH, Klingenberg, Germany). The pressure fluctuations were smaller than the resolution of the pressure transducer (100 Pa). There are two ports in each ebulliometer for adding solvent or solute as well as for taking samples of the coexisting phases (liquid phase and condensed vapor phase). Preliminary experiments show that (e.g., due to the hold up) the composition of the liquid in the equilibrium chamber is somewhat different from that of the solvent/solute mixture charged to the ebulliometer. Therefore, samples from both phases are taken and analyzed by measuring the density. The density of the mixture as well as that of the solvents is determined with a vibrating tube instrument. The uncertainty of the experimental result for the specific density is smaller than $\pm 5\times 10-5$ g cm^{-3}. The mixtures used for calibrating the densimeter are prepared by mixing the liquid components. The mass of each component is determined with a high precision balance with an accuracy of $\pm 10-4$ g.

3.1.3 Experimental Procedure

An ebulliometric experiment starts by flushing both ebulliometers with nitrogen and then filling the ebulliometers with the pure solvent. Next, the pressure is transferred from the pressostat to the ebulliometers; the heating power is set and the cooling fluids are sent through the condensers. The system needs about 30 to 60 min to achieve a steady state for the temperature in the equilibrium cells. The pressure is recorded and the (usually small) temperature difference between both ebulliometers is measured. Then a small amount (typically about 200–300mm^3) of the pure solute is injected by a syringe through a port of that ebulliometer that is supposed to be charged with the solute/solvent mixture. When (typically after about 15–20 min) a new steady state is achieved, the temperatures in both ebulliometers and the temperature difference are recorded, and samples (of about 300mm^3) are taken from the vapor phase condensate (cf. port 3 in Figure 3.2) and from the boiling liquid (cf. port 8 in Figure 3.2). The samples are analyzed by measuring the density. Then some liquid is removed and another small amount of the solute is injected and the corresponding steps are repeated. The experimental data is comprised of the initial amount of mass of the solvent, $m_2^{(0)}$, in that ebulliometer which is used to determine the boiling point temperature of the binary mixture; the amount of mass of the liquid withdrawn from the ebulliometer before an experiment, Δm_{mix}^{liq}; the amount of solute Δm_1^{liq} added to the ebulliometer before that experiment; the amount of mass of the mixture in that ebulliometer during an experiment (i) $m_{mix}^{(i)}$; the density of the liquid mixture, ρ_{liq}; the liquid phase mole fraction of the solute x_1; the temperature difference, ΔT, between the boiling liquids; and the scattering of that difference σΔT. The experimental results for the temperature difference are used to determine the slope $(\partial T/\partial x_1)_p^{\alpha}$. That slope is determined by

$$y = \frac{\sum_k (y_k (y_k / \delta y_k))}{\sum_k (y_k / \delta y_k)} \pm \max(\delta y_k) \tag{3.6}$$

$y = (\partial T / \partial x_1)_p^{\alpha}, y_k = ((T_{mix} - T_{solvent}) / x_1)_k$ and δy_k is the absolute uncertainty of the direct experimental results for *yk*:

$$\delta y_k = \sigma \Delta T/(T_{max} - T_{solvent}) \tag{3.7}$$

The infinite dilution activity coefficient of solute (component 1) in the solvent (component 2) is calculated from Equation (3.3). Derivation of this equation is given in Appendix A.

3.2 VLE Measurement

VLE measurements are tedious and time-consuming as measurement conditions are often controlled and recorded manually. Cost reduction can be achieved by affordable automation, which permits a more efficient operation of the apparatus and, in some cases, an increase in accuracy. One problem associated with automation is that researchers working with experimental thermodynamics seldom seem to have the expertise needed in laboratory automation. When, however, automation expertise has been successfully created in the laboratory, the goal should be to implement data acquisition programs and automation software to increase the measurement output of the experimental devices. It is thereby possible to decrease the cost of one individual measurement point substantially. Suitable methods for determination of VLE vary. In some cases several methods can be applied, but in the most difficult cases measurements are almost impossible. The selection of methods and apparatus depend on the physical properties of the system studied: vapor pressure, component stability, material compatibility, measurement accuracy and safety. The properties determined specifically for binary vapor-liquid equilibrium systems are temperature, pressure and the compositions of the constituent phases. Different types of VLE measurement are discussed as follows.

3.2.1 Dynamic Equilibrium Stills Method

In the dynamic equilibrium stills, the mixture is brought to boil under controlled pressure. The vapor and liquid mixture is separated in the equilibrium chamber and the vapor phase is condensed and returned to the boiling chamber. The liquid phase formed in the equilibrium chamber is also circulated. The composition of the boiling liquid and the vapor change with time until a steady state is achieved [91]. The steady state still represents the true equilibrium values or, in other words, one equilibrium step.

3.2.2 Static Method

In the static method, the degassed components are fed to the equilibrium cell. The volume of the cell can either be controlled or uncontrolled. The temperature and pressure are regulated to assure that two phases are present. The runs carried out with this type of apparatus are most often isothermal. The content of the cell is agitated in order to shorten the equilibration time. Samples are drawn from the liquid and vapor phases and analyzed, for example, with gas chromatography or mass spectrometry. These samples can also be drawn from sample circulation lines the challenging task is to ensure that the samples analyzed represent the equilibrium state. The problems that arise are associated with the partial condensation of the vapor phase and the partial vaporization of the liquid phase, during sampling and sample transfer. Another drawback of this type of apparatus is the time needed for producing one isotherm and the calibration of the analyzer. An advantage is that the results obtained can be tested with consistency tests.

3.3 LLE Data Measurement

Partial miscibility in a liquid mixture at equilibrium is evidence of a highly non-ideal system, and liquid-liquid equilibrium (LLE) computation is difficult. Paradoxically, LLE data are measured much more easily than VLE data. Accurate experimental measurement is essential, since data accuracy can not be tested thermodynamically. There are some experimental methods to measure LLE data. Examples of such methods are turbidity method, analytical method, volume measurement and so on. In our lab several sets of ternary LLE data (Hexane-Butanol-Water, CCl_4-PA-Water, Hexane-PA-

Water) were measured. Detailed descriptions of experimental methods are reported in Javvadi's thesis [1].

Table 3.1. Experimental methods of measuring infinite dilution activity coefficient

Method	Range of α_{12}	Comments
Dew point technique	.01-.4	Rapid measurements(30 min/data point; limited to aqueous systems at present)
Differential Ebuliometry	.3-20.0	General applicability; time consuming (6-12 h/data point).
Headspace Chromatography	.5-1000	Rapid measurements; able to measure more than one solute.
Gas Stripping	>1000	Simultaneously; careful calibration required.
Gas Chromatography	>20	No calibration required; measure more than one solute.
Liquid-liquid chromatography	>20	Well known technique; adsorption problems for aqueous systems.
		Well known technique; adsorption problems for aqueous systems.

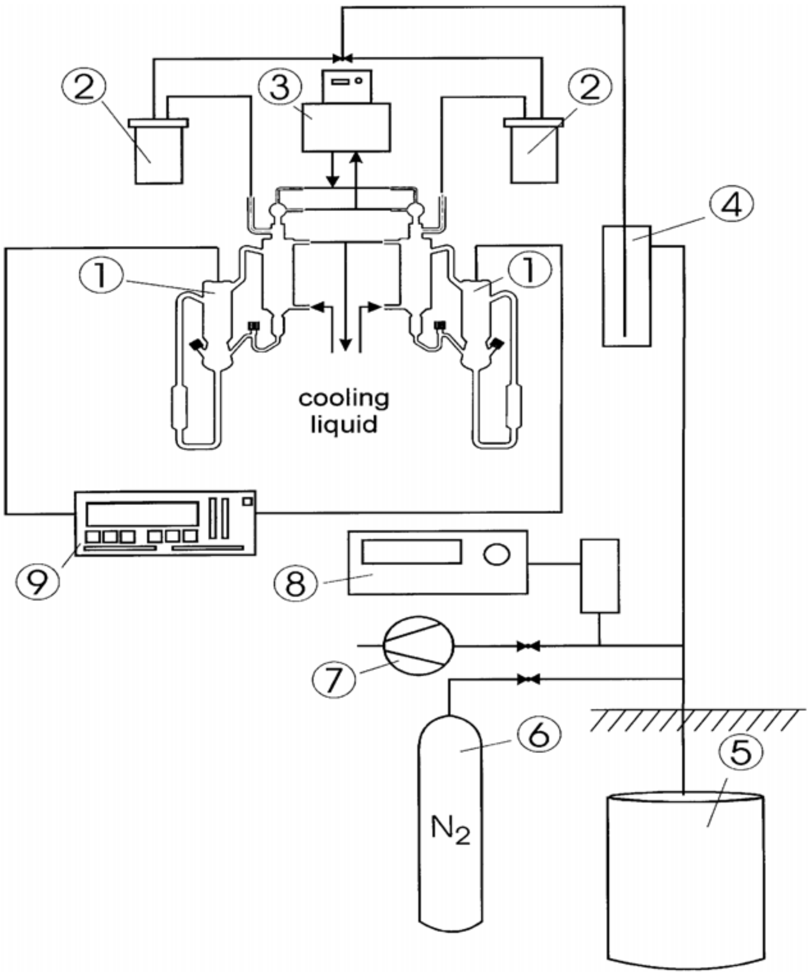

Figure 3.1. Scheme of the experimental arrangement (differential ebulliometers): 1, ebulliometer; 2, recipient vessel; 3, cryostat; 4, cooling trap; 5, manostat (large gas container buried in the ground); 6, nitrogen supply; 7, vacuum pump; 8, pressure gauge; 9, quartz thermometer

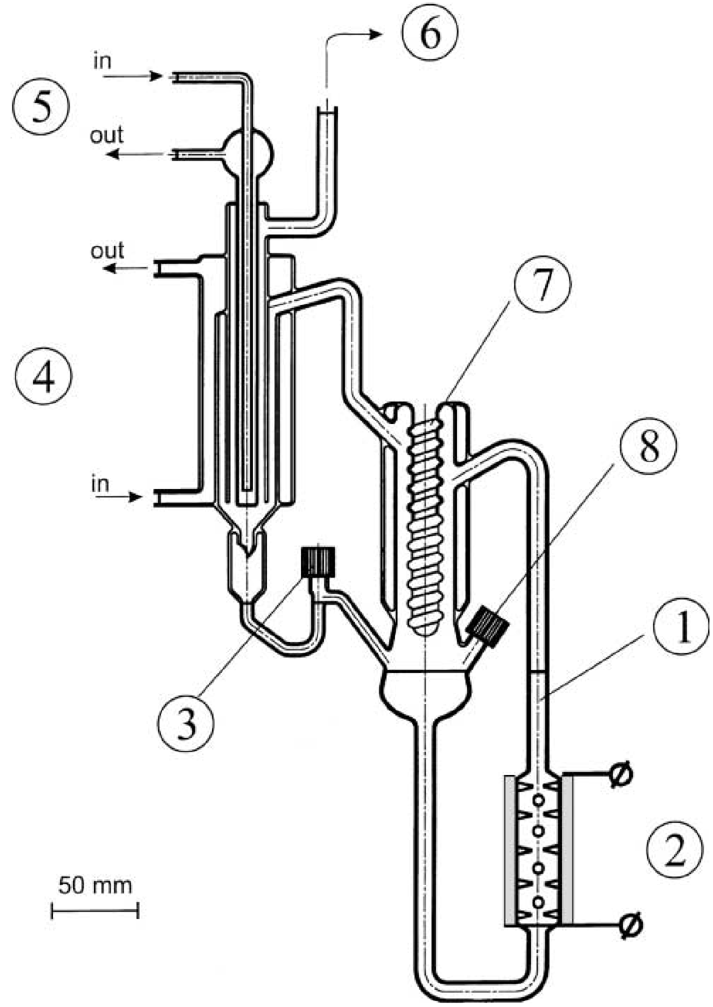

Figure 3.2. Detailed drawing of an ebulliometer: 1, Cotrell pump; 2, electric heater; 3, port for vapor phase sampling; 4, cold water; 5, cold ethyleneglycol–water mixture; 6, to manostat, 7, shaft for quartz thermometer; 8, port for liquid sampling

CHAPTER 4

DATA SELECTION AND RESULTS AT 25 °C

A number of ternary liquid systems have been studied with water as the third component and data being available at 25 °C. An extensive collection of binary, ternary and quaternary data is available in "Liquid-Liquid Data Collection", Chemistry Data Series, DECHEMA [44]. Volume I of this series contains binary systems and volumes II, III and IV contain ternary and quaternary systems. These DECHEMA books also contain the common and specific UNIQUAC parameters for all the systems given in the book. A large collection of log K_{sw} were found in a book titled, "Substituent Constants for Correlations Analysis in Chemistry and Biology", by Hansch and Leo [51]. All ternary systems were categorized from these data books based on minimum solute concentrations in the range of $0 \le x_i \le .01$, $.01 \le x_i \le .02$, $.02 \le x_i \le .03$, $.03 \le x_i \le .04$. Detailed tables are shown in Appendix B. These tables show the variations of the calculated and experimental *Dsw* values for a number of ternary systems. Some systems show an acceptable match, while others display order of magnitude differences. Examples of these systems are shown in Tables 4.1 and 4.2, respectively. More detailed tables are reported in Javvadi's thesis [1].

From these systems, the highly non-ideal system of Hexane-Butanol-Water was investigated in detail to determine whether or not it was possible to calculate γ^{∞}, *Dsw*, mutual solubility data, binary VLE data and ternary LLE data using a single set of parameters suitably. Here, the complete data selection for Hexane- Butanol-Water will be shown.

4.1 Data Selection

A thorough literature search was carried out to obtain mutual solubility, γ^{∞} and VLE data of Hexane-Water, Butanol-Water, Butanol-Hexane pairs, distribution coefficient (*Dsw*), LLE data of Hexane-Butanol-Water and vapor pressure of Hexane, Butanol and Water. From this search, final data was selected which was used to regress the parameters. The criteria for the selections were based on averaged values that were found to be in close proximity. Outliers were not considered. Most of the solubility and γ^{∞} data were taken from Dechema [43, 44, 57 and 58]. Here the data are at 25 °C and in cases where the data was not exactly at 25 °C, then the corresponding temperature was mentioned and marked with *. First, selection of data of pure components Hexane, Butanol and Water will be discussed, then the data corresponding to binary pairs.

4.1.1 Pure Components Data

In this section, all types of pure component data that have been used throughout the calculations are discussed. Vapor pressure (p_i^{sat}) of Hexane, Butanol and Water were taken from different sources. These are reported in Table 4.3. Our selected vapor pressures of Hexane and Butanol are 20.167 and .906 Kpa, respectively, which are the average of values shown in the table. Selected water vapor pressure was 3.165 Kpa which was taken from ASME [53] steam table.

V_i^L of Hexane and Butanol were calculated from temperature dependent correlations given in Daubert and Danner [70]. Saturated Water liquid volume at 25 °C was taken from ASME Table [53].

The Daubert and Danner [57] equation for calculating V_i^L is,

$$V_i^L = A/(B^{(1+(1-T/C)^D)})*1000. \text{ (Here } V_i^L \text{ is in cm}^3\text{/mol)} \qquad (4.1)$$

The Daubert and Danner coefficients (A,B,C,D) for calculating V_i^L for Hexane are .7147, .265, 507.43, .2781 and for Butanol are 9677, .2667,562.93 and .2457, respectively.

The second virial coefficient (B_i) of Hexane and Butanol was calculated by the Tsonopoulos correlation [59]. This method was selected due to the fact that there were no direct experimental data for pure Butanol and B_{ij} for Hexane-Butanol /Water-Butanol in the literature. Since the VLE calculations were at 25 °C and at very low pressures B_i or B_j do not vary much using any method and do not affect x-γ generation significantly. Direct data of B_{ii} for Water was taken from Dymond and Smith [55]. The Tsonopoulos correlation to calculate B_{ii} is as follows

$$\frac{B_{ii}P_c}{RT_c} = f^{(0)}(T_R) + \omega f^{(1)}(T_R) + f^{(2)}(T_R) \tag{4.2}$$

$$f^{(0)}(T_R) = .1445 - .33/T_R - .1385/T_R{}^3 - .000607/T_R{}^8 \tag{4.3}$$

$$f^{(1)}(T_R) = .0637 + .331/T_R{}^2 - .423/T_R{}^3 - .008/T_R{}^8 \tag{4.4}$$

$$f^{(2)}(T_R) = \frac{a}{T_R{}^6} - \frac{b}{T_R{}^8} \tag{4.5}$$

Here $T_R = \frac{T}{T_c}$

The second virial cross coefficient B_{ij} has the same temperature dependence that B_{ii} and B_{jj} have, but the parameters to be used with the above equations are P_{cij}, T_{cij}, ω_{ij}, a_{ij} and b_{ij}. The mixing rules given below make it possible to relate these characteristic constants to pure component parameters.

$$T_{cij} = (T_{ci}T_{cj})^{.5}(1 - k_{ij}) \tag{4.6}$$

$$P_{cij} = \frac{4T_{cij}(P_{ci}v_{ci}/T_{ci} + P_{cj}v_{cj}/T_{cj})}{v_{ci}{}^{1/3} + v_{cj}{}^{1/3}} \tag{4.7}$$

$$\omega_{ij} = .5(\omega_i + \omega_j) \tag{4.8}$$

$$a_{ij} = .5(a_i + a_j) \tag{4.9}$$

$$b_{ij} = .5(b_i + b_j) \tag{4.10}$$

Critical properties were taken from Smith et al. [90]. ω, a_i, b_i, and k_{ij} values were used from Tsonopoulos [59]. These are all shown in Table 4.3. k_{ij} for Hexane-Butanol and Water-Butanol are .15 and .1, respectively. As mentioned earlier, since the calculations were at 25 °C and at very low pressure, selections of cross virial coefficients would not affect the calculations significantly. The experimental values of B_{ij} for Hexane-Butanol and Water-Butanol pairs could not be found in the literature. Hence, Tsonopoulos [59] correlation for B_{ij} calculations was selected. B_{ij} data are reported in the "Binary Data" section. Also there are very simple methods available in literature [2, 47] to calculate B_{ij}. To consider accuracy for these particular pairs, those methods were avoided.

To calculate area fraction (θ_i), volume fraction (φ_i) in UNIQUAC, *r* and *q* were taken from DECHEMA [73]. *r* and *q* of LSG/GEM-RS models were calculated as follows [2]:

$$r_i=\upsilon_i/\upsilon_i^* \tag{4.11}$$

$$q_i=\psi_i/\psi_i^* \tag{4.12}$$

Here, υ_i is a quantity related to some measure of the volume (or size) of the molecules and ψ_i is a quantity related to surface. υ_i is 55% of molar volume of component *i*. ψ_i is calculated from the relation $\psi_i =1.32*10^8* \upsilon_i+6.259*10^8$. υ_i^* and ψ_i^* are equal to 18.92(cm^3/mol), 3.13*10^9(cm^2/mol), respectively. Final values of r and q are reported in Table 4.3.

4.1.2 Binary Data

The details of the selection technique are described in the subsections below.

4.1.2.1 Hexane-Water

Hexane-Water is an immiscible pair. Therefore, the solubility of Hexane in Water is very, very low and vice versa. Solubility and infinite dilution activity coefficient data for this pair are shown in Table 4.4. The closest data were marked with * since some data fall apart to others. Selected solubility of Hexane in Water is 2.577E-6 and that of Water in Hexane is 4.7E-4 which are the average of * values. It is known that for very low solubility, the infinite dilution activity coefficient can be taken as the reciprocal of solubility data [89]. According to this relation, infinite dilution activity coefficient of Hexane in Water is 3.88E+5 and that of Water in Hexane is 2127.65. Binary data are shown in Table 4.4.

4.1.2.2 Butanol-Water

Butanol-Water is a partially miscible pair. Solubility of Butanol in Water is low whereas the solubility of Water in Butanol is high. Our final selection of solubility of Butanol in Water was .01875 and that of Water in Butanol was .5056. These are the average of the data marked with *. As seen in Table 4.4, numerous values of infinite dilution activity coefficient (γ^∞) data of Butanol in Water were found. Our selected value was 51.37 (average of * data). There was only one experimental γ^∞ of Water in Butanol available at 25 °C that was 3.8. However, when the other γ^{∞} values were observed at different temperatures, it was found that the actual value should be greater than 3.8 at 25 °C. Hence, after extrapolation of the temperature versus γ^{∞} values, the final value was 5.06. This is shown in Figure 4.1. This value is also consistent according to our generated x-γ values shown in Table 4.5.

The x-γ values were generated after having worked with VLE data. Here, x-γ means activity coefficient (γ) values for corresponding compositions of a binary pair. From the thermodynamic relation as we know,

$$\gamma_i = \frac{y_i p \varphi_i}{x_i p_i^{sat} \varphi_i^{sat} \exp\left[\frac{V_i^L (p - p_i^{sat})}{RT}\right]} \tag{4.11}$$

Fugacity coefficient (φ_i) was calculated from the virial equation as follows

$$\ln \varphi_i = 2\left(\sum_{j=1}^{m} y_j B_{ij} - B_{mix}\right)\frac{p}{RT} \tag{4.12}$$

where $B = y_i^2 B_{ii} + 2 y_i y_j B_{ij} + y_j^2 B_{jj}$ (4.13)

There were two isothermal (25 °C) VLE datasets of Water-Butanol that were found in literature [71]. By analyzing x-γ values, these two datasets were checked. After combining the data points, the final selection for this pair is shown in Table 4.5. Some data points, which were found to be inconsistent, were disregarded.

4.1.2.3 Hexane-Butanol

This pair is completely miscible. Our selected γ^{∞} of Butanol in Hexane is 38.6 because this is consistent with the *Dsw* value of Hexane-Butanol-Water. For cases in a ternary system when solvent-water are completely immiscible, the *Dsw* value can be defined as the ratio of γ^{∞} of solute in water to γ^{∞} of solute in solvent. γ^{∞} of Hexane in Butanol is 5.12 (average of * values shown in Table 4.4). Isothermal (25 °C) VLE data of this pair was taken from three different sources Smirnova et al. [71], Rodriguez et al. [58] and Gracia et al. [59]. The analyzed x-γ values of these three datasets are shown in Tables 4.6 to 4.8. The data in source Gracia was in isothermal P-x form. Thus, Barker's method [66] was applied to obtain y data and to generate corresponding γ. Coefficients (A_0,A_1,

A_2 and B_1) that were obtained from our calculations to use in Barker's method are 1.8374, -1.108, -.0234 and -.8047, respectively. These coefficients are valid only at 25 °C. Details of this method are discussed in Appendix C.

Once the x-γ data from those three different sources were analyzed, it was simple to observe that data from Rodriguez [58] and Gracia [59] were consistent both in very dilute regions and in finite concentrations. In both data sets, it was noticed that γ_b values increased very rapidly as x_h rose higher. γ^∞ values also follow this trend. However, this case was not found in the dataset from Smirnova [76]. Hence, this dataset was discarded.

4.1.3 LLE and Dsw Data Selection

In Dechema, only one ternary LLE data set of Hexane-Butanol-Water was found. However, this dataset is at only finite concentration. The behaviors in very dilute regions can not be determined based only on one dataset.

Hence, LLE data of this system measured by Javvadi [1] was taken since this dataset covered dilute regions to high concentration regions. Distribution coefficient (Dsw) of Butanol in Hexane-Butanol-Water is 1.2, 1.45. These were taken from Hanch and Leo [65].

4.2 Results of 25 °C

Binary parameters can be regressed in different ways for different pairs. Some parameters are regressed from mutual solubility data if the two components are partially miscible. If the two components are completely miscible, parameters are regressed by taking the number of systems containing the binary pair of interest. First, we will show the variations between calculated and experimental results of binary mutual solubility data, γ^∞, *Dsw*, binary VLE data using the modified UNIQUAC Model. These parameters have been obtained from binary mutual solubility data for Hexane-Water/Water-Butanol pairs and for Hexane-Butanol x-γ data generated from VLE data. The results are shown in Table 4.9. The second column of this table shows the types of data from which parameters have been regressed. Here, symbols w1, w2, w3, w3$^{/}$ represent the weighted Mutual Solubility, γ^∞, VLE data of all concentration ranges, and VLE data of only finite concentration ranges respectively. Corresponding parameters are also reported.

Combinations of weighted functions are shown as regression # in the third column of Table 4.9. All computational work has been carried out using FORTRAN 77 and Absoft 10.1 as the compiler. Regression calculations have been done by using IMSL FORTRAN Numerical Library 5.1. A sample regression calculation is shown in Appendix C. In all cases, the objective function was set as

$$F(obj)=\sum_{k}^{N_k}\sum_{i}^{N_i}\frac{1}{N}w_k\frac{F_i(\exp)-F_i(cal)}{F_i(\exp)} \tag{4.14}$$

where

$$N=N_k*N_i \tag{4.15}$$

Ni=number of data points

N_k=total number of property

w_k=weightage

k=1, mutual solubility

k=2, γ^{∞}

k=3, VLE

k=4, H^E (Excess Enthalpy)

In this table we observed that using only the solubility data for the Water-Butanol pair presented an error of around 40% in the γ^{∞} calculation. On the other hand, using the given γ^{∞} data to calculate solubility, a variation of 40% is observed compared to the experimental data. Regression using VLE data results in the reduction of error in all calculations by 21%. Subsequently, using all data types in conjunction with the necessary weighted objective functions resulted in a further reduced error of 15%. Hence, for this pair the UNIQUAC [12] model performs well.

For the Hexane-Butanol pair, using only the VLE data for parameter regression calculations of γ^{∞} show 68.4% error. Alternately, using γ^{∞} data for overall VLE calculations show around 40% error. In fact, for some data points of VLE(x-γ), error is 100%. This pair was found to be more challenging, and thus studied extensively in order to better understand the problem. We have also checked with the other two-parameter model, LSG [2]. The LSG model presents the same kind of behavior observed when using the UNIQUAC model. In this pair, γ of Butanol in Hexane increases abruptly as the Butanol concentration is reduced and these two-parameter models are unable to take into account this steep behavior. This is clearly shown in Figure 4.2.

In Figure 4.2, it can be seen that the regression of the parameters using finite concentration data to calculate γ^{∞} of Butanol in Hexane shows an order of magnitude difference from the experimental value. To solve this problem, extra weight is given to the data in very dilute regions. This allows the models to predict γ^{∞} suitably; however, γ values in the finite concentration range are inconsistent. Using all of the concentration data slightly improves the γ^{∞} value, yet the values remain unacceptable compared to experimental data. Despite using the best parameters, the results were still within an error of 15-20%. Since weighted objective functions were not able to produce acceptable results, the two-parameter models failed to represent the data for this pair.

Complete results of the LSG model are shown in Table 4.10. Parameters shown in the last row of each pair of Tables 4.9 and 4.10 are the final parameters of the UNIQUAC and LSG models. After this, the NRTL model was used, since it contributes an additional parameter, that is, the non-randomness factor. The NRTL model provided acceptable results for the Hexane-Butanol pair unlike the previous two-parameter models.

Using the NRTL model, the data was fit with an overall error of 5%. To judge the consistency of this result, another three-parameter model (GEM-RS) was used with the Hexane-Butanol pair. GEM-RS also showed similar behavior compared to NRTL. Both NRTL and GEM-RS are able to represent steep functions. The third parameter of these models helps to adjust functionality changes. This fact is shown more clearly in Figure 4.3.

After the success of using NRTL and GEM-RS models on the Hexane-Butanol pair, these said models were used for the entire computational work. For all three pairs, attempts to obtain the best fitted parameters were made using all kinds of data by various combinations of objective functions.

For the Hexane-Water pair, there is no flexibility to regress all three parameters since there are only two datasets (mutual solubility of Hexane in Water and that of Water in Hexane). Hence, a third parameter was fixed (α, λ for NRTL, GEM-RS respectively) and while the other two parameters were regressed. For the Water-Butanol and Hexane-Butanol pairs, α and λ were fitted as independent parameters. Between NRTL and GEM-RS, NRTL provides slightly better results than GEM-RS. Complete results for these models are shown in Tables 4.11 and 4.12, respectively. For fair comparison, all four models used the same weights when regressing the final parameters. Final parameters of these two models are reported in the last rows of each table for each pair.

Parameters of the Hexane-Water pair have been fixed based upon ternary results. In the case of NRTL, different combinations of interaction parameters (g_{12}, g_{21}) and non-random factors ($\alpha_{12}= \alpha_{21}$) are possible for the Hexane-Water pair and correcting this was a challenge. The effects of different non random factors (α) on ternary LLE calculation, especially in a Hexane-rich phase, were investigated. In a Water-rich phase, compositions of all three components are fixed throughout the concentration range. However, in the Hexane-rich phase, addition of more Butanol amounts to considerable changes in the concentration of Hexane and Water. Hence, different α values of the Hexane-Water pair will have substantial effects in ternary LLE calculations, particularly in the Hexane-rich phase.

The value of α should be in between 0 and 1. The calculations were checked at every .05 increment of α, starting at α=.05. In each case the overall percentage of error of the Butanol and Water composition in the Hexane-rich phase was compared. From this comparison, it was observed that the appropriate α value should be in between .15 and .25. Subsequently, starting at α=.15, the error percentage was observed at every .01 increment. This resulted in overall minimum error at α=.22. Hence, the final selection was α=.22. Comparison of results for different α's are shown in Table 4.13. The variations of x-γ for different α's are also shown in Table 4.14. As the α value is increased, the change of γ of the Hexane-Water pair becomes very critical. Higher α values make considerably less change in γ than smaller α values.

Graphical representation of α=.15, .22, and .25 are shown in Figures 4.4 and 4.5. L_1 and L_2 indicate Hexane-rich phase and Water-rich phase, respectively. The same investigation that was conducted on the α parameter was also used to investigate the effect of λ in the GEM-RS model. From NRTL, variations of x-γ based on the appropriate third parameter are known.

In the case of the GEM-RS model, attempts to obtain a third parameter, which would show similar x-γ transformations, were made. Starting at λ=-50 and increasing by increments of 25, changes of x-γ seem to be more similar with NRTL's α variation.

From this observation, the optimal λ value was found to be in between 250 to 260. Again, starting at λ=250 and increasing by increments of 1, the optimal λ value was found to be 254, after checking the error percentage. Thus, λ=254 was selected as the final parameter for our ternary calculation. Comparative results for different λ are shown in Table 4.15.

Changes of x-γ for different λ values are shown in Table 4.16. Similar to the NRTL, as the value of third parameter increases, γ does not change significantly with Hexane composition. Differences between calculated results of Butanol and Water composition in the Hexane-rich phase and experimental values for different λ's are shown in Figures 4.6 and 4.7.

After establishing the third parameters for the NRTL and GEM-RS models, the ternary results using the best parameters of all four models were compared. Results of L_1 and L_2 phase are shown in Figures 4.8 and 4.9, respectively. Quantative experimental ternary data are shown in Appendix E. Comparison of water in the Hexane-rich phase is also shown in Figure 4.10.

According to Figures 4.8 to 4.10, both the UNIQUAC and LSG models fail to represent the ternary data at higher concentration range. These two-parameter models show a peculiar behavior in L_2 phase. In dilute concentration ranges, the calculated data reaches a peak, which is not observed in the experimental data. Three-parameter models do not show this peak. They can predict the data well over the concentration range. Comparisons between calculated and experimental data for all four models in very dilute regions are shown in Figures 4.11 and 4.12.

One very important observation is that the three-parameter models behave similarly when the third parameter is kept constant and the two interaction parameters are regressed. As noticed earlier, the main difficulty was fitting the data of the Hexane-Butanol pair. All three parameters were regressed for this pair; however, keeping the third parameter fixed and regressing the other two parameters in both the NRTL and GEM-RS models results in problems similar to the UNIQUAC and LSG models. Without the third parameter, binary interaction parameters of three-parameter models are unable to represent sharp function. In Figure 4.13, α and λ values are kept fixed to .2 and 200, which results in poor calculated results like two-parameter models.

Since the final parameters of the NRTL and GEM-RS models are used for calculating all types of binary phase equilibrium data (γ^{∞}, Mutual Solubility, VLE), these parameters can be named Universal Parameters since the calculations of the data types mentioned above can be solely obtained using these parameters. Although these parameters have been obtained from binary data, they can also predict ternary LLE data well for all concentration ranges. These can predict correct *Dsw* as well.

Table 4.1. Ternary systems which show good match between experimental and calculated *Dsw*.

Ternary System	Literature D_{sw}	Calculated D_{sw}
Benzene – Ethanol – Water	0.19	0.21
Benzene – Pyridine – Water	14.94	16.46
Benzene – Acetone – Water	4.41	4.14
Toluene – Aniline – Water	45.97	50.16
Toluene – Pyridine – Water	11.54	14.83
Toluene – Acetone – Water	2.90	3.74
Toluene – Methanol – Water	0.04	0.05
Toluene – Ethanol – Water	0.11	0.09
Trichloro Methane – Formic Acid – Water	0.02	0.02
Hexane – Ethanol – Water	0.04	0.03

Table 4.2. Ternary systems which show order of magnitude difference between experimental and calculated Dsw

Ternary System	Literature D_{sw}	Calculated D_{sw}
Hexane – Acetic Acid – Water	0.011	0.091
Hexane – Propanoic Acid – Water	0.002	1.651
Hexane – 1-Propanol – Water	0.221	9.984
Hexane – 1-Butanol – Water	1.212	14.634
Hexane – Acetone – Water	0.879	1.847
Benzene – Methanol – Water	0.064	0.112
Benzene – 2-Propanol – Water	0.543	4.448
Benzene – 2-Butanol – Water	3.841	20.653
Benzene – Acetic Acid – Water	0.031	0.213
Benzene – Propanoic Acid – Water	0.211	4.989
Toluene – Acetic Acid – Water	0.075	0.222
Toluene – Propanoic Acid – Water	0.201	5.946
Toluene – 1-Propanol – Water	0.896	10.500
Trichloro Methane – Ethanol – Water	0.628	1.138
Trichloro Methane – 2-Propanol – Water	1.985	8.182
Trichloro Methane – Formic Acid – Water	0.014	0.022
Trichloro Methane – Acetic Acid – Water	0.122	0.582
Trichloro Methane – Propanoic Acid – Water	0.487	10.060
Tetrachloro Methane – Acetic Acid – Water	0.0428	0.148
Tetrachloro Methane – Propanoic Acid – Water	0.068	3.534
Tetrachloro Methane – 2-Propanol – Water	0.325	4.281
Tetrachloro Methane – Nicotine – Water	46.929	19.977
Heptane – Propanoic Acid – Water	0.284	1.892
Heptane – 1-Propanol – Water	0.247	2.345
Cyclohexane – 1-Propanol – Water	0.182	7.006

Table 4.3. Pure component data

Property	Hexane	Butanol	Water
P_c(Kpa)	3.025[90]	4.423[90]	22.025[90]
T_C(K)	507.6[90]	563.1[90]	647.1[90]
V_c(cm^3/mol)	371[90]	275[90]	55.9[90]
ω_i	.301[90]	.594[90]	.345[90]
a_i	0[59]	.0878[59]	.0279[59]
b_i	0[59]	.0367[59]	.0229[59]
r_i	4.49(UNIQUAC)[73] 3.77(LSG,GEM-RS)[2]	3.45(UNIQUAC)[73] 2.66(LSG,GEM-RS)[2]	.92(UNIQUAC)[73] .73(LSG,GEM-RS)[2]
q_i	3.85(UNIQUAC)[73] 3.21(LSG,GEM-RS)[2]	3.05(UNIQUAC)[73] 2.32(LSG,GEM-RS)[2]	1.4(UNIQUAC)[73] 1.19(LSG,GEM-RS)[2]
B_{ii}(cm^3/mol)	-1749.1[59], -1917.8[54], -1918[70]	-3475.9[59],-6382.7[70], -6495[54]	-1162.1[55], -1281[70], -1160[77]
V_i^L (cm^3/mol)	131.6[57]	91.96[57]	18.045[53]
P_i^{sat} (Kpa)	20.158*[43], 20.132[43],20.15*[46], 20.174*[47], 20.136[48], 20.169*[49],20.167**	.921[43],.823[47],.901*[48] .948[49],.905*[49],.912*[49], .933[50], .933[51],906**	3.165[53]

** average of values marked with * which is our final value

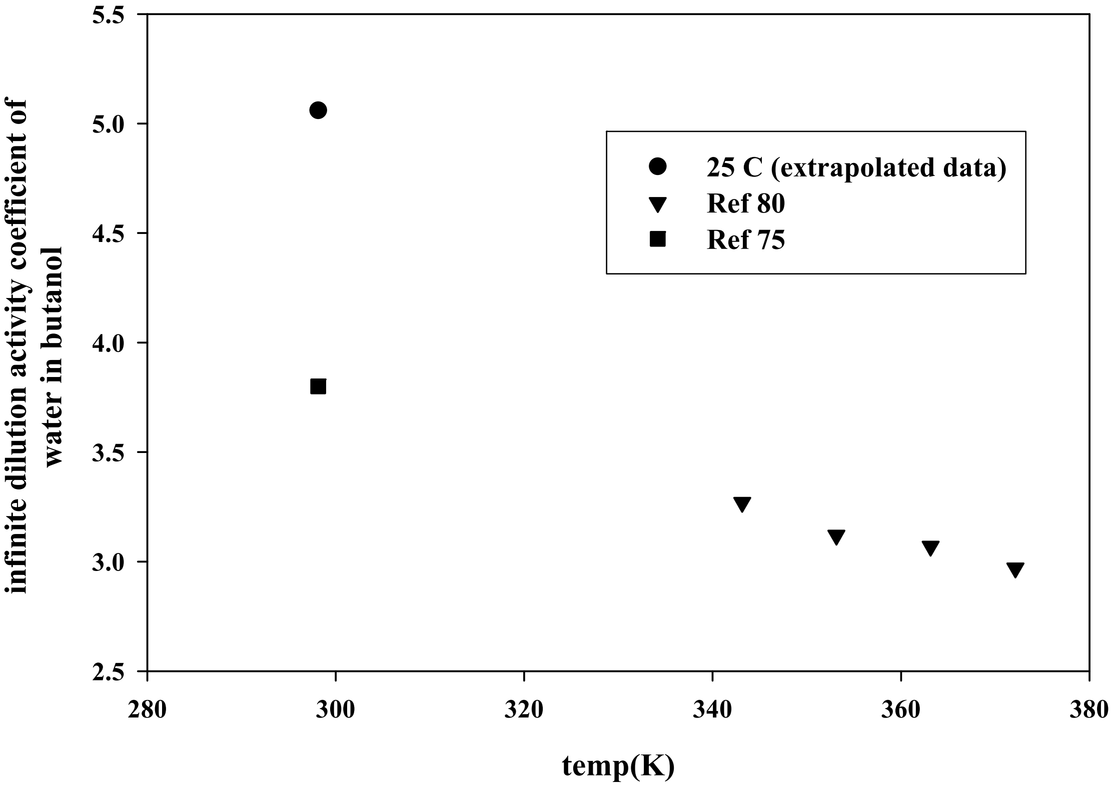

Figure 4.1. Infinite dilution activity coefficient of Water in Butanol at different temperatures

Table 4.4. Binary data selection

Binary pair	Type of data	Data[Ref]
Hexane-Water	Solubility of Hexane in Water	2.699E-6[15], 1.986E-6[16], 2.592E-6*[17], 2.571E-6*[18], 1.984E-6[19],2.570E-6*[20], 2.986E-6[21], 2.406E-6[22], 3.830E-6[43], 2.780E-6[43],2.57E-6**
	Solubility of Water in Hexane	4.3E-4*[17],5.1E-4*[22],3.84E-4[23], 4.41E-4[20], 6.06E-4[43],4.7E-4**
Butanol-Water	Solubility of Btanol in Water	.01892*[24],.01905*[25], .01797[43], .01851*[43], .01854*[43],.01869[26], .0192[43],.0187**
	Solubility of Water in Butanol	.5055*[43], .5058*[43], .512[43],.5112[36],.5178[37],.506**
	γ^{∞} of Butanol	45.1[27],50.5*[58],51.6*[28], 52.8*[29], 53.7[30], 205.6[31], 53.33[32], 52.24*[33], 48.2[34], 50.9*[35], 50.2*[58] ,51.37**
	γ^{∞} of Water	3.8[38]
	B_{ij}	-2465[2],-2514[47],-2090[59]
Hexane-Butanol	γ^{∞} of Hexane	5.12*[40],5.25*[58], 5.00*[58],5.123**
	γ^{∞} of Butanol	33.0[41]
	B_{ij}	-2009[2],-2119[47],-596[59]

Table 4.5. P-x-y-γ data of Water-Butanol

P(Kpa)	x_w	y_w	γ_w	γ_b
0.906	0.0000	0.0000	5.0650	1.0000
1.0226	0.0081	0.1036	4.1283	1.0197
2.5571	0.1500	0.6882	3.4198	1.1301
3.4091	0.3000	0.7900	2.8352	1.1531
3.7157	0.5124	0.8253	1.9282	1.4749
3.7157	0.9812	0.8253	1.0070	38.2524
3.5157	0.9900	0.8874	1.0055	43.6943
3.1650	1.0000	1.0000	1.0000	51.3700

Table 4.6. P-x-y-γ data of Hexane-Butanol from Smirnova

P(Kpa)	x_h	y_h	γ_h	γ_b
0.906	.000	0.00	5.12000	1.00000
8.305	.082	.901	4.98000	1.25587
12.87	.171	.939	4.00720	1.32830
15.38	.276	.95	3.00071	1.48981
18.14	.488	.964	2.03070	1.78824
19.02	.681	.969	1.53330	2.59180
19.31	.715	.972	1.48600	2.65820
19.55	.765	.976	1.41260	2.79760
19.95	.867	.984	1.28230	3.36194
19.97	.894	.987	1.24098	3.43225
20.17	1.00	1.00	1.00000	38.6000

Table 4.7. P-x-y-γ data of Hexane-Butanol from Rodriguez

P(Kpa)	x_h	y_h	γ_h	γ_b
0.906	0.0000	0.0000	5.12000	1.00000
2.7339	0.0181	0.6320	4.82350	1.00040
6.8289	0.0710	0.8678	4.19880	1.00690
9.3450	0.1138	0.9154	3.77110	1.01800
13.2880	0.2057	0.9412	3.03800	1.06080
15.9079	0.3128	0.9555	2.42150	1.14850
17.3079	0.4086	0.9592	2.02240	1.27150
17.7929	0.4541	0.9594	1.87050	1.34910
18.7759	0.5962	0.9641	1.51020	1.71120
19.5769	0.7767	0.9731	1.21860	2.76700
19.9480	0.8770	0.9757	1.10170	4.54720
20.1379	0.9331	0.9750	1.04430	7.69140
20.2499	0.9709	0.9755	1.01210	14.6782
20.2289	0.9878	0.9860	1.00260	23.1481
20.1670	1.0000	1.0000	1.00000	38.6000

Table 4.8. P-x-y-γ data of Hexane-Butanol from Gracia

P(Kpa)	x_h	y_h	γ_h	γ_b
0.906	0.0000	0.0000	5.1200	1.0000
4.0970	0.0390	0.8080	4.3030	1.0000
6.7660	0.0730	0.8850	4.0680	1.0030
8.6310	0.1090	0.9140	3.6860	1.0130
9.5080	0.1220	0.9200	3.5410	1.0190
11.3230	0.1760	0.9350	2.9920	1.0490
13.5420	0.2810	0.9500	2.3090	1.1320
15.5780	0.3630	0.9580	2.0210	1.2050
17.8750	0.5290	0.9680	1.6350	1.4320
18.4820	0.5740	0.9700	1.5460	1.5350
19.3450	0.6990	0.9730	1.3340	1.9930
19.7900	0.7740	0.9760	1.2330	2.4880
19.8210	0.7950	0.9760	1.2060	2.6930
19.7980	0.8320	0.9770	1.1600	3.1900
20.0020	0.8470	0.9770	1.1420	3.4700
20.1140	0.9550	0.9800	1.0210	10.677
20.1670	1.0000	1.0000	1.0000	38.600

Table 4.9. Comparison between experimental and calculated results using UNIQUAC

Pair i-j	Weightage Parameter (Aij,Aji)	Reg #	Solubility				γ^∞				Average error in γ		Average error		Dsw	
			i in j		j in i		i		j		i	j				
			exp	cal	exp	cal	exp	cal	exp	cal			P	y	exp	cal
Hexane-Water	1545.48, 845.14	1	2.57 E-6	2.57 E-6	4.7 E-4	4.7 E-4	3.89 E+5	3.89 E+5	2.13 E+3	2.13 E+3					1.2, 1.4 5	
Butanol-Water	w1=1, w2=1 w3=1 274.45,144.7	1	.0187	.021	.505	.42	51.37	54.74	5.06	4.58	3.37	5.61	2.91	3.7		
	w1=0, w2=1 w3=0 214.9,209.7	2	.0187	.026	.505	.30	51.37	51.37	5.06	5.06	13.37	5.16	11.5	6.6		
	w1=0, w2=0 w3=1 286.16,142.28	3	.0187	.022	.505	.38	51.37	54.53	5.06	3.97	3.0	4.47	2.59	3.34		
	w1=1, w2=0 w3=0 362.73,77.4	4	.0187	.0187	.505	.505	51.37	56.9	5.06	3.04	14.44	5.67	12.5	7.3		
	w1=5, w2=10 w3=1 355.56,82.72	5	.0187	.0186	.505	.47	51.37	59.05	5.06	4.43	6.95	4.52	6.01	5.8		
Hexane-Butanol	w2=1,w3=1 520.25,60.71	1					5.12	4.75	38.6	14.9	4.89	22.43	28.9	2.94		3.96*
	w2=1,w3=0 723.17,67.51	2					5.12	5.12	38.6	38.6	.98	39.76	39.4	3.0		1.53*
	w2=0,w3$^{/}$=1 295.41,106.48	3					5.12	5.30	38.6	5.89	2.73	9.34	12.0	1.64		10.0*
	w2=5,w3=1 703.45,64.2	4					5.12	4.98	38.6	38.14	.89	38.97	35.8	2.98		1.54*

*using γ^∞ of Butanol in Water 59.05 and that of Butanol in Hexane in corresponding row

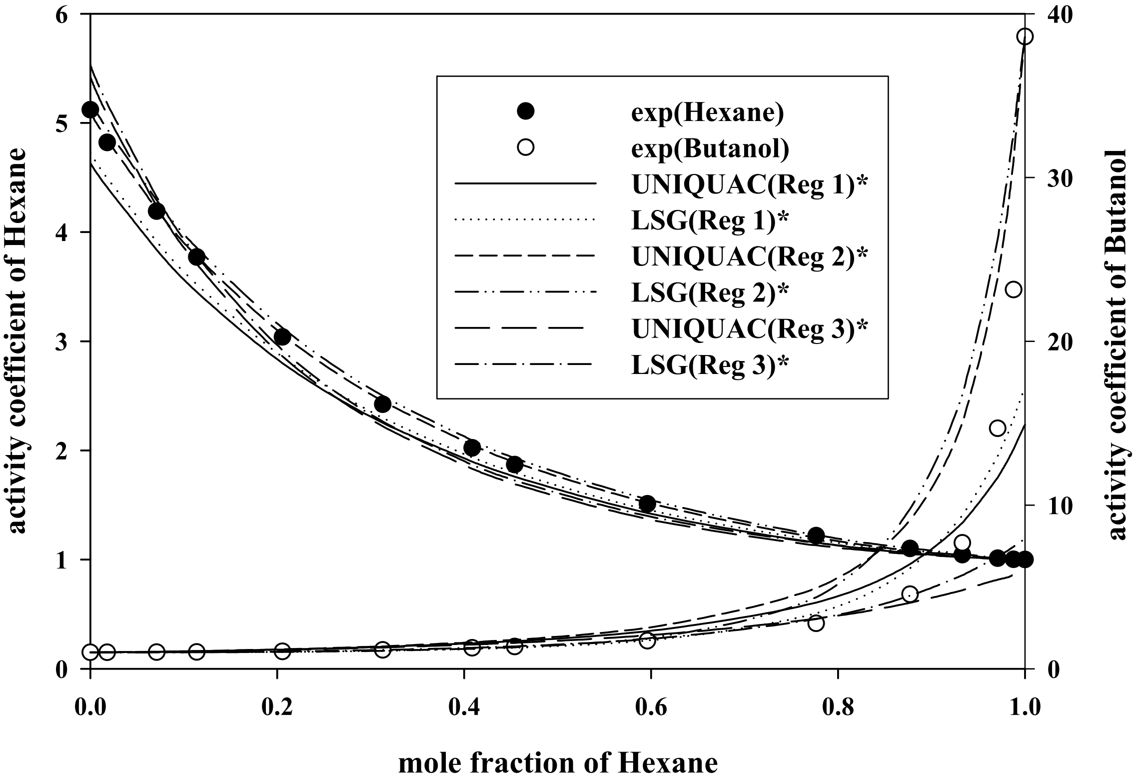

Figure 4.2. Variation of experimental and calculated γ's in the binary Hexane-Butanol liquid mixture by two parameter models. γ_{Hexane} scale is given on the y-axis to the left and $\gamma_{Butanol}$ on the y-axis to the right of the figure.(* parameters used are according to the regression # in table 4.9 and 4.10)

Table 4.10. Comparison between experimental and calculated results using LSG model

Pair i-j	Weightage	Reg #	Solubility				γ^∞				Average error in γ		Average error		Dsw	
			i in j		j in i		i		j		i	j				
			exp	cal	exp	cal	exp	cal	exp	cal			P	y	exp	cal
Hexane-Water	-9.04, 384.06	1	2.57 E-6	2.57 E-6	4.7 E-4	4.7 E-4	2.13 E+3	2.13 E+3	3.89 E+5	3.89 E+5					1.2, 1.45	
Butanol - Water	w1=1, w2=1 w3=1 81.18,-16.62	1	.0187	.019	.505	.44	51.37	53.88	5.06	4.27	3.19	5.0	3.01	3.92		
	w1=0, w2=1 w3=0 39.22,25.13	2	.0187	.027	.505	.28	51.37	51.37	5.06	5.06	12.57	4.98	11.2	6.2		
	w1=0, w2=0 w3=1 103.65,-36.3	3	.0187	.02	.505	.40	51.37	53.63	5.06	3.81	2.98	4.17	2.78	3.81		
	w1=1, w2=0 w3=0 198.31,-111.2	4	.0187	.0187	.505	.505	51.37	58.1	5.06	3.07	15.05	5.17	13.1	7.9		
	w1=5, w2=10 w3=1 192.33,-104.15	5	.0187	.0185	.505	.48	51.37	58.95	5.06	4.72	6.15	4.19	6.34	5.91		
Hexane-Butanol	w2=1,w3=1 -150.45,270.08	1					5.12	4.83	38.6	17.17	4.14	20.98	27.7	2.98		3.43*
	w2=1,w3=0 -160.36,307.58	2					5.12	5.12	38.6	38.6	.87	38.06	38.6	2.92		1.54*
	w2=0,w3=1 -102.36,176.68	3					5.12	5.26	38.6	6.03	2.53	8.95	11.9	1.87		9.76*
	w2=5,W3=1 -161.31,308.7	4					5.12	5.01	38.6	38.32	.78	38.69	34.1	2.32		1.54*

*using γ^∞ of Butanol in Water 58.95 and that of Butanol in Hexane in corresponding row

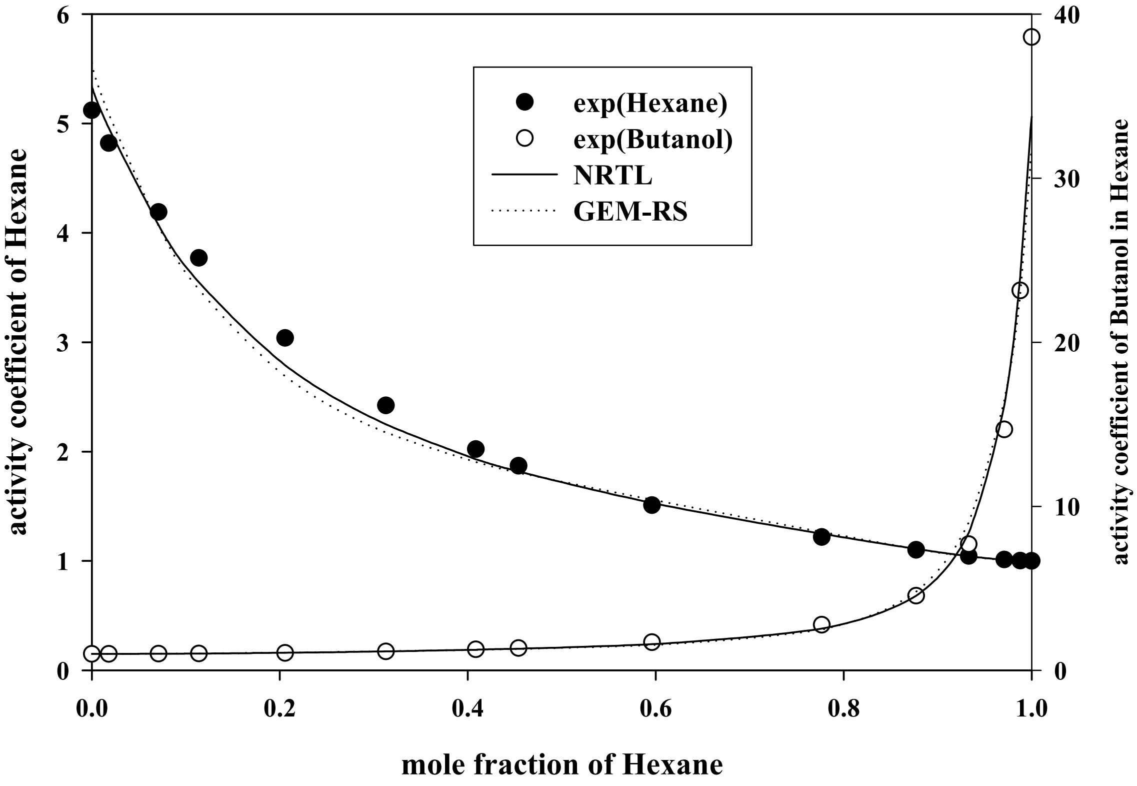

Figure 4.3. Variation of experimental and calculated γ's in the binary Hexane-Butanol liquid mixture by three parameter models. γ_{Hexane} scale is given on the y-axis to the left and $\gamma_{Butanol}$ on the y-axis to the right of the figure

Table 4.11. Comparison between experimental and calculated results using NRTL

Pair i-j	Weightage Parameter (Aij,Aji,α)	Reg #	Solubility				γ^{∞}				Average error in γ		Average error		Dsw	
			i in j		j in i		i in j		j in i		i in j	j in i				
			exp	cal	exp	cal	exp	cal	exp	cal			P	y	exp	cal
Hexane-Water	3381.1,2013.86,.22	1	2.57 E-6	2.57 E-6	4.7 E-4	4.7 E-4	3.89 E+5	3.89 E+5	2.13 E+3	2.13 E+3					1.2, 1.45	
Butanol-Water	w1=1, w2=1,w3=1 1070.01,146.32,.35	1	.505	.42	.0187	.021	51.37	54.74	5.06	4.58	5.34	3.37	1.23	2.91		
	w1=0, w2=0,w3=1 1099.3,133.41.,.34	2	.505	.39	.0187	.023	51.37	58.65	5.06	4.32	5.06	2.87	1.16	2.47		
	w1=5, w2=10,w3=1 1031.46,229.43,.41	3	.505	.49	.0187	.02	51.37	55.8	5.06	5.02	5.6	3.8	1.29	3.24		
Hexane-Butanol	w2=1,w3=1 871.16,329.66.,55	1					5.12	5.42	38.6	33.91	2.71	3.63	2.68	1.95		1.64 *
	w2=5,w3=1 910.21,323.42,.56	2					5.12	5.23	38.6	38.5	3.03	4.48	3.0	2.41		1.45 *

*using γ^{∞} of Butanol in Water 55.8 and that of Butanol in Hexane in corresponding row

Table 4.12. Calculated results by GEM-RS model using best fitted parameters for all three pairs

Pair i-j	Weightage Parameter (Aij,Aji,λ)	Reg #	Solubility				γ^{∞}				Average error in γ		Average error		Dsw	
			i in j		j in i		i in j		j in i		i in j	j in i				
			exp	cal	exp	cal	exp	cal	exp	cal			P	y	exp	cal
Hexane-Water	-438.05,1380.45, 254.0		2.57 E-6	2.57 E-6	4.7 E-4	4.7 E-4	3.89 E+5	3.89 E+5	2.13 E+3	2.13 E+3						
Butanol-Water	w1=1, w2=1 w3=1 -198.86, 271.76,75.87	1	.505	.41	.0187	.022	51.37	55.14	5.06	4.93	5.42	3.51	1.31	3.01		
	w1=0, w2=0 w3=1 -234.34,339.57, 84.73	2	.505	.37	.0187	.024	51.37	59.67	5.06	4.57	5.21	2.93	1.23	2.52	1.2 1.4	
	w1=5, w2=10 w3=1 -85.68,104.79, 58.58	3	.505	.48	.0187	.021	51.37	56.2	5.06	4.98	5.78	3.93	1.41	3.32		
Hexane-Butanol	w2=1,w3=1 -272.87, 464.36,70.56	1					5.12	5.42	38.6	31.72	2.71	3.63	2.68	1.95		1.65*
	w2=5,w3=1 -278.75,485.91, 70.56	2					5.12	5.25	38.6	38.2	3.23	4.83	3.26	2.74		1.47*

*using γ^{∞} of Butanol in Water 56.2 and that of Butanol in Hexane in corresponding row

Table 4.13. Average percentage of error of Butanol and Water composition in Hexane phase for different α's

α	Xh	Xw	γ_h	γ_w
.15	0.0000	1.0000	387966	1.00
	0.0001	0.9999	384010.	1.0
	0.001	0.999	350374	1.0
	0.01	0.99	147619	1.004
	0.1	0.9	764.4	1.31
	0.5000	0.5000	4.37	7.4
	0.9900	0.100	1.0	1670
	1.0000	0.0000	1.00	2153
.22	0.0000	1.0000	388144	1.00
	0.0001	0.9999	377610	1.0
	0.001	0.999	296015	1.0
	0.01	0.99	37159	1.01
	0.1	0.9	33.56	1.36
	0.5000	0.5000	2.95	2.8
	0.9900	0.100	1.0	1240
	1.0000	0.0000	1.00	2186
.25	0.0000	1.0000	388489	1.00
	0.0001	0.9999	372142	1.0
	0.001	0.999	155306	1.0
	0.01	0.99	13199	1.01
	0.1	0.9	11.4	1.34
	0.5000	0.5000	2.48	2.05
	0.9900	0.100	1.0	1025
	1.0000	0.0000	1.00	2211

Table 4.14. Change of activity coefficient values with the change of Hexane-Water concentrations in different α's

α	Average % err of Butanol composition in Hexane phase	Average % err of Water composition in Hexane phase
.05	27.83	27.96
.1	20.13	21.32
.15	13.2	15.18
.16	12.04	14.13
.17	11.3	13.40
.18	10.68	12.12
.19	10.1	11.61
.2	9.91	10.91
.21	9.33	10.23
.22	9.02	10.41
.23	9.53	11.03
.24	10.01	12.21
.25	10.78	13.32
.35	21.38	24.62

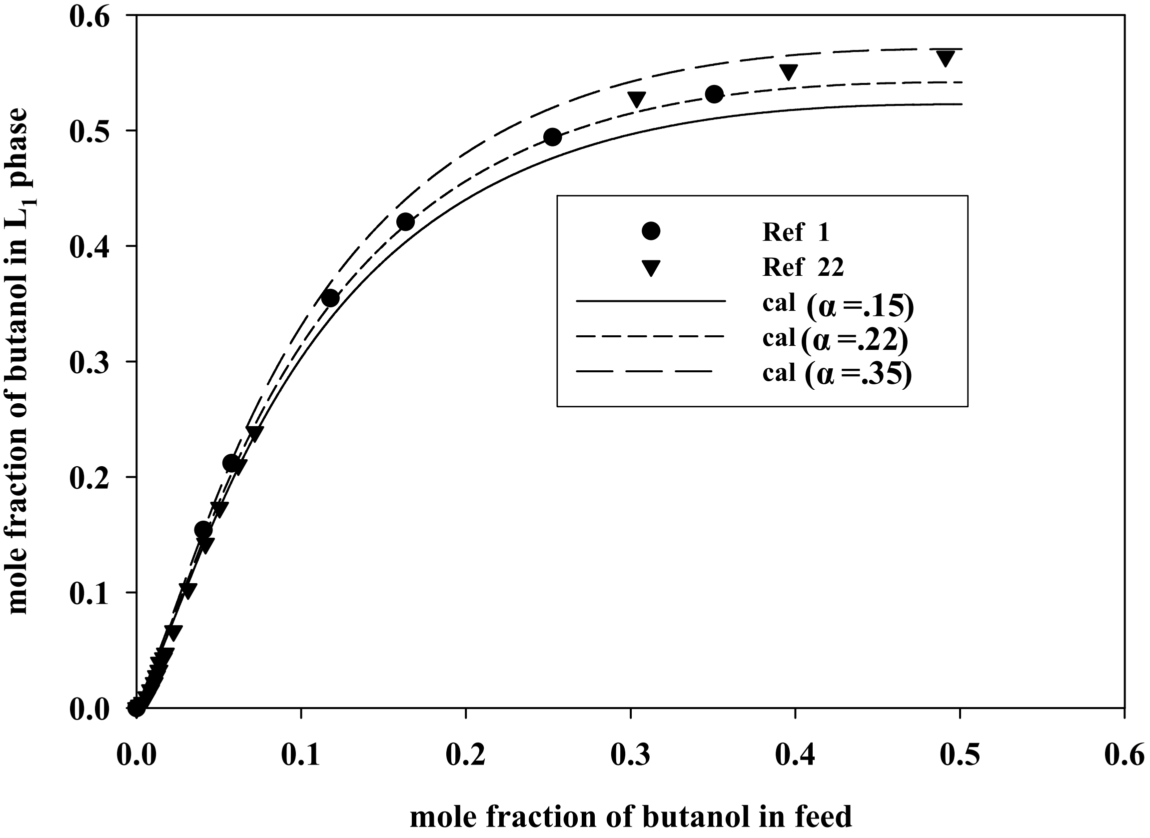

Figure 4.4. Comparison of experimental data and results calculated by NRTL for different α of Hexane-Water pair

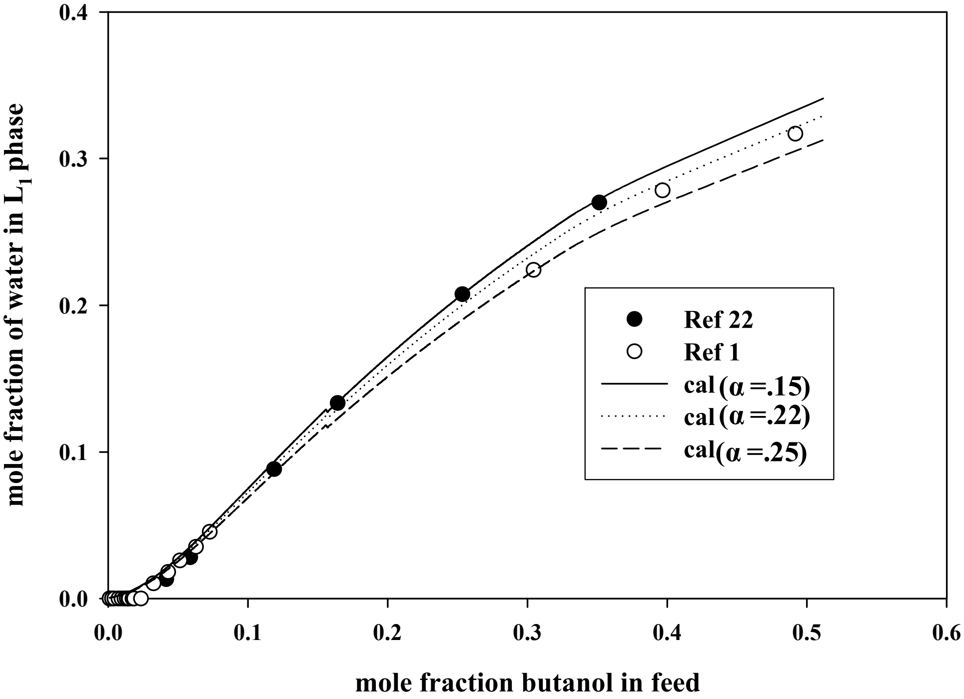

Figure 4.5. Comparison of experimental data and results calculated by NRTL for different α of Hexane-Water pair

Table 4.15. Average percentage of error of Butanol and Water composition in Hexane phase for different λ's

λ	Average % err of Butanol composition in Hexane phase	Average % err of Water composition In Hexane phase
250	13.68	14.92
251	12.83	13.38
252	11.21	12.91
253	10.12	11.18
254	9.13	10.73
255	9.82	11.08
256	10.10	12.13
257	11.2	13.23
258	12.41	14.51
259	13.39	15.68
260	14.08	16.71

Table 4.16. Change of activity coefficient values with the change of Hexane-Water concentrations in different λ's

λ	Xh	Xw	γ_h	γ_w
250	0.0000	1.0000	387986	1.00
	0.0001	0.9999	384110	1.0
	0.001	0.999	350348	1.0
	0.01	0.99	147599	1.003
	0.1	0.9	742.4	1.28
	0.5000	0.5000	4.28	7.3
	0.9900	0.100	1.0	1659
	1.0000	0.0000	1.00	2148
254	0.0000	1.0000	388126	1.00
	0.0001	0.9999	377589	1.0
	0.001	0.999	296008	1.0
	0.01	0.99	37139	1.01
	0.1	0.9	32.68	1.27
	0.5000	0.5000	2.73	2.7
	0.9900	0.100	1.0	1228
	1.0000	0.0000	1.00	2174
260	0.0000	1.0000	388458	1.00
	0.0001	0.9999	372119	1.0
	0.001	0.999	155292	1.0
	0.01	0.99	13159	1.01
	0.1	0.9	10.9	1.28
	0.5000	0.5000	2.31	2.03
	0.9900	0.100	1.0	1018
	1.0000	0.0000	1.00	2209

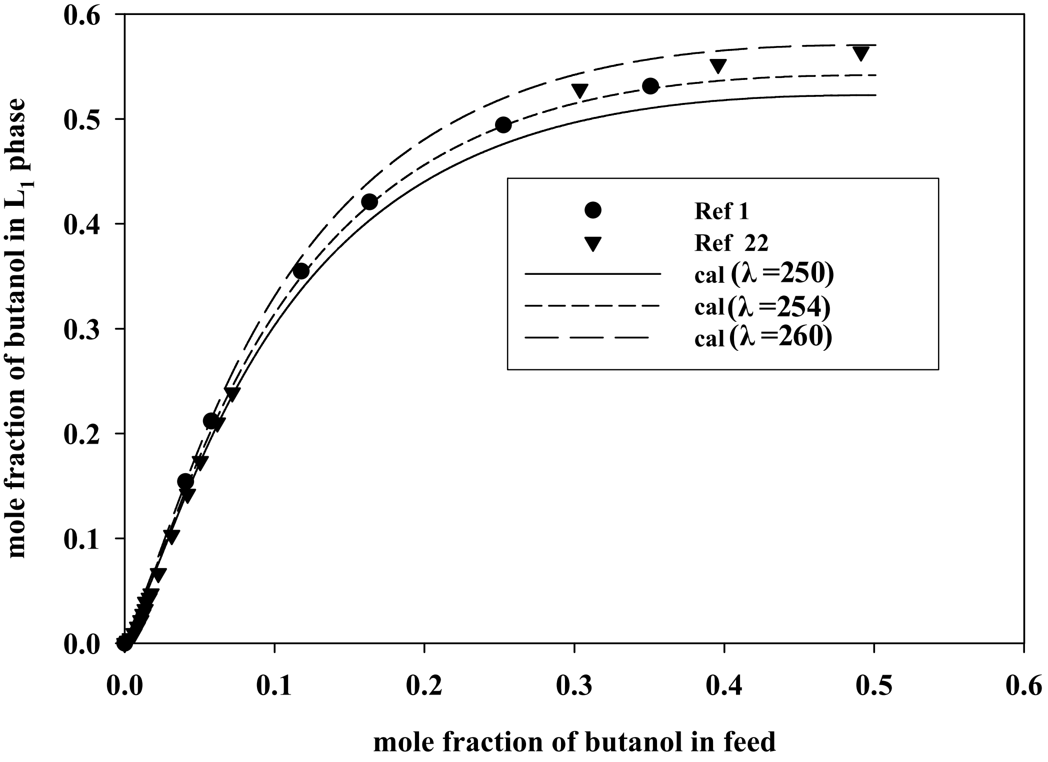

Figure 4.6. Comparison of experimental data and results calculated by GEM-RS for different λ of Hexane-Water pair

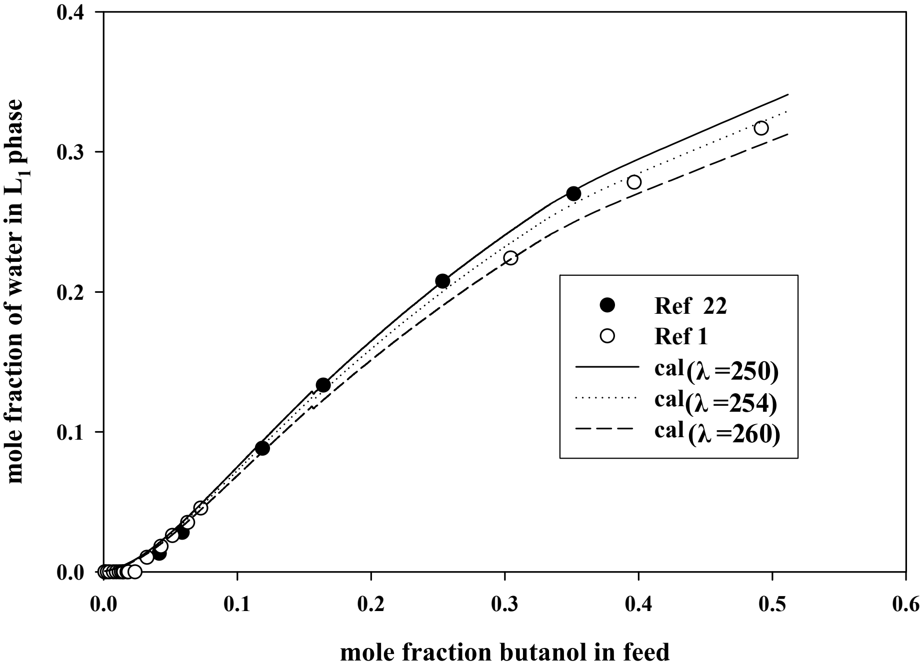

Figure 4.7. Comparison of experimental data and results calculated by GEM-RS for different λ of Hexane-Water pair

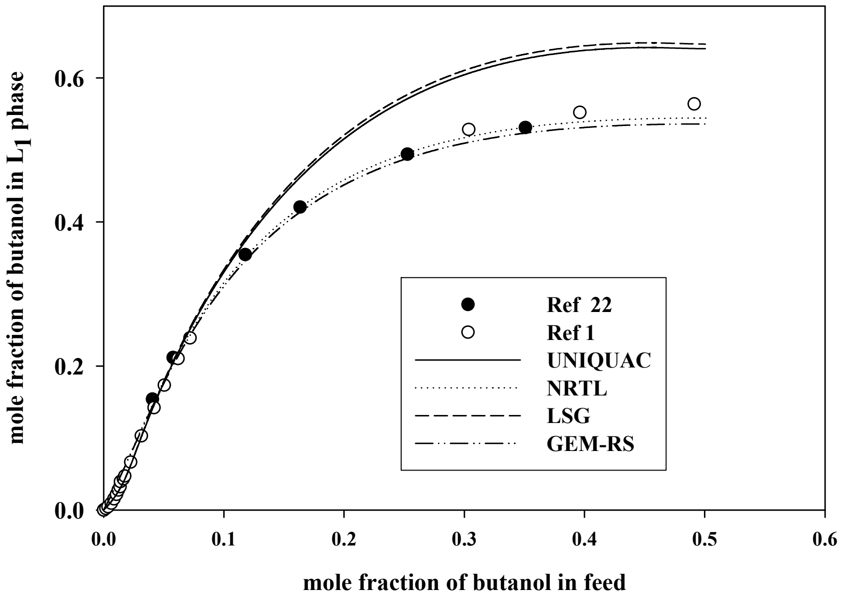

Figure 4.8. Comparison of experimental data and results calculated by UNIQUAC, NRTL, LSG, GEM-RS model over the concentration range

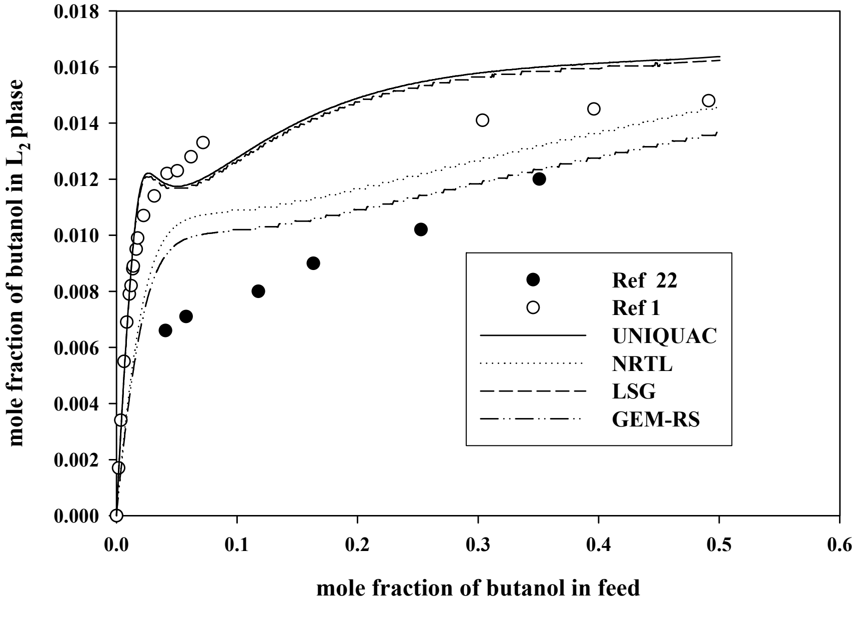

Figure 4.9. Comparison of experimental data and results calculated by UNIQUAC, NRTL, LSG, GEM-RS model over the concentration range in L_1 phase

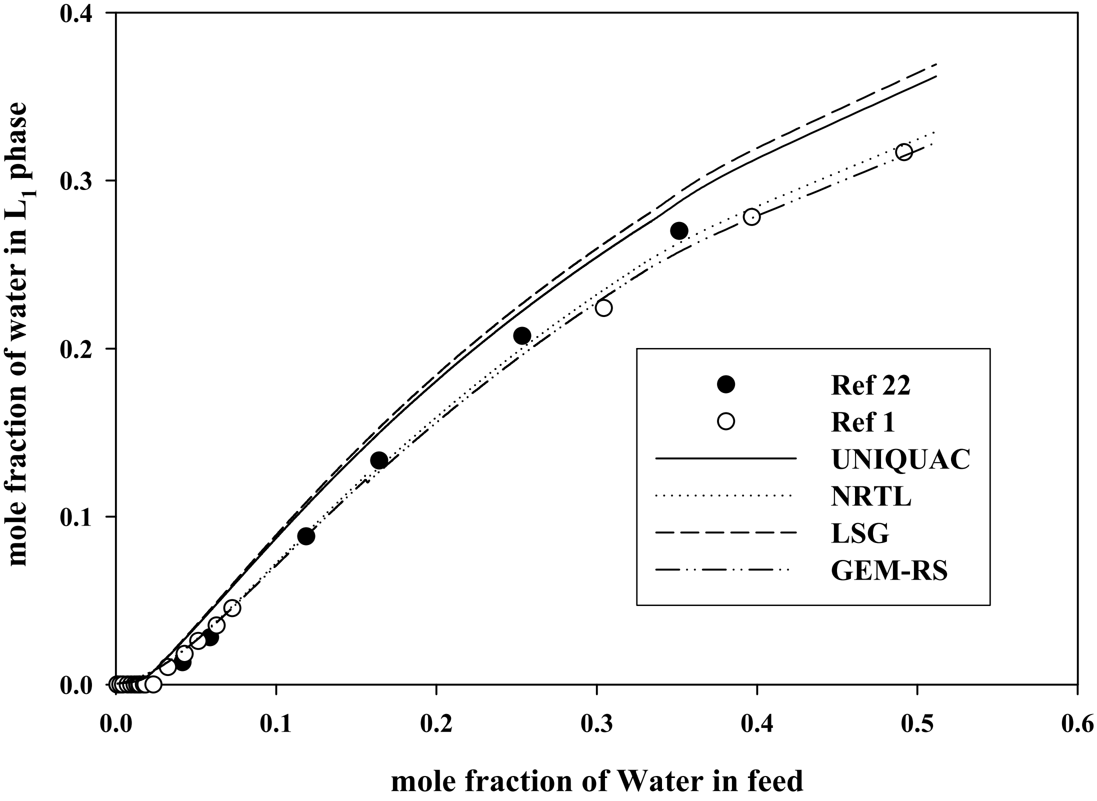

Figure 4.10. Comparison of experimental data and results calculated by UNIQUAC, NRTL, LSG, GEM-RS model over the concentration range in L_2 phase

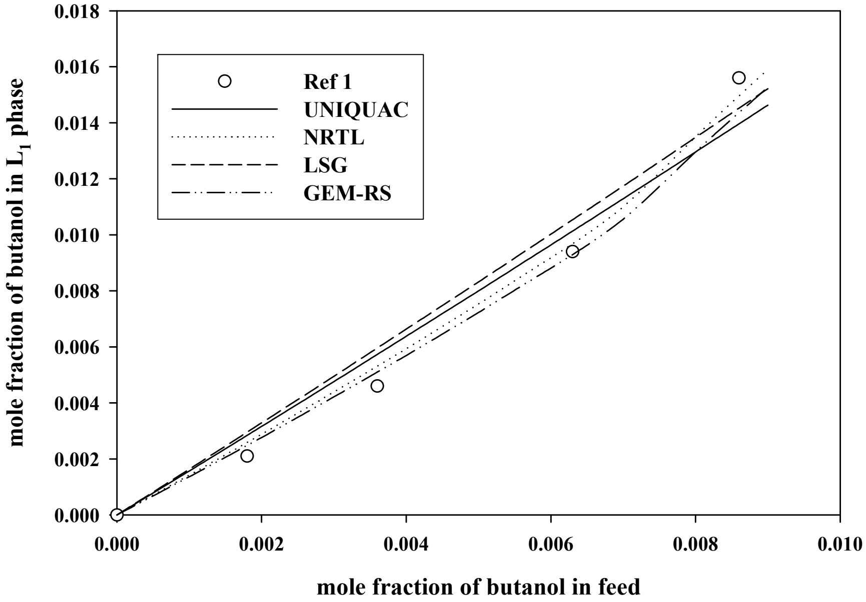

Figure 4.11. Comparison of experimental data and results calculated by UNIQUAC, NRTL, LSG, GEM-RS model in very dilute region

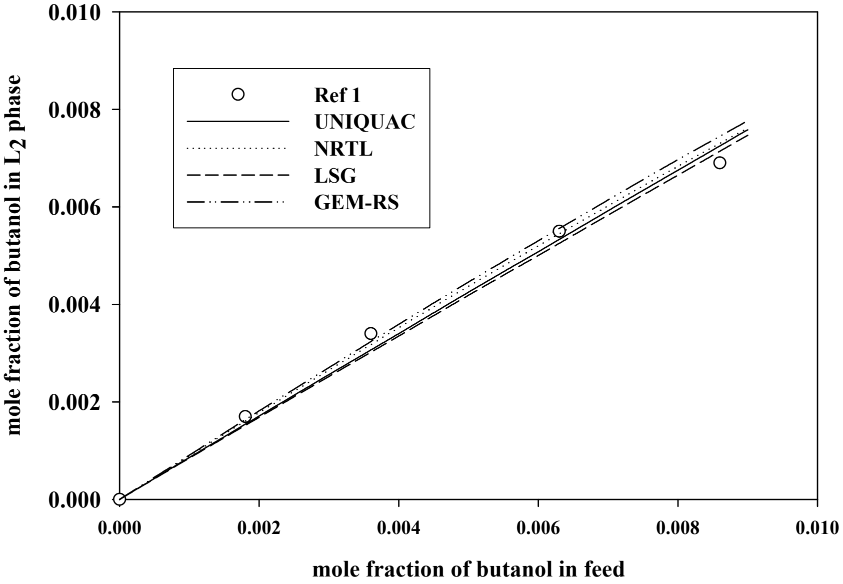

Figure 4.12. Comparison of experimental data and results calculated by UNIQUAC, NRTL, LSG, GEM-RS model in very dilute region

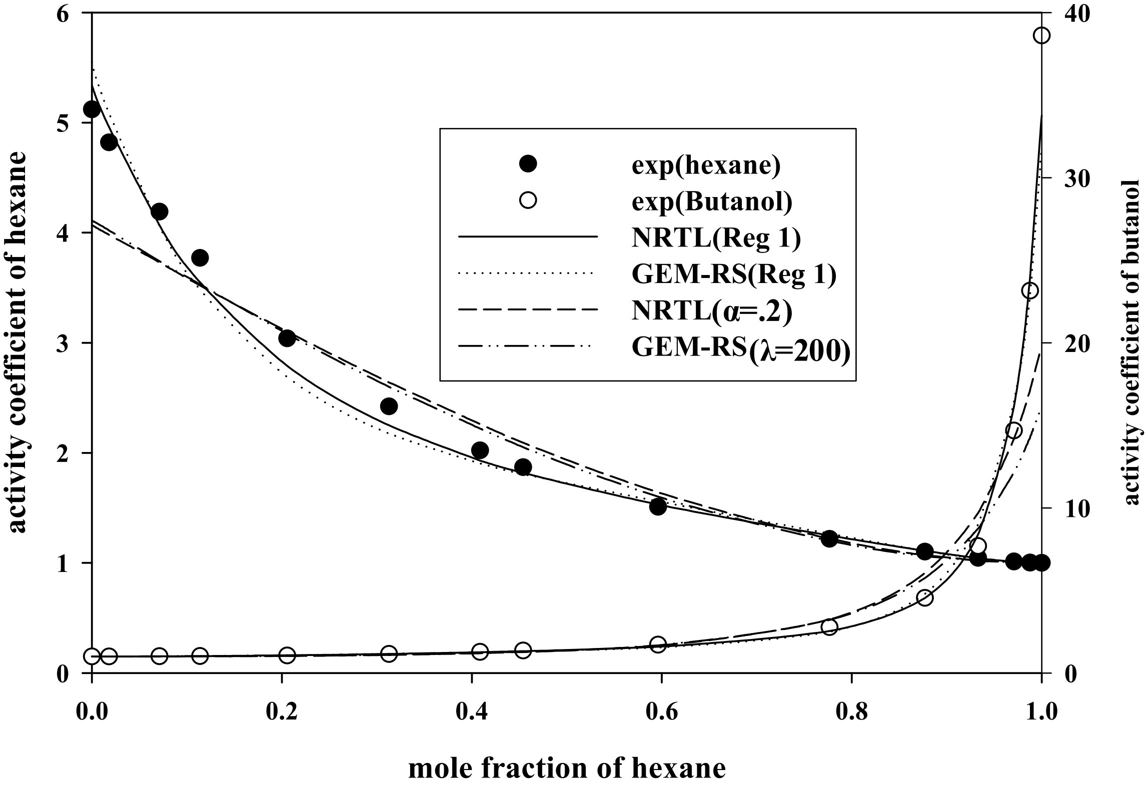

Figure 4.13. Variation of experimental and calculated γ's in the binary Hexane-Butanol liquid mixture by three parameter models if 3rd parameter is kept constant. γ_{Hexane} scale is given on the y-axis to the left and γ_{Butanol} on the y-axis to the right of the Figure

CHAPTER 5

SELECTION OF DATA FOR TEMPERATURE DEPENDENT WORK

5.1 Data Selection

After obtaining satisfactory results at 25 °C, a set of universal parameters that can be used within a temperature range of 10 to 100 °C was to be found. Hence, similar to previous methods, an extensive literature search was carried out to obtain mutual solubility, γ^{∞} and VLE data of Hexane-Water, Butanol-Water, and Butanol-Hexane pairs; distribution coefficient (Dsw) and LLE data of Hexane-Butanol-Water; vapor pressure, and liquid density of Hexane, Butanol and Water ranging from 10 to 100 °C. Most of the solubility, γ^{∞} and excess enthalpy (H^E) data was taken from Dechema [43, 44, 57, 58, 73, 74]. Complete descriptions of the data selection are discussed by pairs as follows.

5.1.1 Hexane-Water

In the literature [15-26], numerous values for solubility were found at several temperatures for this pair. However, these values vary between each source. The data was selected from Tsonopoulos et al. [23] since it follows a non-erratic trend throughout. Figure 5.1 illustrates the difficulty in selecting solubility data of Hexane in Water. Generally, it is known that solubility of oil in water increases with temperature and using this criterion, the data points were selected. From Figure 5.2, it was observed that the solubility of Water in Hexane at 293.15 K does not follow the trend at other temperatures, such as at 298.15, 303.15 and 313.15 K (Englin et al. [43]). Hence, data at 293.15 K was discarded. The final selected data are shown in Appendix F.

5.1.2 Water-Butanol

There are numerous values of infinite dilution activity coefficients (γ^{∞}) and solubility data for this pair [44-53, 71, 72]. In this case some data points were discarded due to discontinuity. For VLE data selection, x-γ values were generated by the previously mentioned procedure. This time also the second virial coefficients (B_{ii}), saturated liquid volume (V_i^L) and saturated vapor pressure (p_i^{sat}**)** data or corresponding expressions from literature [56, 77-80] were chosen carefully.

V_i^L and p_i^{sat} of Hexane and Butanol were calculated from the temperature dependent correlation by Daubert and Danner [56] and for Water from the ASME Table [67]. Equations for calculating V_i^L and p_i^{sat} by Daubert and Danner [56] are as follows:

$$V_i^L = A/(B^{(1+(1-T/C)^D)})*1000 \text{ (Here } V_i^L \text{ is in cm}^3\text{/mol)} \tag{5.1}$$

$$p_i^{sat} = \exp\left[A + B/T + C\log T + DT^E\right] \div 1000 \tag{5.2}$$

B_{ii} of Hexane and Butanol and mixed virial coefficient (Bij) of Hexane-Butanol/Water-Butanol pairs were calculated by the Tsonopoulos correlation [20], and for Water it was taken from Harvey and Lemon [77]. The Harvey and Lemon correlation is as follows:

$$B(T)/B^o = \sum_{i=1}^{4} a_i (T^*)^{b_i} \tag{5.3}$$

All the parameters of Daubert and Danner [56], Harvey and Lemon [77], are shown in Table 5.1.

There are enormous solubility datasets, which are available for this pair, as seen in Figures 5.3 and 5.4. In Figure 5.3, solubility data for Water in Butanol at different temperatures do not differ much from one source to another. It seems that solubility of Water in Butanol increases with temperature. Hill et al. [36] showed smooth solubility data from lower temperature to higher temperature and these data were taken for our final selection.

In Figure 5.4, most of the reference data showed a decline of solubility of Butanol in Water with temperature; however, Lesteva et al. [43] showed reverse behavior. Fuehner et al. [43] reported smooth trend data with temperature ranging from lower to higher and this dataset was finally selected. For γ^∞ data of Water in Butanol, Loblein et al. [80] was finally selected since this was the only reference data which was consistent with values at 25 °C. This is shown in Figure 5.5**.**

Different literature show different trends of γ^{∞} data of Butanol in Water with temperatures as shown in Figure 5.6. Tochigi et al. [63] showed that γ^{∞} of Butanol in Water decreases with temperature whereas other sources showed the opposite manner. Since Vrbka et al. [45] reported from lower temperature to higher temperature, his dataset was used.

Five excess enthalpy (H^E) dataset was found for Water-Butanol. These are shown in Figure 5.7. Ponner et al. [74] data was not selected since the dataset did not show the solubility gap between Water and Butanol. Hence for this regression purpose, Pannov [74] and Goodwin [83] datasets were used. Excess enthalpy data are also very important for an activity coefficient model because excess enthalpy is the first derivative of activity coefficient at constant pressure and composition.

5.1.3 Hexane-Butanol

Large amounts of VLE data of Butanol-Hexane over the temperature range were found in the literature. Barker's method [52] was also applied to get y data and to generate corresponding γ. Coefficients that were calculated to use in Barker's method are listed in Table 5.2 and the VLE dataset of Hexane-Butanol which was used for the calculations are reported in Appendix F.

Five excess enthalpy datasets for this pair were collected [82]. Brown et al. [82] reported datasets at temperatures of 25, 35 and 45 °C. Those datasets were part of the final selection. Nguyen's [89] dataset seemed to be uncertain since data points were erratic. Mukrami's [82] also had the same problem. All the datasets are shown in Figure 5.8.

There was a scarcity of γ^{∞} data of Hexane in Butanol and that of Butanol in Hexane in literature. For these datasets, the final selections are shown in Figures 5.9 and 5.10, respectively.

5.2 Results of Temperature Dependent Work

The temperature dependent work was done using the NRTL model over the temperature range of 10-100 °C. In this case parameters at 25 °C were taken as reference parameters. As mentioned earlier, the temperature dependent functions are as follows:

$$g_{1,2} = A_{1,2} + B_{1,2}(T - 298.15) + C_{1,2}(T - 298.15)^2 \tag{5.1}$$

$$g_{2,1} = A_{2,1} + B_{2,1}(T - 298.15) + C_{2,1}(T - 298.15)^2 \tag{5.2}$$

For this work, all types of phase equilibrium data in addition to excess enthalpy data were used. In this case A_{12}, A_{21}, and α were kept fixed at 25 °C and only four parameters, B_{12}, B_{21}, C_{12} and C_{21}, were regressed. Overall percentage of error was minimized for each data point. Based on the work done at 25 °C, to obtain the best parameters for each pair (Hexane-Water, Hexane-Butanol, Water-Butanol), several combinations of objective functions were tried. For each objective function in the regression, overall average percentage of error and percentage of error in each data point was recorded. The target was to minimize overall percentage of error in each data point of binary LLE, binary VLE, H^E and γ^∞ data. Here H^E is a new type of data set. Weight on this data set was mentioned by w_4. w_1, w_2, w_3 were the same as in Chapter 4. Samples of regression work are shown in Tables 5.3 and 5.4.

The objective was to obtain the parameters which will give overall average percentage of error within 15%. After thorough computation work, these parameters were successfully obtained. The complete overall results are reported in Table 5.5 and the parameters are shown in Table 5.6.

After obtaining a universal set of parameters for the temperature dependent work, a ternary diagram was plotted with calculated results at 25 °C as well as at 75 °C. This is shown in Figure 5.11. Like the experimental data, the calculated results also clearly show phase split. Although in the literature, ternary LLE data was not available at higher temperatures, a prediction can be made based on these calculated results. From this figure it was seen that at higher temperatures, the Water-rich phase behaves the same as in 25 °C; however, the Hexane-rich phase behaves differently. At higher temperatures, there is more Butanol in the Hexane-rich phase than in 25 °C. Calculated ternary data at 40, 60 and 75 °C are also shown in this figure. Variations of Butanol concentrations in the Hexane-rich phase at high temperatures are shown in Figure 5.12. Calculated *Dsw* at 40, 60 and 75 °C are 1.81, 2.31 and 2.98, respectively.

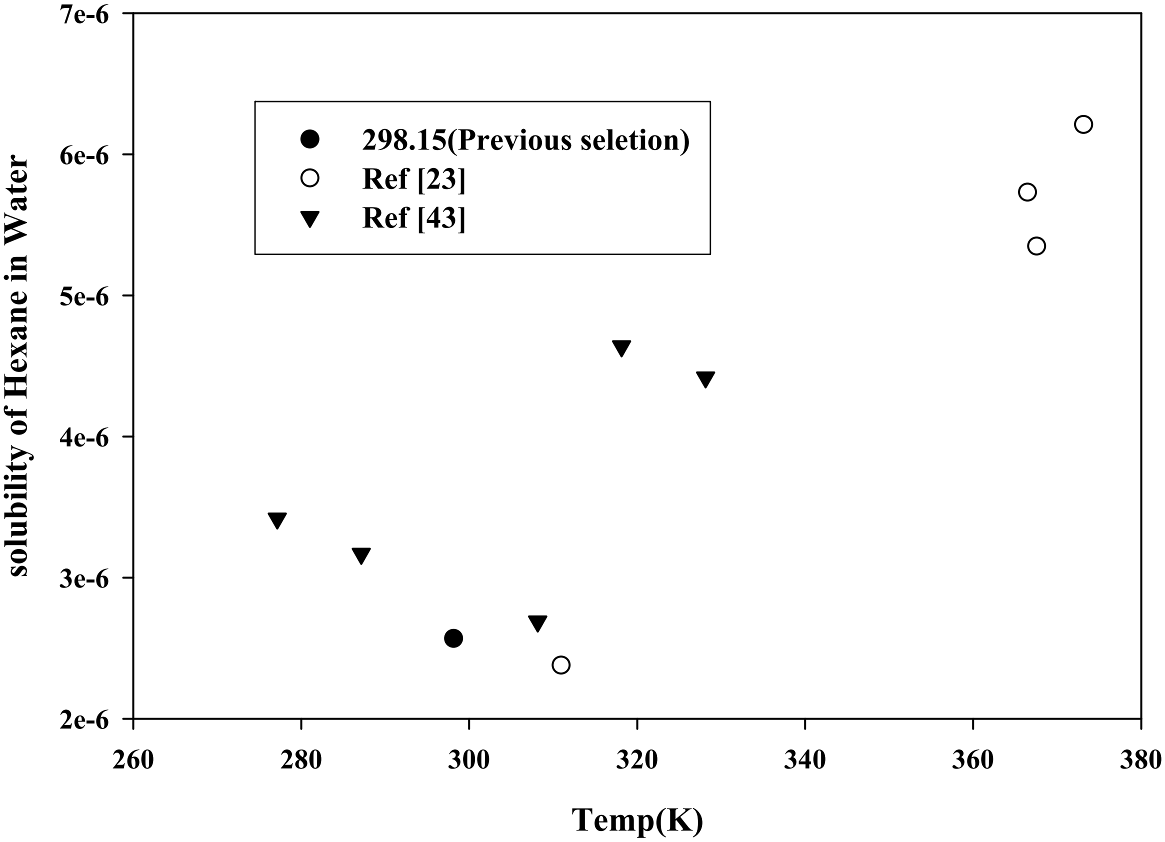

Figure 5.1. Solubility of Hexane in Water at different temperatures

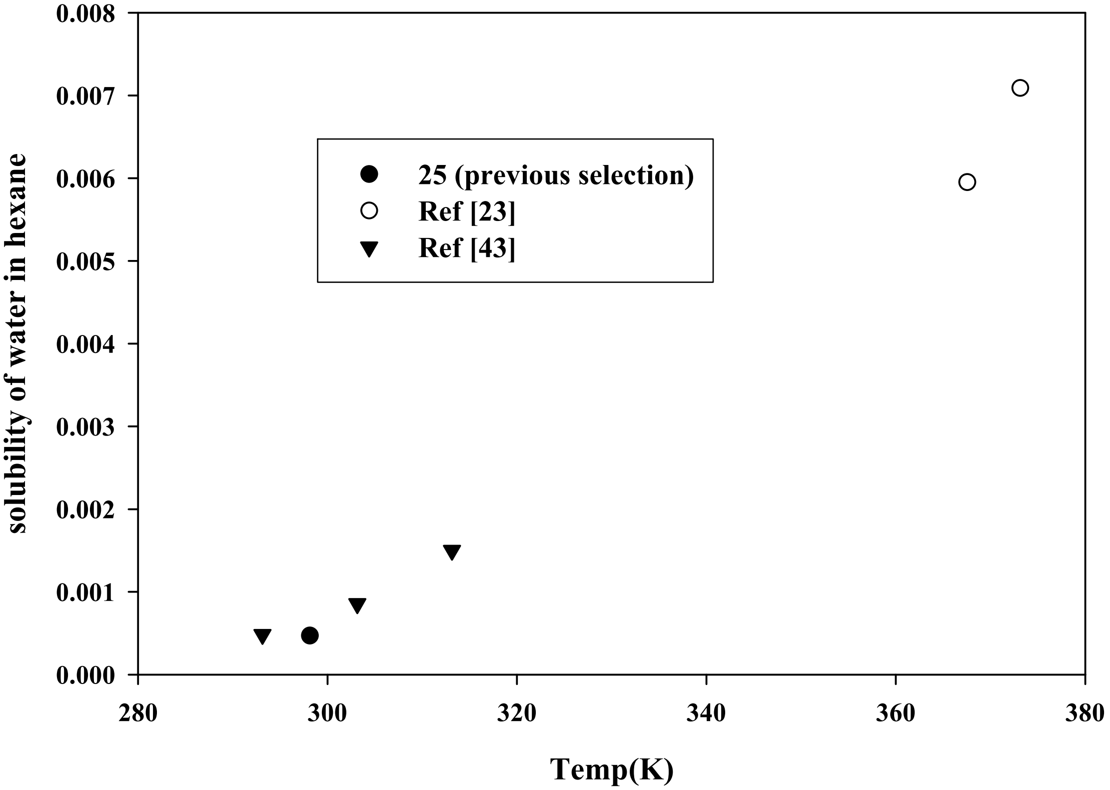

Figure 5.2. Solubility of Water in Hexane at different temperatures

Table 5.1. Parameters of Daubert and Danner [56], Harvey and Lemon [77]

Parameter of Ref [56]	V_i^L		p_i^{sat}		**parameter of Ref [77]**	$\mathbf{B_i}$	
	Hexane	**Butanol**	**Hexane**	**Butanol**	**i**	**Water**	
						$\mathbf{a_i}$	$\mathbf{b_i}$
A	.7147	.9677	165.47	96.23	1	.34	-0.5
B	.265	.26674	-8353.3	-9214.3	2	-.76	-0.8
C	507.43	562.93	-23.972	-10.295	3	-24.22	-3.35
D	.2781	.2457	.02949	.000002	4	-3978.2	-8.3
E	0.	0.	1.0	2.0			

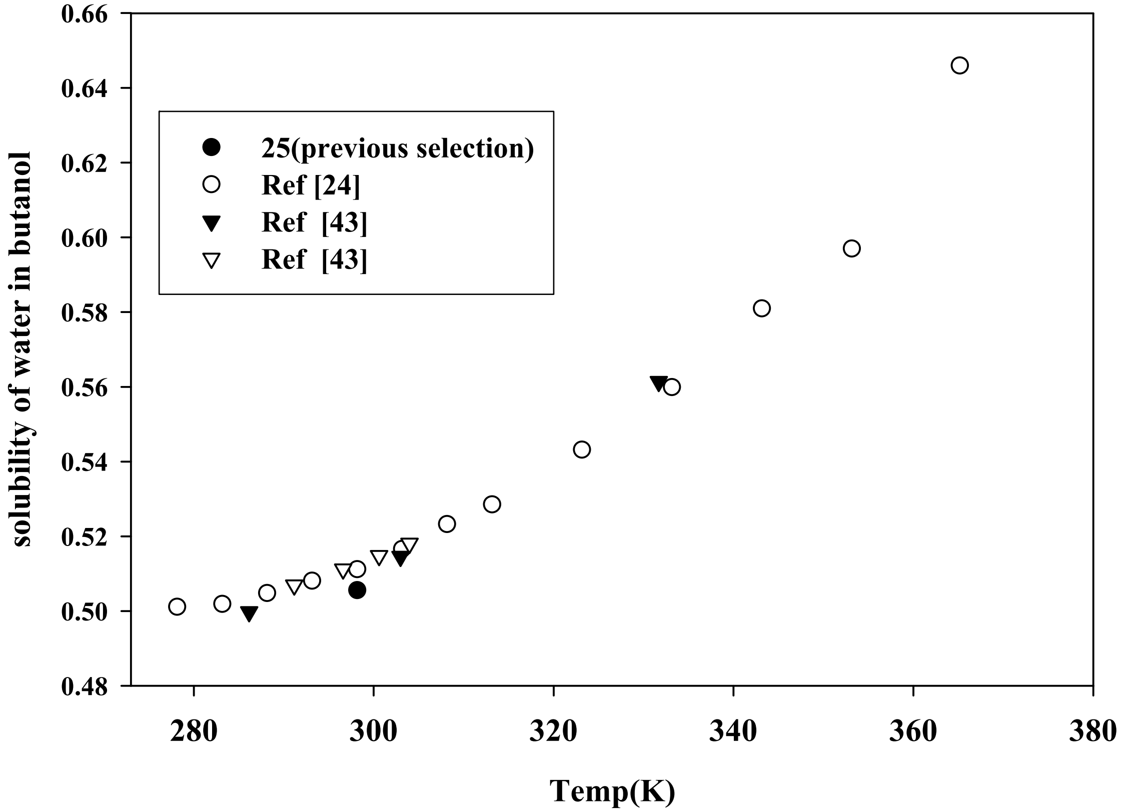

Figure 5.3. Solubility of Water in Butanol at different temperatures

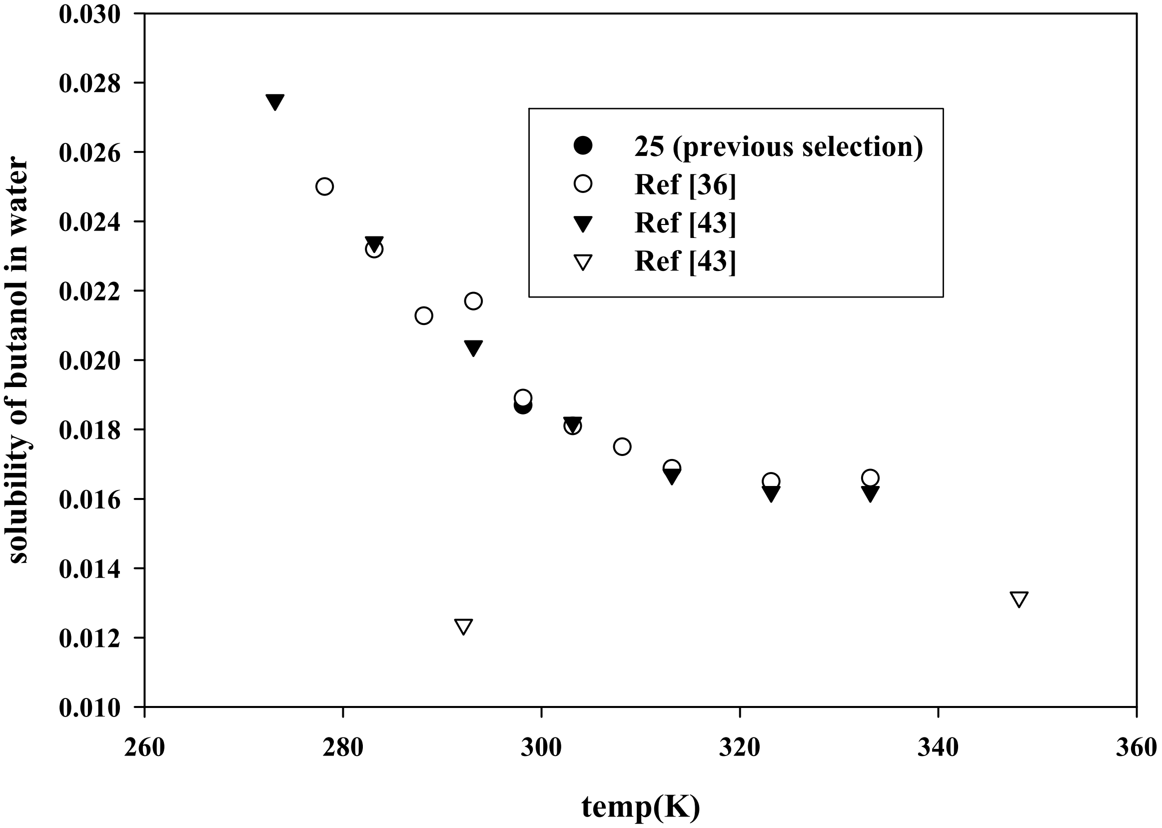

Figure 5.4. Solubility of Butanol in Water at different temperatures

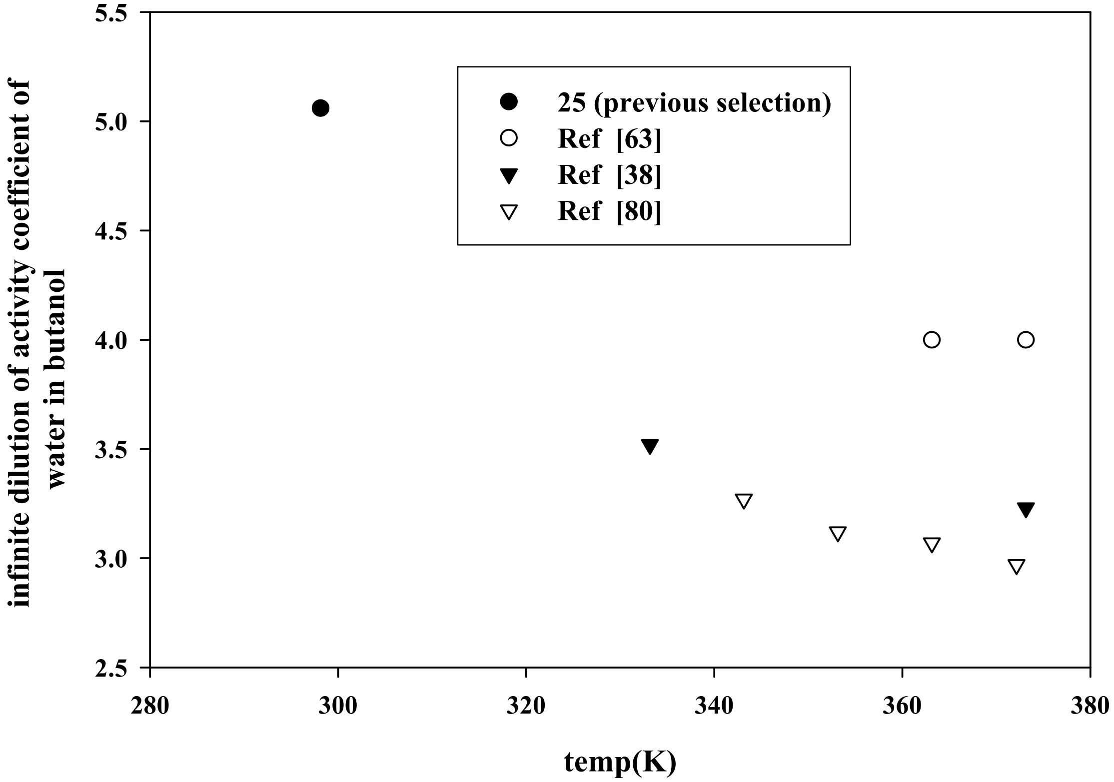

Figure 5.5. Infinite dilution activity coefficient of Water in Butanol at different temperatures

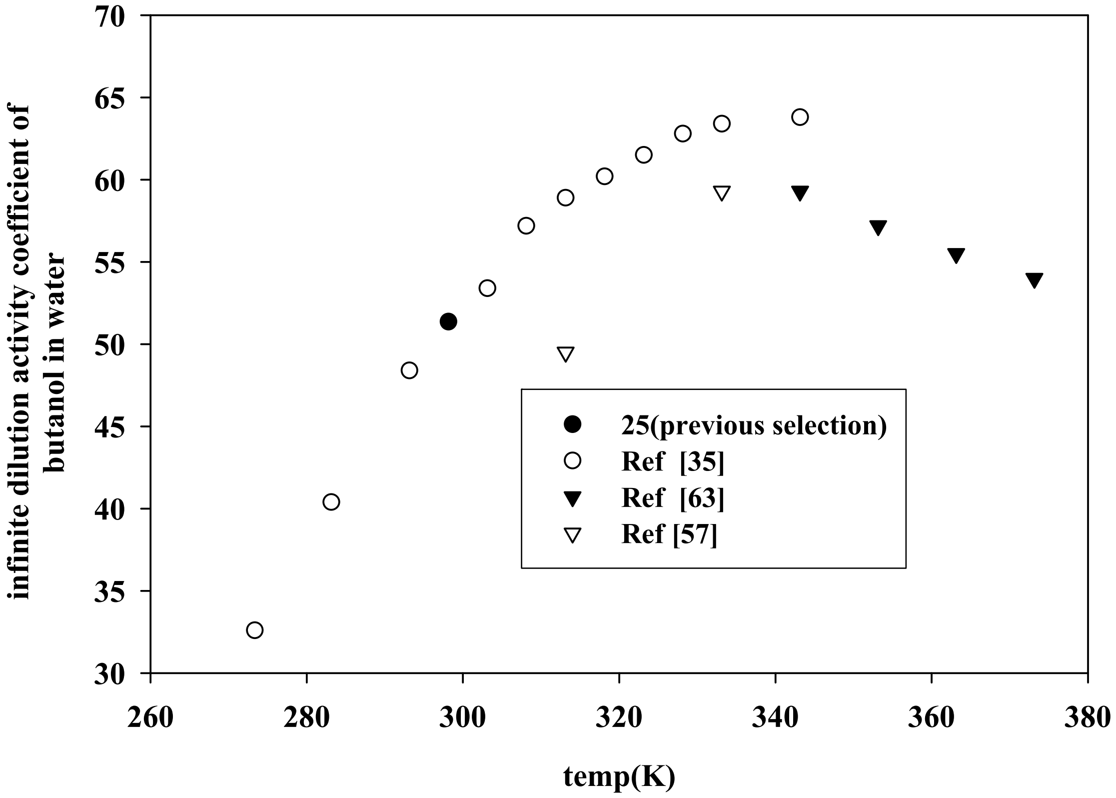

Figure 5.6. Infinite dilution activity coefficient of Butanol in Water at different temperatures

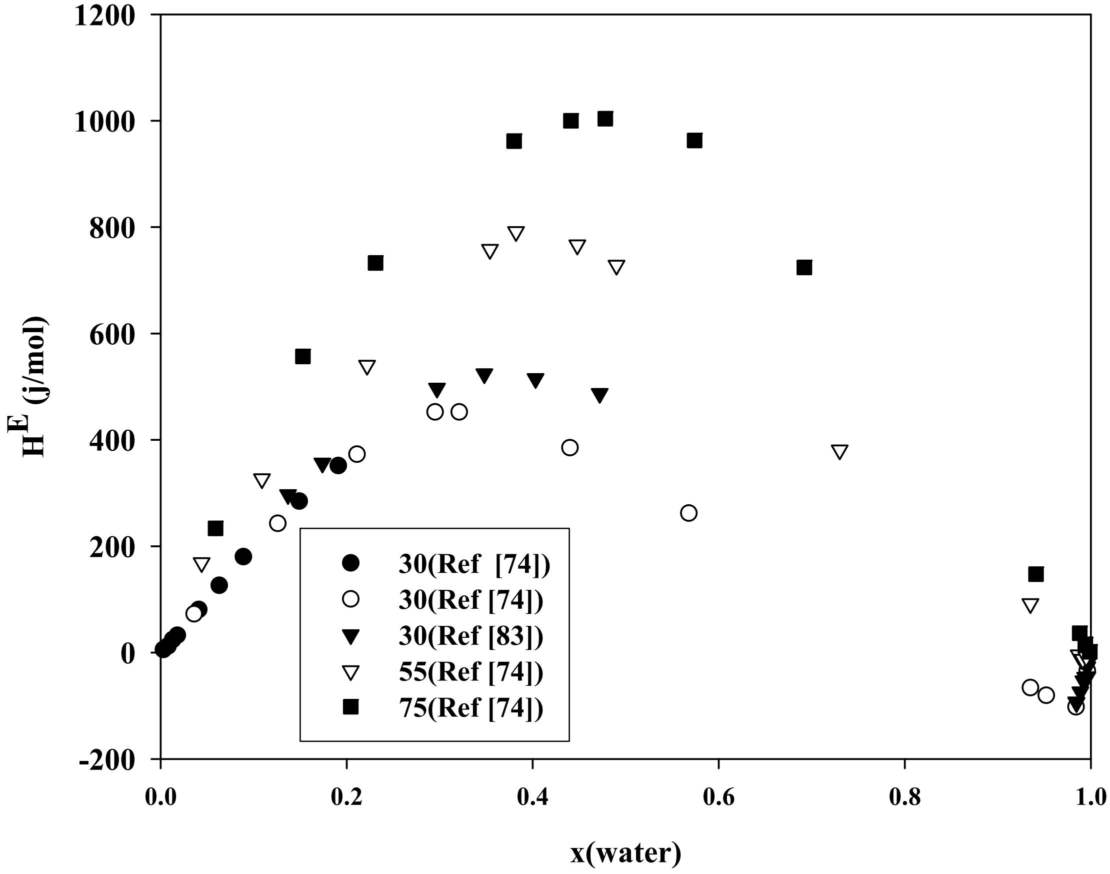

Figure 5.7. Excess Enthalpy of Water-Butanol at different temperatures

Table 5.2. Coefficients for use in Barker's method in Equations 2.23 and 2.24

T(K)	A_0	A_1	A_2	B_1
288.15	1.8698	-1.1973	-.0527	-.8453
293.15	1.8553	-1.1564	-.0348	-.8254
298.15	1.8374	-1.108	-.0234	-.8047
303.15	1.8204	-1.1015	-.031	-.8025
308.15	1.8049	-1.0658	-.0182	-.7852
313.15	1.788	-1.0416	-.031	-.7745
318.15	1.7741	-1.0031	.0118	-.7487
323.15	1.7538	-.9645	.0163	-.7305

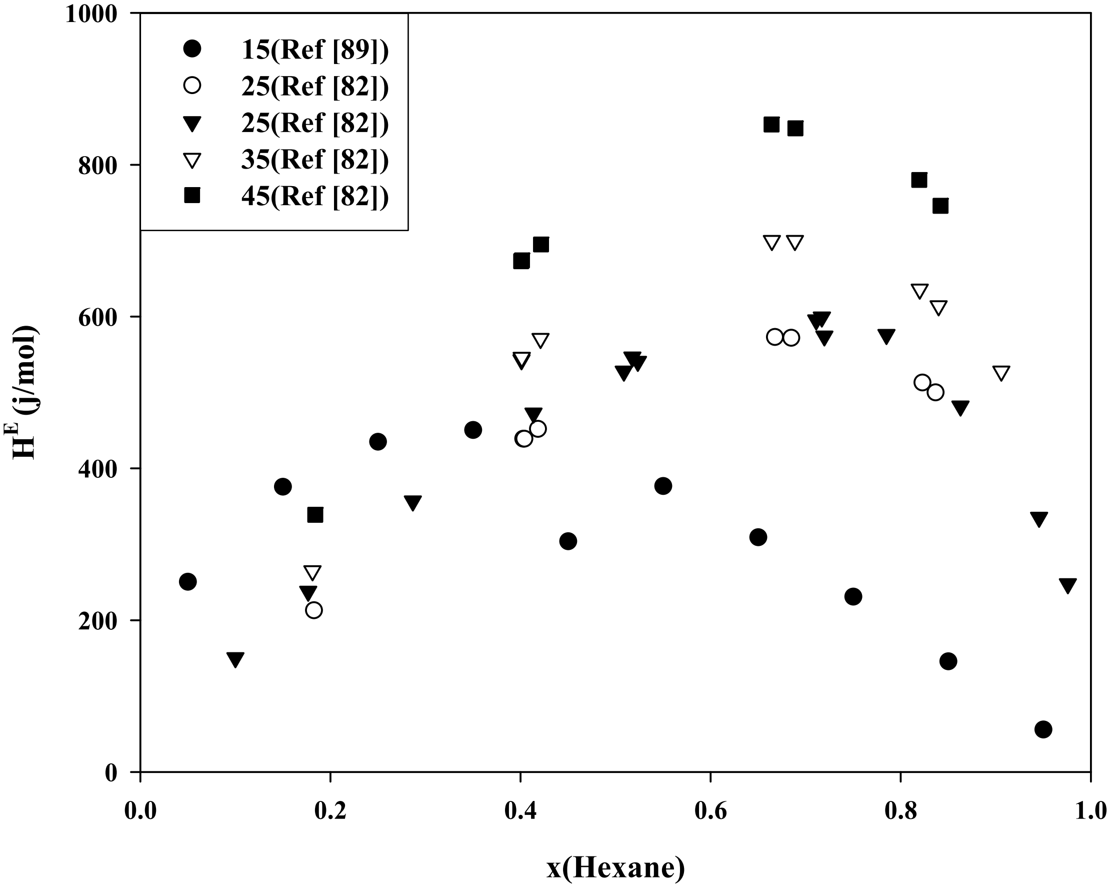

Figure 5.8. Excess Enthalpy of Hexane-Butanol

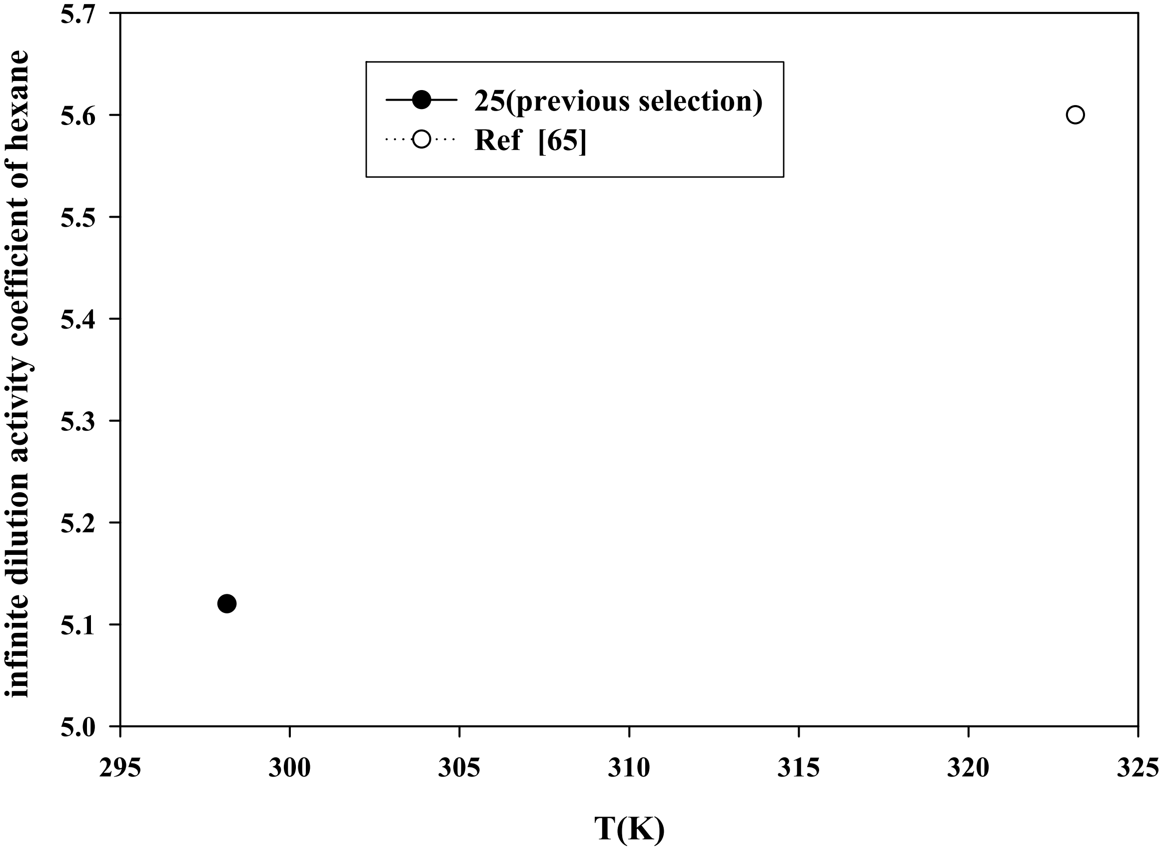

Figure 5.9. γ^{∞} of Hexane-Butanol at different temperatures

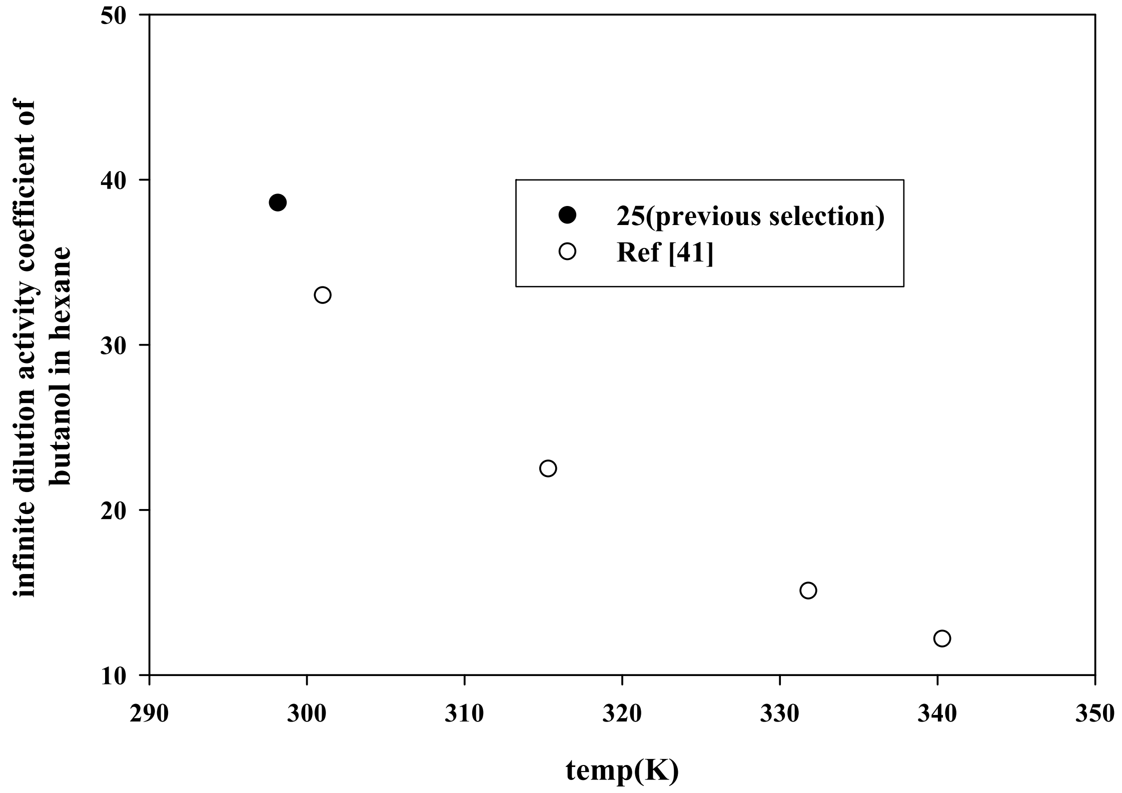

Figure 5.10. γ^{∞} of Hexane-Butanol at different temperature

Table 5.3. Parameter estimation for Water-Butanol(for temperature dependent work)

Objective function	Average error in solubility (%)		Average error in γ^{∞}(%)		Average error in γ (%)		Average error in H^E (%)
	1 in 2	**2 in 1**	**1**	**2**	**1**	**2**	
w1=1,w_2=1,$w_{3=}$1,w_4=1	12.61	4.1	5.89	4.37	3.7	4.43	14.41
w_4=10	23.38	36.21	15.58	13.37	7.18	11.02	8.92
w_2=4.5	18.36	4.82	2.99	5.99	2.44	3.88	16.73
w_1=10	18.51	5.99	3.02	4.5	2.47	4.04	15.9
w_2=10	1.21	4.86	2.81	7.51	5.39	4.48	19.0
w_2=10,w_4=5	4.34	6.38	10.14	2.4	13.04	6.99	12.91
w_2=5,w_4=10	14.6	26.43	6.5	10.68	9.52	9.82	9.75
w_4=10,w_2=10	8.69	17.9	9.75	7.37	113.65	8.83	10.89
w_4=5,w_2=5	4.94	9.84	4.78	7.31	4.4	5.9	16.32
w_2=10,w_4=8,w_1=5	8.41	11.46	6.16	4.74	5.85	6.69	13.67
w_2=10,w_1=5	8.57	4.33	3.97	3.19	6.46	5.52	14.04
w_1=10,w_4=15,w_2=5	10.9	7.73	7.78	1.09	6.72	6.16	12.54

Table 5.4. Parameter estimation for Hexane-Butanol(for temperature dependent work)

Objective function	Average error in H^E	Average error in γ^{∞}(%)		Average error in γ (%)	
		1	2	1	2
$w_2=1$,$w_3=1$,$w_4=1$	8.95	10.02	14.08	3.41	5.17
$w_2=2$	7.48	11.7	15.51	3.83	6.19
$w_3=3$	6.42	12.39	17.14	4.06	6.93
$w_4=5$	6.05	12.43	11.49	4.33	7.64
$w_2=2$, $w_4=5$	9.18	9.48	13.69	2.48	3.51
$w_2=5$, $w_4=5$	8.82	10.31	12.97	2.73	3.85
$w_2=2.5$,$w_4=5$***	8.53	11.02	12.13	2.57	3.52

*** objective function for our final parameters.

Table 5.5. Calculated results by NRTL using best fitted parameters (temperature dependent function) for all three pairs

Hexane-Water	1.13	5.49						
Water-Butanol	5.52	12.48	8.47	8.98	3.14	6.49	12.21	1.2, 1.45/ 1.45
Hexane-Butanol			11.02	2.13	2.57	3.52	8.53	

Table 5.6. Best fitted parameters for all three pairs (for temperature dependent work)

Pair(i-j)		**A**	**B**	**C**	**α**
Hexane-Water	i,j	3381.24	7.478	-.0167	.22
	j,i	2013.85	-17.886	.1527	
Water-Butanol	i,j	1031.46	6.315	.00096	.41
	j,i	229.43	.585	-.0387	
Hexane-Butanol	i,j	910.21	-.307	-.003	.55
	j,i	323.42	-2.157	.018	

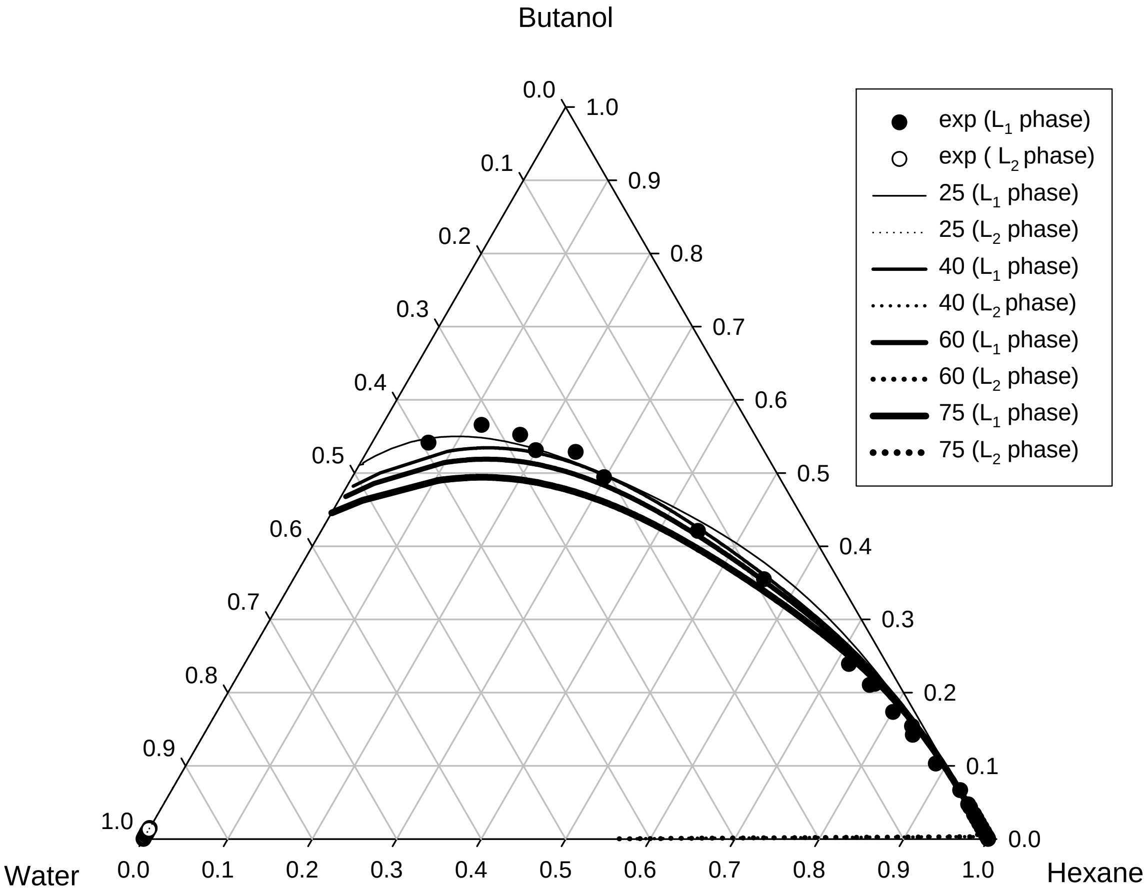

Figure 5.11. Ternary diagram for Hexane-Butanol-Water at higher temperatures

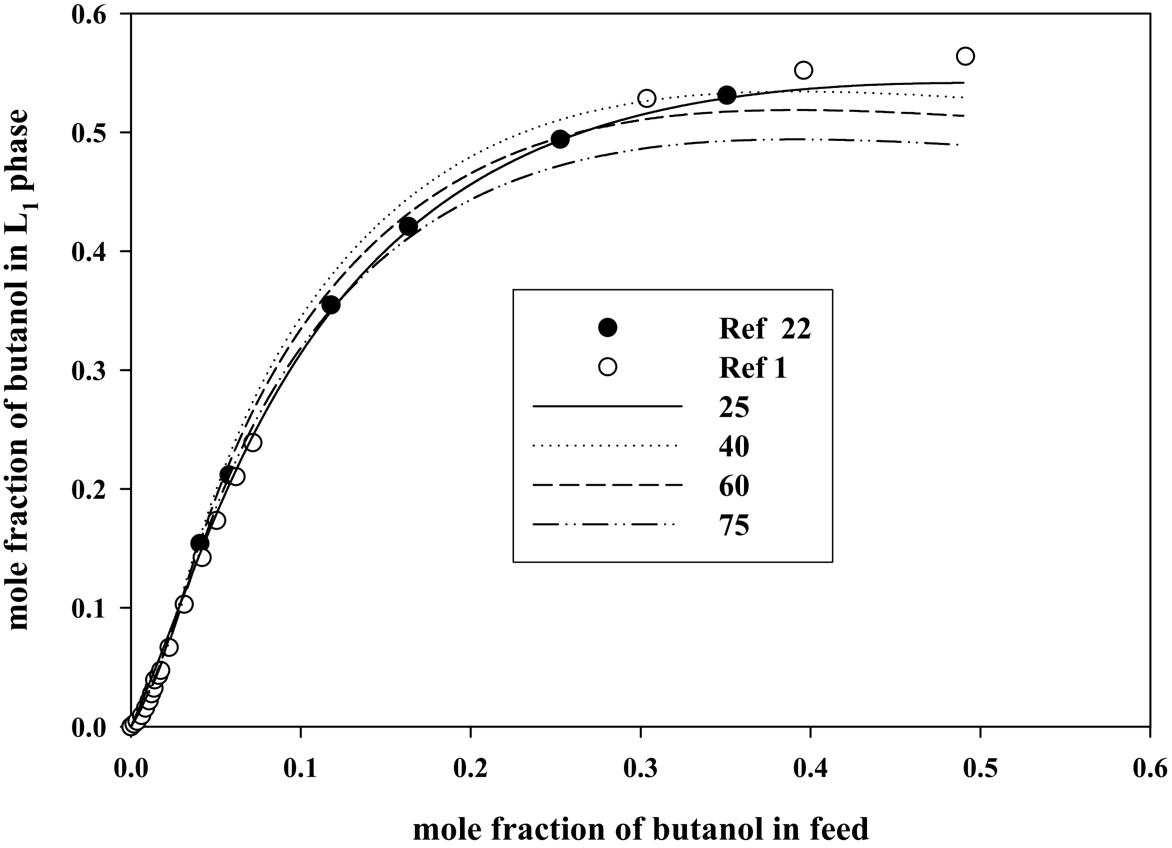

Figure 5.12. Variation of Butanol concentration in L_1 phase at higher temperatures

CHAPTER 6
DISCUSSION

Throughout this work, it was observed that careful selection of data and regression of parameters using x vs. γ data generated from VLE, all γ^{∞}, binary mutual solubility (LLE) and excess enthalpy data (H^E) data made it possible to obtain a universal liquid state model as well as a universal set of parameters for 25 °C and also for a temperature range of 10-100 °C. These parameters are not only able to predict binary data but also ternary data very well. For the Hexane-Water and Water-Butanol pairs, either two parameter or three-parameter models provide good results. The Hexane-Water pair does not show any problems due to the fact that the solubility itself is in infinite dilution and appropriate γ^{∞} values can be obtained using any model. Also, problems do not arise for the Water-Butanol pair since they are partially miscible and the x-γ functionality change within the miscibility gap is not known and cannot be described by any of the models. For these Hexane-Water and Water-Butanol pairs, any of the models can be used to fit the data at infinite dilution and finite concentration simultaneously. These two pairs did not show large deviations between calculated and experimental data. However, it was not possible to fit the data for all concentration ranges for the Hexane-Butanol pair. From x-γ analysis, it was found that at dilute concentrations γ values of Butanol increases very sharply. So any model which can represent sharp functionality changes can only be able to fit the data of this pair. The two-parameter models were found unable to show rapid changes of x-γ values. For the other two pairs, since γ changes smoothly with concentration, the two-parameter models perform well. Three-parameter models are capable of showing steep γ changes. The third additional parameter (in terms of non-randomness) helps to adjust the fit. It is also very important that the three-parameter models can only fit the data when the third parameter is regressed independently. Otherwise, there would be no difference between the three and two-parameter models. This additional parameter has the flexibility to fit the data for all concentration ranges. As seen in Figure 4.13, using the three-parameter models to fit the data showed the same behavior as in the UNIQUAC or LSG model. This is due to the fact that the third parameters were kept fixed and other two interaction parameters were regressed.

For ternary systems, using the three-parameter models is not straightforward. Due to the immiscible pair, Hexane-Water, many combinations of third parameters and binary parameters are possible. Although every combination will give reasonable solubility values for this binary pair, they will not necessarily give good ternary results. The Water-rich phase calculations can be done using any set of parameters, unlike the Hexane-rich phase. In the Water-rich phase, the amount of Hexane and Water remain nearly fixed throughout the entire concentration range. In the Hexane-rich phase, as the Butanol concentration increases, the concentration of Hexane and Butanol changes substantially. Hence, different third parameters will give different results for this phase. The most accurate way of selecting suitable third parameters is to compare the calculated results with the experimental data, which is very tedious work. As seen from the results, optimum ternary data can be achieved at α=.22 (NRTL) and λ=254 (GEM-RS) after a thorough investigation with this third parameter.

Following the same procedures of the work at 25 °C, it is also possible to acquire a single set of parameters for the temperature range between 10 and 100 °C. In addition to phase equilibrium calculations, excess enthalpy data can be reasonably predicted with these parameters, all within fair error.

CHAPTER 7

CONCLUSION

From our observations the following conclusions can be drawn:

- Data selections should be done very cautiously.
- Hexane-Butanol pair was the main problem for fitting data since x-γ shows steep function.
- Two-parameter models can not fit this steep function; however, three-parameter models can represent that.
- Regression has to be done using all kinds of possible data.
- The Third parameter has to be regressed independently.
- Selecting the appropriate third parameter of three parameter model for an immiscible pair (Hexane-water) is very important since only a fixed α or λ of NRTL and GEM-RS are able to predict ternary data well.

From our results it is observed that, NRTL/GEM-RS (three-parameter models) are the universal models for Hexane-Butanol-Water system because these models can

- fit the data for Hexane-Butanol pair which show sharp x-γ change,
- predict all kinds of binary phase equilibrium data,
- represent ternary data from very dilute region to finite concentration simultaneously, and
- calculate *Dsw* correctly.

Hence, it is possible to obtain universal liquid mixture models for VLE and LLE, meaning that separate sets of parameters are not needed to calculate different types of phase equilibrium data. The work based on a typical non-ideal ternary system that is Hexane-Butanol-Water was satisfactory. However, more work is needed to be done to show that this process provides acceptable universal parameters for other non-ideal ternary systems like Benzene-Methanol-Water, Hexane-Propanol-Water and so on. This process can be further validated if used on quaternary systems.

REFERENCES

[1] Javvadi, A. Partitioning of Higher Alcohols in Alkane-Water at Dilute Concentrations, MS Thesis, 2000. North Carolina A&T State University.

[2] Prausnitz, J.M.; Lichtenthaler, R. N.; Azevedo, E.G. Molecular thermodynamics for fluid phase equilibria. *Prentice Hall International Series in the Physical and Chemical Engineering Sciences. Third Edition,2005*

[3] Vera, J.H.; Sayegh, S.G.; Ratcliff, G.A. A Quasi Lattice-Local Composition Model for the Excess Gibbs free energy of Liquid *Mixtures. Fluid Phase Equilibria 1977,1,113*

[4] Renon, H.; Prausnitz, J.M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE Journal. 1968, 14, 135*

[5] Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of liquid Mixtures: A New Expression for the Excess Gibbs energy of Partly or Completely Miscible systems. *AIChE Journal,* 1975, *116*

[6] Maurer. G.; Praunirz. J.M. On the Derivation and extension of uniquac equation. *Fluid Phase Equilibria.1978,2, 91*

[7] Anderson, T. F.; Prausnitz, J. M. Appication of the Uniquac Equation to Calculation of Multicomponent Phase Equilibria. 2. Liquid-Liquid Equilibria *Ind. Eng. Chem., Process Des. Dev.,* 1978*, 17, 561*

[8] Nagata, I.; Katoh, K. Effective UNIQUAC Equation in Phase Equilibrium Calculation. *Fluid Phase Equilibria,* 1981*, 5, 225.*

[9] Larsen. B. L.; Ramussen. P; Fredenslund. A. A Modified UNIFAC Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing. *Ind. Eng. Chem. Res. 1987, 26, 2274*

[10] Weidlich. U.; Gmehling. J. A Modified UNIFAC Model. 1. Prediction of VLE, h^E, and γ^{∞}. *Ind. Eng. Chem. Res. 1987, 26, 1372*

[11] Nagata. I. Modification of the Extended Uniquac Model for Ternary and Quaternary Liquid-Liquid Equilibrium Calculations. *Fluid Phase Equilibria, 1989, 51, 53*

[12] Tamura. K.; Chen. Y.; Tada. K.; Yamada. T.; Yamada. T.; Nagata. I.; Representation of Multicomponent Liquid-Liquid Equilibria for aqueous and Organic Solutions Using a Modified UNIQUAC Model. *Journal of Solution Chemistry. 2000,29, 463*

[13] Tse, G.; Sandler, S. I. Determination of Infinite Dilution Activity Coefficients and 1-Octanol/Water Partition Coefficients of Volatile Organic Pollutants. *J. Chem. Eng. Data, 1994, 39, 354*

[14] P. Alessi, M.; Fermeglia, M.; Kikic, I. Significance of Dilute Regions. *Fluid Phase Equilibria, 1991,70,239*

[15] Chapoy, A.; Haghighi, H.; Tohidi, B. Development of a Henry's constant correlation and solubility measurements of n-pentane, I pentane, Cyclopentane,n hexane, and toluene in water. *J. Chem. Therm, 2008, 40, 1030*

[16] Macauliffe, C. Solubility in Water of C_1-C_9 Hyderocarbon.*Nature (London). 1963, 200,1092*

[17] Polak J.; B.C. Lu. Mutual Solubilities of Hydrocarbons and Water at 0 and 25 C. *Can. J. Chem. 1973,51,4018*

[18] Leinonen, P.J.; Mackay. D. The Multicomponent Solubility of Hydrocarbons in Water. *Can. J. Chem. 1973,51,230*

[19] Mackay, D.; Shiu, W.Y. A Critical Review of Henry's Law Constants for Chemicals and Environmental Interest. J. Phys. Chem. Ref. Data. *1981,10,1175*

[20] Tsonopoulos, C.; Wilson, G.M. High Temperature Mutual Solubilities of hydrocarbons and Water .*AIChE Journal. 1983, 29, 990*

[21] Deal, C. H.; Derr, E. L. Selectivity and Solvency in Aromatics Recovery. *Ind. Eng. Chem. Process Des. Dev. 1964,3, 394*

[22] Sugi, H.; Katayama, T. Liquid-Liquid Equilibrium Data for Three Ternary Systems of Aquous Alcohol Solutions and Applicability of The Analytical Solutions of Groups.*J. Chem. Eng. Jpn. 1977,10, 400*

[23] Roddy, J. W.; Coleman, C. F. Solubility of Water in Hydrocarbons as a Function of Water Activity. *Talanta*. 1968, 15,1281

[24] Hill, A.E. ; Malisoff, W. M. The Mutual Solubility of Liquids. III. The Mutual Solubility of Phenol and Water . IV. The Mutual Solubility of Normal Butyl Alcohol and Water. *J. Am. Chem. Soc 1926,48,918*

[25] Kinoshita, K. ; Ishikawa, H.; Shinoda, K. Solubility of Alcohols in Water Determined by the Surface Tension Measurements. *Chem. Soc. Jpn. 1958,31, 1081*

[26] Yaws, C.L.; Hopper, J.R.; Sheth, S.D.; Hen, M.; Pike, R.W. Solubility and Henry's Law Constant for Alcohols in Water. *Waste Management.1997, 17,541*

[27] Lebert, A.; Richon, D. Infinite Dilution Activity Coefficients of N-Alcohols as a function of Dextrin Concentration in Water-Dextrin Systems.*J. Agri. Food Chem.1984,32,1156*

[28] Mash, C.J.; Pemberton, R.C. Activity Coefficient at very low concentrations for organic solutes in Water determined by an Automatic Chromatographic Method. *NPL Report Chem. 111 Natl Phys. Lab., Middlesex., U.K., July 1980.*

[29] Rytting, J.H.; Huston, L.P.; Higuchi, L.P. Thermodynamic Group Contributions for Hydroxyl, Amino, and Methyl Groups. *J. Pharm. Sci 1978,67,615*

[30] Landau, L.; Belfer, A.J; Locke, D.C. Measurements of Limiting Activity Coefficients Using Non-Steady State Gas Chromatography. *Ind. Eng. Chem. Res.1991,30,1900*

[31] Djerki, R.A.; Laub, R.J. Solute Retention in Column Liquid Chromatography. X. Determination of Solute Infinite-Dilution Activity Coefficients in Methanol, Water, and Their Mixtures by Combined Gas-Liquid and Liquid-Liquid Chromatography. *J. Liquid Chromatgr.1988,11, 585*

[32] Li. J.J.; Carr, P.W. Measurement of Water-Hexadecane Partition Coefficients by Headspace Gas Chromatography and Calculaton of Limiting Activity Coefficients in Water. *Anal. Chem. 1993,65,1443*

[33] Abraham, M.H.; Whitting, G.S; Fuchs, R.; Chambers, E.J. Thermodynamics of Solute Transfer from Water to Hexadecane. *J. Chem. Soc., Perkin Trans.1990,2, 291*

[34] Paul, G.W.; Sandler,S.I. Headspace gas chromatography for measurement of infinite dilution activity coefficients of C4 alcohols in water. *Fluid Phase Equilibria. 1999,157,111*

[35] Vrbka, P.; Fenclova, D.; Lastovka, V.; Dohnal, V. Measuremnt of inifinite dilution activity coefficients of 1-alkanols (C1-C5) in water as a function of temperature (273-373 K). *Fluid Phase Equilibria 2005,237, 123*

[36] Hill, A.E.; Malisoff, W. M. The Mutual Solubility of Liquids. III. The Mutual Solubility of Phenol and Water. IV. The Mutual Solubility of Normal Butyl Alcohol and Water. *J. Am. Chem. Soc 1926,48,918*

[37] Petrisis V.E.; Geankoplis C.J. Phase Equilibria in 1-Butanol-Water-Lactic Acid System. *J. Chem. Eng. Data 1959,4,197*

[38] Pierotti G. J.; Deal C.H.,Derr E.L. Activity Coefficients and Molecular Structures. *Ind. Eng. Chem. 1959,51,95*

[39] Gmehling J.; Menke J.; Schiller, M. Activity Coefficients at infinite dilution. *Chemistry Data Series, Vol. IX, Part 4, 1994*

[40] Castells C.B.;Carr. P.W.; Eikens D.I.; Bush D. Comparative Study of Semitheoritical Models for Predicting Infinite Dilution Activity Coefficients of Alkanes in Organic Solvents. *Ind. Eng. Chem. Res. 1999,38,4104*

[41] Thomas, E. R.; Newman, B.A.; Long, T.C.; Wood, D.A.; Eckert, C.A. Limiting Activity Coefficients of Polar and non polar solutes in both volatile and non volatile solvents by Gas Chromatography. *J. Chem. Eng. Data 1982, 27,399*

[42] Thomas, E. R.; Newman, B.A.; Nicolaides, G. L.; Eckert C.A.; Limiting Activity Coefficients from Differential Ebulliometry. *J. Chem. Eng. Data 1982, 27,233*

[43] Ghemehling, G.; Onken U. Vapor Liquid Equilibrium Data Collection. *DECHEMA, Chemistry Data Series,Vol 1. Part 1, 1977*

[44] Sorensen J. M.; Arlt W. Liquid-Liquid Equilibrium Data Collection. *DECHEMA, Chemistry Data Series, 1979, Vol V,Part 1*

[45] Thomas, E. R.;Newman, B.A.; Nicolaides, G. L.; Eckert C.A. Limiting Activity Coefficients from Differential Ebulliometry. *J. Chem. Eng. Data 1982, 27,233*

[46] Reid, R.C.; Prausnitz, J.M.; Polling, B.E. The properties of Gases And Liquids. *McGraw Hill, New-York, 4th ed.,1987*

[47] Rodriguez, V.; Pardo, J.; Lopez, M.C.; Royo, F.M.; Urieta, J.S. Vapor Pressures of Binary Mixtures of Hexane+1 Butanol,+2 butanol,+2 Methyl 1 Propanol, or+ 2 Methyl 2 Propanol at 298.15 K. *J. Chem. Eng. Data 1993,38,350*

[48] Gracia, M.; Sanchez, F.;Perez, P;Valero, J.; Losa, C.G. Vapor Pressure of (butan-1 ol+hexane) at temperatures between 283.1 and 323.12 K. *J. Chem. Therm 1992, 24, 463*

[49] Garriza, R.; Mertinez, S.; Perez, P.; Gracia,M. Vapor Pressure at Several Temperatures between 278.15 and 323.15 K and Excess Functions at T=298.15 for 1 Bromobutane with 1 Butanol or 2 Methyl-2-propanol. *J. Chem.Eng.Data 2002, 47, 322*

[50] Ambrose D.; Ghiasse, N.B. Vapor pressure and critical temperatures of some alkanoic acids; C1 to C10. *J. Chem. Therm. 1987, 19, 505-519*

[51] Hansch, C.; Leo, A. Substituent Constants for Correlation analysis in Chemistry and Biology. *Wiley – Interscience, NY, 1979*

[52] Barker, J.A. Determination of Activity Coefficients from Total Pressure Measurements. *Aust. J. chem.1953,6,207*

[53] ASME Steam Tables. *American Society of Mechanical Engineers, NY, 1993.*

[54] Selected Values of Chemicals Compounds. *TRC Tables. Thermodynamic Research Center Data Project, College Station, TX,1995*

[55] Dymond, J.H.; Marsh, K.N.; Wilhoit, R.C. Virial Coefficients of Pure Gases and Mixtures. *Group IV: Volume 21,Springer,2003*

[56] Daubert, T.E.; Danner, R. P. Physical and Thermodynamic Properties of Pure Chemicals. *Data Compilation. Part 2 &3, Taylor & Francis, 1992*

[57] Gmehling J.; Menke J. Activity Coefficients at Infinite Dilution.*Chemistry Data Series, Vol. IX, Part 4*

[58] Gmehling, J; Menke J. Activity Coefficients at infinite dilution, C_1-C_{16}. *DECHEMA, Chemistry Data Series, 2007, Vol IX, Part 5*

[59] Tsonopoulos, C. An Empirical Correlation of Second Virial Coefficients. *AIChE Journal, 20, 263*

[60] Tarakad, R.R.; Danner, R.P. An Improved Corresponding States Method for Polar Fluids: Correlation of Second Virial Coefficients. *AIChE J.1977,23,685*

[61] Lin, S.T.; Sandler, S. I. Prediction of Octanol-Water Partition Coefficients Using a Group Contributoion Solvation Model. *Ind. Eng. Chem. Res, 1999, 38,4081*

[62] Lin, S.T.; Sandler, S. I. A Priori Equilibrium Prediction from a Segment Contribution Solvation Model. *Ind. Eng. Chem. Res, 2002, 41,899*

[63] Tochigi, K.; Tiegs, D.; Gmheling, K.; Kojima, K. Determination of New ASOG Parameters. *J.Chem.Eng.Japan,1990,23,453*

[64] Li, J.; Carr, P.W. Gas chromatographic study of salvation enthalpy by solvatochromically based linear salvation energy relationships. *J. Chrom, 1994,659,367*

[65] Dobrjakov, Y.G.; Balashova, I.M.; Maurer, G. The limiting activity coefficient of phenol in Water and Some organic solvents from Differential Ebuliometry. *Fluid Phase Equilibria. 2001,181,59*

[66] Gmehling, J.; Mollmann, C. Synthesis of Distillation Process using Thermodynamic Models and the Dortmund Data Bank. *Ind.Eng.Chem.Res. 1988,37,3112*

[67] McCann, D.W.; Danner, R.P. Prediction of Second Virial Coefficients of Organic compounds by a Group Contribution Method. *Ind.Eng.Chem.Process Des.Dev. 1984,23,529*

[68] Vetere, A. On the Calculation of the Second Virial Coefficients of Pure Compound And Mixture. *Chem.Eng.Sci.1991,46,1787*

[69] Hendi, H.; Vogel, E. Second Cross Virial coefficient of the Binary Vapor Mixture n-Hexane/Methanol from Quasi-isochoric ppT Measurements. *Fluid Phase Equilibria. 1996,125,55*

[70] Vetere, A. An Improved Method to Predict Second Cross Virial Coefficients. *Fluid Phase Equilibria. 2005,230,15*

[71] Ghemehling G.; Onken U. ; Arlt W. Vapor Liquid Equilibrium Data Collection. *DECHEMA, Chemistry Data Series,Vol 1. Part 1a, 1981*

[72] Ghemehling G.; Onken U.; Rarey-Nies, J.R. Vapor Liquid Equilibrium Data Collection. *DECHEMA, Chemistry Data Series, Vol 1. Part 1b, 1987*

[73] Sorensen J. M.; Arlt W. Liquid-Liquid Equilibrium Data Collection. *DECHEMA, Chemistry Data Series, 1980, Vol V,Part 2-3*

[74] Christensen, C.; Gmehling, J.; Rasmussen, P.; Weidlich, U. Heats of Mixing Data Collection, Binary System. *Chemistry Data series. 1984, Vol 3,part 1.*

[75] Kojima, K.; Zhang, S; Hiaki, T. Measuring Methods of Infinite Dilution Activity Coefficients and a Database for Systems Including Water. *Fluid Phase Equilibria, 1997,131,145*

[76] Ghemehling G.; Onken U. Vapor Liquid Equilibrium Data Collection. *DECHEMA, Chemistry Data Series,Vol 1. Part 1c, 2003*

[77] Harvey, A. H.; Lemon, E.W. Correlation for the Second Virial Coefficient of Water. *J. Phys. Chem. Ref. Data. 33, 369,2004*

[78] Fischer, K.; Gmehling, J. P-x and γ^{∞} Data for the Different Binary Butanol-Water systems at 50^{0} C. *J. Chem. Eng. Data. 1994, 39, 309*

[79] Butler, J.A.V.; Thomson, D.W.; Maclennan, W.H. The Free Energy of the Normal Alcohols in Aqueous Solution. Part I. The Partial Vapor Pressures of Aqueous Solutions of Methyl, n-Propyl, and n-Butyl Alcohols. Part II. The Solubilities of Some Normal Aliphatic Alcohols in Water. Part III. The Theory of Binary Solutions, and its Application to Aqueous-Alcoholic Solutions. *J. Chem. Soc(London) 1933, 674*

[80] Loblein, G.M.; Prausnitz, J.M. Infinite Dilution Activity Coefficients from Differential Ebulliometry. *Ind.Eng.Chem.Fundum.1982,21,109*

[81] Tochigi, K.; Kojima, K. The Determination of Group Wilson Parameters to Activity Coefficients by Ebulliometer. *J.Chem.eng.Jpn. 1976,9,267*

[82] Christensen, C.; Gmehling, J; Rasmussen, P.; Weidlich, U. Heats of Mixing Data Collection, Binary System. *Chemistry Data series. Vol 3,part 1.1984*

[83] Goodwin, S.R.; Newsham, D.M. A flow calorimeter for the determination of enthalpies of mixing of liquids: enthalpies of mixing of water+n-propanol and water+n butanol at 30^0 C. *J. Chem. Thermodyn.1971,3,325*

[84] Berro, C.; Rogalski, M.; Peneloux, A. Excess Gibbs Energies and excess volumes of 1 -Butanol-n-Hexane and 2-methyl-1-propanol-n-Hexane binary systems. *J.Chem.Eng.Dat.1982,27,352*

[85] Regina, M.W.; Maciel, A.Z.F. Vapor-Liquid phase equilibrium measurements for the n-hexane-1-butanol system at 323.15, 338.15 and 348.15 K. *Fluid Phase Equilibria.1989,50,201*

[86] Castells C.B.; Carr. P.W; Eikens D.I.; Bush D. Comparative Study of Semitheoritical Models for Predicting Infinite Dilution Activity Coefficients of Alkanes in Organic Solvents. *Ind. Eng. Chem. Res. 1999,38,4104*

[87] Thomas, E.R.; Newman, B.A.; Long, T.C.; Wood, D.A.;Eckert, C.A. Limiting Activity Coefficients of Polar and non polar solutes in both volatile and non volatile solvents by Gas Chromatography. *J. Chem. Eng. Data. 1982, 27,39*

[88] Arlt, W.;Sphul, O.; Klamt, A. Challenges of Thermodynamics. *Chemical Engineering and Proceeding.2004,43,221*

[89] Nguyen, T.H.; Ratcliff, G, A. Heats of Mixing of n-Alcohol-n-Alkane Systems at15 and 55 C. *J.Chem.Eng.Data.1975,20,252*

[90] Introduction of Chemical Engineering Thermodynamics. Smith, J.M; Van Ness, H.C; Abbot, M.M. *5th edition. McGraw-Hill International Editions, 1996.*

[91] Abbot, M., M.; Low pressure phase equilibria: Measurement of VLE, *Fluid Phase Equilib, 1986,29, 193*

[92] Rarey, J., R.; Gmehling, J. Computer-operated static apparatus for the measurement of vapor-liquid equilibrium data, *Fluid Phase Equilib. 1993,83, 279*

[93] Malanowski S.; Experimental methods for vapour-liquid equilibria. II. Dew- and bubble-point method, *Fluid Phase Equilib*. 1982,9,311

APPENDIX A

DERIVATION OF EQUATION IN CHAPTER 3

Here, the thermodynamic relations to derive Equation 3.3 (in Chapter 3) are shown. This technique is based on no assumptions concerning liquid-phase nonideality other than the obvious one of the finiteness of the activity coefficient and of its composition derivative at infinite dilution. The fugacity coefficient terms, not too critical at the atmospheric or lower pressure used here, are obtained from virial coefficients.

At equilibrium,

$$\gamma_{1L} x_1 f_{1L}^0 = \gamma_{1V} y_1 f_{1V}^0 \quad => \frac{\gamma_{1L}}{\gamma_{1V}} = \frac{y_1 f_{1V}^0}{x_1 f_{1L}^0} \tag{A1}$$

as x_1 approaches zero, the right hand side approaches form 0/0. Applying L' Hospital's rule yields

$$\left(\frac{\gamma_{1L}}{\gamma_{1V}}\right)_{x_1=0} = \left[\left(\frac{\partial y_1}{\partial x_1}\right)\left(\frac{f_{1V}^0}{f_{1L}^0}\right)\right]_{x_1=0} = \left[K_1\left(\frac{f_{1V}^0}{f_{1L}^0}\right)\right]_{x_1=0} \tag{A2}$$

Here K is the equilibrium vaporization ratio. An equation for component *2* analogous to equation (A2) becomes

$$y_1 = 1 - y_2 = \frac{\gamma_{2V} f_{2V}^o - \gamma_{2L} x_2 f_{2L}^0}{\gamma_{2V} f_{2V}^0} \tag{A3}$$

Differentiating with respect to x_1 and noting that $x_1=0$, $\gamma_{2V}=\gamma_{2L}=1.0$, $f_{2L}^0=f_{2V}^0=f_2^0$

$$\left(\frac{\partial y_1}{\partial x_1}\right)_{x_1=0} = \frac{\partial}{\partial x_1}\left\{\frac{1}{f_2^0}\left[f_{2V}^0-\left(1-x_1\right)f_{2L}^0\right]\right\}_{x_1=0} = \left[\frac{f_2^0+\frac{\partial\left(f_{2V}^0-f_{2L}^0\right)}{\partial x_1}}{f_2^0}\right]_{x_1=0} \qquad \text{(A4)}$$

This equation is applicable to both constant pressure and constant temperature data
At constant pressure,

$$\left[\frac{\partial\left(f_{2V}^0-f_{2L}^0\right)}{\partial x_1}\right]_P = \left[\frac{\partial\left(f_{2V}^0-f_{2L}^0\right)}{\partial T}\right]_P\left(\frac{\partial T}{\partial x_1}\right)_P \qquad \text{(A5)}$$

here $\left(\frac{\partial T}{\partial x_1}\right)$ is the slope of an isobaric temperature-liquid composition curve.

now,

$$f_{2L}^0 = \varphi_{P_2^{sat},T}P_2^{sat}\exp\left[\frac{V_{2L}}{RT}\left(\pi-P_2^{sat}\right)\right] \qquad \text{(A6)}$$

$$f_{2V}^0 = \varphi_{P,T} = \varphi_{P_2^{sat},T}P_2^{sat}\exp\left[\frac{V_{2V}}{RT}\left(P-P_2^{sat}\right)\right] \qquad \text{(A7)}$$

$$\left(\frac{\partial f_{2L}^0}{\partial T}\right)_\pi = \varphi_{P_2^{sat},T}\exp\frac{V_{2L}\left(P-P_2^{sat}\right)}{RT}\left(\frac{\partial P_2^{sat}}{\partial T}\right)_\pi + P_2^{sat}\exp\frac{V_{2L}\left(P-P_2^{sat}\right)}{RT}\left(\frac{\partial\varphi_{P_2^{sat},T}}{\partial T}\right)_\pi +$$
$$P_2^{sat}\varphi_{P_2^{sat},T}\exp\frac{V_{2L}\left(P-P_2^{sat}\right)}{RT}\left[-\frac{V_{2L}\left(P-P_2^{sat}\right)}{RT^2}+\frac{\left(P-P_2^{sat}\right)}{RT}\left(\frac{\partial V_{2L}}{\partial T}\right)_P-\frac{V_{2L}}{RT}\left(\frac{\partial P_2^{sat}}{\partial T}\right)_\pi\right] \qquad \text{(A8)}$$

$$\left(\frac{\partial f_{2V}^0}{\partial T}\right)_\pi = \varphi_{P_2^{sat},T}\exp\frac{V_{2V}\left(P-P_2^{sat}\right)}{RT}\left(\frac{\partial P_2^{sat}}{\partial T}\right)_\pi + P_2^{sat}\exp\frac{V_{2V}\left(P-P_2^{sat}\right)}{RT}\left(\frac{\partial\varphi_{P_2^{sat},T}}{\partial T}\right)_\pi +$$
$$P_2^{sat}\varphi_{P_2^{sat},T}\exp\frac{V_{2V}\left(P-P_2^{sat}\right)}{RT}\left[-\frac{V_{2V}\left(P-P_2^{sat}\right)}{RT^2}+\frac{\left(P-P_2^{sat}\right)}{RT}\left(\frac{\partial V_{2V}}{\partial T}\right)_P-\frac{V_{2V}}{RT}\left(\frac{\partial P_2^{sat}}{\partial T}\right)_P\right] \qquad \text{(A9)}$$

now, at $x_1=0$, we assume that, $P_2^{sat} \approx P \approx f_2^0$ and $\Phi\, P_2^{sat}{}_{,T} \approx 1$

so, from equation (A6) and (A7)

$$\left[\frac{\partial\left(f_{2V}^{0}-f_{2L}^{0}\right)}{\partial T}\right]_{\pi}=-P_{2}^{sat}\left(\frac{\partial P_{2}^{sat}}{\partial T}\right)_{\pi}\left(\frac{V_{2V}}{RT}-\frac{V_{2L}}{RT}\right) \tag{A10}$$

$$=-\frac{P_{2}^{sat}}{P_{2}^{sat}}\left(\frac{\partial P_{2}^{sat}}{\partial T}\right)_{P}\left(\frac{V_{2V}}{RT}-\frac{V_{2L}}{RT}\right) \tag{A11}$$

$$=-f_{2}^{0}\left(\frac{d\ln P_{2}^{sat}}{dT}\right)_{\pi}\left(\frac{PV_{2V}}{RT}-\frac{PV_{2L}}{RT}\right) \tag{A12}$$

from Eq. (A4) we get that,

$$\left[\frac{\partial\left(f_{2V}^{0}-f_{2L}^{0}\right)}{\partial x_{1}}\right]_{P,x_{1}=0}=f_{2}^{0}\left(\frac{\partial T}{\partial x_{1}}\right)_{\pi}\left(-\frac{d\ln P_{2}^{sat}}{dT}\right)\left(\frac{PV_{2V}}{RT}-\frac{PV_{2L}}{RT}\right) \tag{A13}$$

combining eqn (A2), (A4) and (A9)

$$\left\{\left(\frac{\gamma_{1L}}{\gamma_{1V}}\right)\right\}_{x_{1}=0}=\frac{f_{1V}^{0}}{f_{1L}^{0}}\left[1-\left(\frac{\partial T}{\partial x_{1}}\right)_{P}\left(\frac{d\ln P_{2}^{sat}}{dT}\right)\left(\frac{PV_{2V}}{RT}-\frac{PV_{2L}}{RT}\right)\right] \tag{A14}$$

Now, for low pressure equations

Assumptions:

$$\gamma_{1V}\approx 1$$
$$f_{1v}^{0}\approx P$$
$$f_{1L}^{0}\approx P_{1}^{sat}$$
$$\frac{PV_{2V}}{RT}\approx 1$$

$$\left(\gamma_{1}\right)_{x_{1}=0}=\frac{\gamma_{1V}f_{1V}^{0}}{f_{1L}^{0}}\left[1-\left(\frac{\partial T}{\partial x_{1}}\right)_{P}\left(\frac{d\ln P_{2}^{sat}}{dT}\right)\right] \tag{A15}$$

$$\Rightarrow\qquad \left(\gamma_{1}\right)_{x_{1}=0}=\frac{P}{P_{1}^{sat}}1\left[1-\left(\frac{\partial T}{\partial x_{1}}\right)_{P}\left(\frac{d\ln P_{2}^{sat}}{dT}\right)\right] \tag{A16}$$

this is same as equation 3.3 in chapter 3

from equation. (A1),

$$\frac{\gamma_{1L}}{\gamma_{1V}} = \frac{\frac{f_{1V}^0}{f_{1L}^0}}{\left(\frac{\partial x_1}{\partial y_1}\right)_{x_1=0}} \tag{A17}$$

$$\left(\frac{\partial y_1}{\partial x_1}\right)_{x_1=0} = \frac{f_2^0 + \frac{\partial\left(f_{2V}^0 - f_{2L}^0\right)}{\partial x_1}}{f_2^0} \tag{A18}$$

$$= \frac{f_2^0 + \frac{\partial\left(f_{2V}^0 - f_{2L}^0\right)}{\partial y_1}\left(\frac{\partial y_1}{\partial x_1}\right)_{x_1=0}}{f_2^0} \tag{A19}$$

$$= 1 + \frac{1}{f_2^0}\left(\frac{\partial y_1}{\partial x_1}\right)_{x_1=0} \frac{\partial\left(f_{2V}^0 - f_{2L}^0\right)}{\partial y_1} \tag{A20}$$

$$\Rightarrow \left(\frac{\partial y_1}{\partial x_1}\right)_{x_1=0} \left\{1 - \frac{1}{f_2^0}\frac{\partial\left(f_{2V}^0 - f_{2L}^0\right)}{\partial y_1}\right\} = 1 \tag{A21}$$

$$\Rightarrow \left(\frac{\partial y_1}{\partial x_1}\right)_{x_1=0} = \frac{1}{\frac{f_2^0 - \frac{\partial\left(f_{2V}^0 - f_{2L}^0\right)}{\partial y_1}}{f_2^0}} \tag{A22}$$

at constant pressure,

$$\left[\frac{\partial\left(f_{2V}^0 - f_{2L}^0\right)}{\partial y_1}\right]_P = \left[\frac{\partial\left(f_{2V}^0 - f_{2L}^0\right)}{\partial T}\right]_P \left(\frac{\partial T}{\partial y}\right)_P \tag{A23}$$

$$= -f_2^0\left(\frac{d\ln P_2^{sat}}{dT}\right)_P\left(\frac{PV_{2V}}{RT}-\frac{PV_{2L}}{RT}\right)\left(\frac{\partial T}{\partial y}\right)_P \tag{A24}$$

so, from equations. (A2), (A11) and (A12)

$$\left(\frac{\gamma_{1L}}{\gamma_{1V}}\right)_{x_1=0} = \frac{f_{1V}^0}{f_{1L}^0}\frac{1}{1+\left(\frac{\partial T}{\partial y_1}\right)_P\left(\frac{d\ln P_2^{sat}}{dT}\right)\left(\frac{PV_{2V}}{RT}-\frac{PV_{2L}}{RT}\right)} \tag{A25}$$

For low pressure equation considering previous assumptions,

$$\left(\gamma_{1L}\right)_{x_1=0} = \frac{P}{P_1^{sat}}\left[\frac{1}{1+\left(\frac{\partial T}{\partial y_1}\right)_P\left(\frac{d\ln P_2^{sat}}{dT}\right)}\right] \tag{A26}$$

At constant temperature from equation. A5 we can write,

$$\left[\frac{\partial\left(f_{2V}^0-f_{2L}^0\right)}{\partial x_1}\right]_T = \left[\frac{\partial\left(f_{2V}^0-f_{2L}^0\right)}{\partial P}\right]_T\left(\frac{\partial P}{\partial x}\right)_T \tag{A27}$$

Now,

$$\frac{\partial f_{2L}^0}{\partial P} = \frac{\partial \varphi_{P_2^{sat},T}}{\partial P}P_2^{sat}\exp\left[\frac{V_{2L}}{RT}\left(P-P_2^{sat}\right)\right]+\frac{\partial P_2^{sat}}{\partial P}\varphi_{P_2^{sat},T}\exp\left[\frac{V_{2L}}{RT}\left(P-P_2^{sat}\right)\right]$$
$$+\varphi_{P_2^{sat},T}P_2^{sat}\exp\left[\frac{V_{2L}}{RT}\left(P-P_2^{sat}\right)\right]\left\{\frac{V_{2L}}{RT}\left(1-\frac{\partial P_2^{sat}}{\partial P}\right)+\frac{\left(P-P_2^{sat}\right)}{RT}\frac{\partial V_{2L}}{\partial P}\right\} \tag{A28}$$

considering same assumptions

$$\frac{\partial f_{2L}^0}{\partial P} = P_2^{sat}\frac{V_{2L}}{RT} \tag{A29}$$

similarly, $$\frac{\partial f_{2V}^0}{\partial P} = P_2^{sat}\frac{V_{2V}}{RT} \tag{A30}$$

$$\left[\frac{\partial\left(f_{2V}^0-f_{2L}^0\right)}{\partial P}\right]_T = P_2^{sat}\left(\frac{V_{2V}}{RT}-\frac{V_{2L}}{RT}\right) = f_2^0\left(\frac{V_{2V}}{RT}-\frac{V_{2L}}{RT}\right) \tag{A31}$$

APPENDIX B

COMPARISON OF CALCULATED AND EXPERIMENTAL *Dsw* OF TERNARY SYSTEMS

In this section, all the ternary systems that were studied from DECHEMA [73] are listed from Tables B1 to B4. From these tables, it is simple to observe for which systems the calculated *Dsw* show good match with literature values and which systems show significant errors. The first component is the solvent and the second component is the solute. The first and second columns have the calculated and literature distribution coefficient, D_{sw} values using common UNIQUAC parameters.

Table B1. Ternary systems with minimum solute concentration in the range of 0≤x≤.01

System	Dsw(calc)	Dsw(lit)	x_i (phase 1)	x_i (phase2)	Reference [73], page/vol	Parameters available
1. Benzene-2-Methyl-1-propanol-water	3.06	4.11/ 3.84	.00967	.00228	142/2	Yes
2. Benzene-2-Methyl-2-propanol-water	3.07	1.27/ 1.33	.00682	.00399	143/2	Yes
3. Nitrobenzene-phenol-water		49.91/ 41.51/ 44.48	.0009	.00002	259/3	No
4. 1-butanol-3-Methyl 1,3 butanediol-water	3.0557	--	.003	.002	116/3	Yes
5. 1-butanol-succinic acid-	2.7275	2.67	.00011	.00003	11/3	Yes
water		--	.009	.002	17/3	Yes
6. 2-butanone-2-butanol-		--	.00667	.00102	23/3	No
water						
7. 2-butanone-1,2,3						
propanetricarboxylic acid-		--	.00281	.00296	31/3	No
water		--	.00046	.00018	335/3	No
8. 2-butanone-nicotine-water						
9. 1-aza cycloheptane-6		--	.00730	.00036	190/3	Yes
amino lactam hexanoic	2.609	2.2	.00213	.0011	533/2	Yes
acid-water						
10. Benzene-furfural-water	9.807	--	.00231	.00242	159/2	Yes
11. 1-butanol-2 hydroxy propanoic acid-water	1.874	--	.00568	.00276	532/2	Yes
12. Tri chloro ethane-6-amino	1.9928	--	.00317	.00093	59/2	Yes

lactam hexanoic acid-water						
13. 2-butanone-2-hydroxy propanoic acid-water	9.821	--	.00231	.00242	159/2	Yes
14. 4,4 dimethyl 1,3 dioxane-formic acid-water	1.7925	--	.00512	.0099	50/2	Yes
15. Tri chloro ethane-6-amino lactam hexanoic acid-water	2.496	.52/ .42/ .63	.0049	.00889	456/2	Yes
16. Furfural-formic acid-water	3.505	--	.00677	.00310	333/3	Yes
17. Diethyl ether-malonic acid-water	3.63	--	.00174 .00569	.00022 .00184	301/3 495/2	Yes Yes
18. 4 methyl-2-pentanone-1,2,3-propanetricarboxylic acid-water	1.874	2.88 --	.00568 .00374	.00276 .00705	532/2 213/2	Yes No
19. Iso-propyl-phenol-water	2.31	--	.00851	.000307	218/2	Yes
20. Toluene-2-propanone-water	3.07	3.33 2.28/	.00886	.00385	229/2	Yes
21. 2-butanone-2 hydroxy propanoic acid-water		2.56/ 2.395/				
22. Water-Ethanol-Oleic acid		2.23/				
23. 2 butanone-acetic acid-water	9.96	2.34 1.27/	.00682	.00399	142/3	Yes
24. diethyl ether-acetic acid-water	1.54	1.33	.003	.002	116/3	Yes

Table B2. Ternary systems with minimum solute concentration in the range of $.01<x\leq.02$

System	Dsw(calc)	Dsw(lit)	x_i (phase 1)	x_i (phase 2)	Reference [73],page/vol	Parameter available
1. Tetrachloro methane-nicotine-water	86.51	22.38	.01803	.00022	15/2	Yes
2. Water-methanol-acetic acid, ethyl ester	2.68	.089/ .635	.01331	.001014	90/2	Yes
3. Phenol-methanol-water	1.75	--	.01983	.00731	125/2	Yes
4. Acetic acid, butyl ester-methanol-water	2.77	.115/ .32	.01689	.01894	131/2	Yes
5. Butanoi c acid, ethyl ester-methanol-water	--	--	.01355	.01951	132/2	No
6. Water-methanol-toluene	--	.041	.01422	0.0	135/2	Yes
7. 1 butanol-acetic acid-water	2.17	3.28	.01054	.00281	226/2	Yes
8. Acetic acid, isobutyl ester-acetic acid-water	2.9	--	.01197	.00556	273/2	Yes
9. Water-acetic acid,amide,amide,n,n dimethyl-formic acid, methyl ester	--	--	.013	.01	316/2	No
10. Acetic acid, ethyl ester-ethanol-water	2.6	--	.00175	.01646	334/2	Yes
11. Ether, dibutyl-ethanol-water	3.55	--	.01139	.01119	389/2	Yes
12. Furfural-ethanol, 2 amino-water	--	6.64	.0186	.00328	437/2	No
13. Acetic acid, ethyl ester-2 propanone-water	2.97	--	.01983	.0036	466/2	Yes
14. 2 butanone-2 propanol-water	1.99	--	.01253	.00463	467/2	Yes
15. Acetic acid, propyl ester-2 propanone-water	3.21	--	.01451	.01198	473/2	Yes
16. Cyclohexanone-propanoic	2.486	--	.01938	.00918	536/2	Yes

acid, 2 hydroxy-water						
17. 1 hexanol-propanoic acid, 2 hydroxy-water	2.987	--	.01387	.00894	537/2	Yes
18. Water-formic acid, amide, n,n dimethyl-furfural	--	--	.0122	.01078	539/2	No
19. Benzene-1 propanol-water	2.56	.66/ .98/ 1.13/ 1.1/	.01677	.01076	569/2	Yes
20. Cyclohexane-1 propanol-water	3.00	1.108	.01256	.01813	572/2	Yes
21. Furfural-2 propanol-water	2.948	.11/	.0189	.01456	591/2	Yes
22. Benzene-2 propanol-water	2.55	.107/ .08	.01035	.0088	595/2	Yes
23. Phenol-2 propanol-water	2.67	--	.01427	.00193	607/2	Yes
24. 2 butanone-2 butanol-water	2.66	.54/	.015	.001	19/3	Yes
25. 2 butanone-nicotine-water	--	.59	.01806	.00409	33/3	No
26. Nicotine-2 butanone-water	--	--	.01212	.01151	35/3	No
27. Aniline-butanoic acid-water	2.85	--	.01689	.00224	64/3	Yes
28. 1 butanol-2,3 butanediol-water	--	--	.01942	.01493	112/3	Yes
29. 2 butanol-2 propanol, 2 methyl-water	2.27	--	.0166	.0044	125/3	Yes
30. Benzene-2 butanol-water	3.08	--	.01616	.00539	129/3	Yes

31. 1 propanol-butanoic acid, 3 methyl-water	3.45	--	.01637	.00037	138/3	Yes
32. Water-2,3 butanediol-acetic acid, 1 ethenylethyl ester	--	--	.0174	.002218	151/3	No
33. Water-amine, diethyl, 2,2 dihydroxy-aniline	3.71	4.11/3.84	.00924	.01086	181/3	Yes
34. 3 buten 1 ol 3 methyl-1,3 dioxane 4 4 dimethyl-water	4.66	--	.019	.001	250/3	Yes
35. Aniline-amine,triethyl,2,2,2 tridydroxy-water	5.22	--	.01364	.01525	313/3	Yes
36. Toluene-2 propanol, 1,3 bis(dimethylamino)-water	6.28	--	.00627	.01654	361/3	Yes
37. Water-n-methyl 2 pyrrolidone-1 pentanol	.21	.156/.118/.22/.16/4.73	.01177	.00994	351/2	Yes
38. dipropyl ether-1 propanol-Water	2.9	--	.01197	.00556	273/2	Yes
39. Water-acetic acid-2 methyl 2 butanol	--	--	.01942	.01493	112/3	No
40. benzene-ethanol-water	--	--	.0174	.002218	151/3	No

Table B3. Ternary systems with minimum solute concentration in the range of .02<x≤.03

System	Dsw(calc)	Dsw(lit)	x_i (phase 1)	x_i (phase 2)	Reference [73],page/vol	Parameter available
1. Tetrachloro methane-2 propanone-Water	3.04	2.28/ 2.39/ 2.45/ 2.68	.0209	.01066	7/2	Yes
2. Water-6 amino lactam hexanoic acid-tetra chlo methane	9.78	--	.02389	.00543	12/2	Yes
3. Acetic acid, ethyl ester-formic acid-water	2.09	--	.02836	.01073	48/2	Yes
4. Formic acid, propyl ester-formic acid-water	--	--	.0211	.01904	49/2	No
5. Water-formic acid, amide-furfural	1.83	--	.02672	.01737	65/2	Yes
6. Water-acetic acid-trichloro ethane	2.53	--	.02918	.01088	151/2	Yes
7. Water-dichloro acetic acid-chloro benzene	3.75	--	.02944	.0107	166/2	Yes
8. 1,2 dichloro ethane-6 amino lactam hexanoic acid-water	10.35	--	.0261	.01102	209/2	Yes
9. Acetic acid, ethyl ester-acetaldehyde-water	2.59	--	.02069	.00827	210/2	Yes
10. Furfural-acetic acid-water	2.07	--	.02306	.00778	230/2	Yes
11. Cyclohexanol-acetic acid-water	2.348	3.11	.02836	.00667	260/2	Yes
12. 4 methyl 2 pentanone-acetic acid-water	2.77	--	.02736	.00885	261/2	Yes

13. 3 methylbutyl ester-acetic acid-water	3.03	--	.02186	.01073	298/2	Yes
14. 1-butanol-ethanol-water	2.22	--	.02206	.00486	340/2	Yes
15. 4 heptanone-ethanol-water	--	--	.02851	.00839	374/2	No
16. Water-1,2 ethane dilo-1 butanol	2.41	--	.02787	.02531	420/2	Yes
17. Water-1,2 ethane diol-furfural	--	--	.024	.02907	421/2	Yes
18. Water-ethanol, 2 amino-aniline	2.51	--	.02749	.01256	441/2	Yes
19. Propanoic acid, nitril-cyclohexane, methyl-octane, 1,8 oxy-perfluro	--	--	.0282	.0151	458/2	Yes
20. 1 butanol-2 propanone-water	2.468	--	.02454	.00735	469/2	Yes
21. Water-acetic acid, amide, n,n dimethyl-formic acid, ethyl ester	4.64	--	.022	.011	509/2	Yes
22. Cyclo hexane-propanoic acid-water	2.72	--	.02544	.01963	519/2	Yes
23. 1 butanol-propanoic acid, 2 hydroxy-water	2.87	--	.02051	.01185	535/2	Yes
24. 1 propanol, 2 methyl-1 propanol-water	2.69	--	.0212	.0054	555/2	Yes
25. Cyclohexane-2 propanol-water	2.97	--	.02241	.0028	613/2	Yes
26. Water-acetic acid, amide,n,n dimethyl-acetic acid, ethyl ester	4.72	--	.024	.013	48/3	Yes
27. Acetic acid, ethyl ester-2 propanol, 2 methyl-water	2.57	--	.02842	.00997	55/3	Yes

28. Toluene, 2-amino-butanoic acid-water	2.95	--	.02096	.0014	68/3	Yes
29. Water-acetic acid,amide,n,n, dimethyl-acetic acid, isobutyl ester	5.64	--	.024	.002	102/3	Yes
30. Water-acetic acid,amide,n,n, dimethyl-ether, dibutyl	6.34	--	.025	.005	104/3	Yes
31. Benzene-1 butanol-water	3.01	3.19/ 2.26/ 3.75/ 3.93/ 2.06/ 4.21	.02526 .0174	.00469 .002218	118/3 151/3	Yes Yes
32. Water-2,3 butanediol-acetic acid, 1 ethenylethyl ester	--	--	.02403	.01869	153/3	No
33. Acetic acid, 1 ethenylethyl ester- 2,3 butanediol-water	--	--	.02003	.00335	154/3	No
34. 2,3 butanediol diacetate-2,3 butandiol-water	10.06	--	.02091	.02577	155/3	No
35. Water-hexanoic acid, 6 amino, lactam-benzene	--	--	.02028	.01524	272/3	No
36. trichloro methane-acetic acid-water	3.04	--	.02047	.01968	18/2	Yes
37. cyclohexane-2 propanol-water	6.67	--	.022441	.0028	613/2	Yes
38. dibutyl ether-acetic acid, amide, n,n,dimethyl-water	3.039	--	.025	.005	104/3	Yes
39. acetic acid, ethyl ester-2 propanol, 2 methyl-water	2.58	--	.02842	.00997	55/3	Yes

Table B4. Ternary systems with minimum solute concentration in the range of .03<x≤.04

System	Dsw(calc)	Dsw(lit)	x_i (phase 1)	x_i (phase 2)	Reference [73],page/vol	Parameter available
1. Tetrachloro methane-2 propanol-Water	3.02	.58/ .32	.01521	.03681	10/2	Yes
2. Dichloro methane-acetic acid-water	2.06	--	.03008	.00928	37/2	Yes
3. 1,3 dioxane 4,4 dimethyl-formic acid-water	2.02	--	.0317	.00093	59/2	Yes
4. Acetic acid, ethyl ester-methanol-water	2.2	--	.00746	.03179	94/2	Yes
5. 1 butanol-methanol-water	1.95	--	.03148	.02813	100/2	Yes
6. Water-methanol-propenoic acid,2 methyl, methyl ester	2.54	--	.03164	.02999	113/2	Yes
7. Water-methanol-benzene	1.81	.075/ .063	.03027	.01328	121/2	Yes
8. Tetrachloro ethene-propanoic acid-water	3.06	--	.03081	.02186	149/2	Yes
9. Trichloro ethene-furfural-water	--	--	.03522	.00081	158/2	Yes
10. Trichloro ethane-nicotine-water	--	--	.03939	.00055	163/2	Yes
11. Acetic acid, ethyl ester-acetic acid-water	2.37	2.97	.03091	.00899	220/2	Yes
12. Water-acetic acid-benzene	2.049	.053/ .078/ .0495/ .031/	.03023	.00597	241/2	Yes

		.09/ .042/ .027				
13. Hexanoic acid-acetic acid-water	2.75	--	.03753	.02382	280/2	Yes
14. Water-acetic acid-toluene	2.23	.074	.03833	.00914	289/2	Yes
15. Water-acetic acid-anilene, n,n dimethyl	2.48	--	.03771	.0257	301/2	Yes
16. Water-acetic acid-tetralin	--	--	.03194	.00701	310/2	Yes
17. Acetic acid, octyl ester-acetic acid-water	3.84	--	.0359	.02275	312/2	Yes
18. Diisopropyl ether-ethanol, 2 chloro-water	3.53	--	.03131	.00799	319/2	Yes
19. 1 pentanol-ethanol-water	--	--	.03157	.01601	348/2	No
20. Water-ethanol-toluene, 2-chloro	2.5	--	.03079	.01085	369/2	Yes
21. Water-1,2 ethane diol-2 butanone	2.04	--	.03551	.00435	418/2	Yes
22. Toluene-propenoic acid-water	1.01	.27/ .276/ .2	.039	.02651	454/2	Yes
23. Furfural-propanoic acid-water	2.48	--	.03834	.0056	512/2	Yes
24. Benzene-propanoic acid-water	2.39	.31/ .34/ .21/ .298/ .216/ .124	.03326	.01582	518/2	Yes

25. 1 octanol-propanoic acid, 2 hydroxy-water	3.14	--	.03319	.02704	538/2	Yes
26. Toluene-1 propanol-water	2.7		.037	.02618	580/2	Yes
27. Acetic acid, iso butyl ester-propenoic acid, 2 methyl amide	2.85	.89 --	.0303	.00979	16/3	Yes
28. 2 butanone-ethanol, 2 butoxy-water	--	--	.03698	.00812	28/3	Yes
29. Acetic acid, ethyl ester-2 propanol, 2 methyl-water	6.8	--	.03738	.001	58/3	Yes
30. Acetic acid, ethyl ester-furfural-water	--	--	.0379	.01635	76/3	Yes
31. Cyclo hexane-benzene-water	2.976	--	.02438	.03277	98/3	Yes
32. Benzene-pyridine-water	9.32	13.0/12.15/14.95/13.63/12.72	.03021	.00036	190/3	Yes
33. Water-2 pyrolidone, 1 methyl-tridecane	19.89	--	.03609	.00269	227/3	Yes
34. Tetralin-toluene, alpha hydroxyl-water	6.14	--	.03942	.01654	361/3	Yes

APPENDIX C

BARKER'S ACTIVITY COEFFICIENT METHOD

There is a numerical method to calculate activity coefficient. This method is called Barker's method [52]. The method is discussed here in detail. From Thermodynamics as we know total pressure P for a binary system is written

$$P = x_1\gamma_1 p_1^{/} + x_2\gamma_2 p_2^{/} \tag{C1}$$

The symbols $p_1^{/}$ and $p_2^{/}$ are the "corrected" vapor pressure of component *1* and *2* respectively.

These are defined by

$$p_1^{/} = x_1 P_1^{sat} \exp\left[\frac{(V_1^L - B_{11})(P - p_1^{sat})}{RT} - \frac{P\delta_{12} y_2^2}{RT}\right] \tag{C2}$$

$$p_2^{/} = x_2 P_2^{sat} \exp\left[\frac{(V_2^L - B_{22})(P - p_2^{sat})}{RT} - \frac{P\delta_{12} y_1^2}{RT}\right] \tag{C3}$$

Here, P_1^{sat} and P_2^{sat} are the vapor pressure of the pure components, x and y are liquid and vapor molar fractions respectively, γ_1 and γ_2 are activity coefficients, V_1^L and V_2^L are liquid molar volumes, B_{11}, B_{22} and B_{12} are second virial coefficients in the equations of state of the pure and mixed vapors, and

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \tag{C4}$$

At constant temperature, activity coefficients are functions only of composition. Equation (C1) is rigorous provided we assume that the vapor phase of the mixture, as well as the vapors in equilibrium with the pure components, are adequately described by the volume-explicit virial equation terminated after the second virial coefficient; that the pure component liquid volumes are incompressible over the pressure range in question; and that the liquid partial molar volume of each component is invariant with composition. The standard states for the activity coefficients in equation (C1) are the pure components at the same temperature and pressure as those of mixture. From these assumptions it follows that

$$\ln\gamma_1 = \ln\left(\frac{Py_1}{x_1P_1^{sat}}\right) - \frac{(B_{11}-V_1^L)\left(P-P_1^{sat}\right)}{RT} + \frac{P_1y_2^2\delta_{12}}{RT} \tag{C5}$$

$$\ln\gamma_2 = \ln\left(\frac{Py_2}{x_2P_2^{sat}}\right) - \frac{(B_{22}-V_2^L)\left(P-P_2^{sat}\right)}{RT} + \frac{P_2y_1^2\delta_{12}}{RT} \tag{C6}$$

C1. Description of Barker's Method

Barker's method is used to reduce experimental data that give the variation of total pressure with liquid composition at constant temperature. One further relation is needed in addition to Eqs. (C1) to (C3), and that is an equation relating the activity coefficients to mole fractions. This relation may contain any desired number of undetermined numerical coefficients that are then found from the total pressure data as shown below. For example, suppose we assume that

$$\ln\gamma_1 = (1-z)^2\left\{AB + (1+z)(A'B - AB')\right\}/4B^2 \tag{C7}$$

$$\ln\gamma_1 = (1+z)^2\left\{AB - (1-z)(A'B - AB')\right\}/4B^2 \tag{C8}$$

here $A' = \sum_{m=0}^{n} mA_m z^{m-1}$; $B' = \sum_{n=0}^{m} nA_n z^{n-1}$ and z=1-2x

Equations (C1) to (C6) contain unknowns A_0, A_1, A_2, and B_1 (since B_0 is taken as one). (It is assumed that values for the quantities V, B, P^s, and δ_{12} are available. It is true that y is also unknown but once A_0, A_1, A_2, B_1 are known, y can be determined).

In principle, Equations (C1) to (C6) could yield A_0, A_1, A_2, B_1 using only two points on the experimental P-x curve. In practice, however, more than two points are required; we prefer to utilize all reliable experimental points and then optimize the values of A_0, A_1, A_2, B_1 to give the best agreement between the observed total pressure curve and that calculated with parameters A_0, A_1, A_2, B_1.

The calculations are iterative because y_1 and y_2 can only be calculated after A_0, A_1, A_2, B_1 have been determined; the method of successive approximation must be used. In the first approximation, y_1 and y_2 are set equal to zero in Equations (C2) and (C3). Then A_0, A_1, A_2, B_1 are found, and immediately thereafter y_1 and y_2 are computed (from the first approximation of the parameters A_0, A_1, A_2, B_1) using Equations (C1) to (C6). The entire calculation is then repeated except that the new values of y_1 and y_2 are now used in Equations (C5) and (C6). We proceed in this way until the assumed and calculated values of y_1 and y_2 are in agreement; usually three or four successive approximation is sufficient. But in some cases it requires more number of iteration based upon tolerance setting. For our calculation it required >100 iterations and we set tolerance 10E-4. The form of Equations (C1) to (C6) is arbitrary; we may use any desired set of equations with any desired number of constants, provided that the equations satisfy the Gibbs-Duhem equation.

Proof of Equations (C1), (C2) and (C3)

$$f_i^v = f_i^L \tag{C9}$$

$$=> P y_1 \varphi_1 = x_1 \gamma_1 f_1^0 \tag{C10}$$

$$=> P y_1 = x_1 \gamma_1 \frac{f_1^0}{\varphi_1} \tag{C11}$$

similarly

$$P y_2 = x_2 \gamma_2 \frac{f_2^0}{\varphi_2} \tag{C12}$$

$$\therefore P\left(y_1 + y_2\right) = x_1 \gamma_1 \left(\frac{f_1^0}{\varphi_1}\right) + x_2 \gamma_2 \left(\frac{f_2^0}{\varphi_2}\right) \tag{C13}$$

$$\therefore P = x_1 \gamma_1 P_1^{S'} + x_2 \gamma_2 P_2^{S'} \tag{C14}$$

where corrected pressure,

$$P_1^{S'} = \frac{f_1^0}{\varphi_1} \tag{C15}$$

$$= \frac{f_1^{sat} \exp\left[\frac{V_1^L\left(P-P_1^{sat}\right)}{RT}\right]}{\varphi_1} \tag{C16}$$

$$= \frac{P_1^s \varphi_1^s \exp\left[\frac{V_1^L\left(P-P_1^{sat}\right)}{RT}\right]}{\varphi_1} \tag{C17}$$

$$= \frac{\varphi_1^s}{\varphi_1} P_1^s \exp\left[\frac{V_1^L\left(P-P_1^{sat}\right)}{RT}\right] \tag{C18}$$

$$\frac{P_1^{s'}}{P_1^s} = \frac{\varphi_1^s}{\varphi_1} \exp\left[\frac{V_1^L\left(P-P_1^{sat}\right)}{RT}\right] \tag{C19}$$

$$\ln\left(\frac{P_1^{s'}}{P_1^s}\right) = \ln\left(\frac{\varphi_1^s}{\varphi_1}\right) + \frac{V_1^L\left(P-P_1^s\right)}{RT} \tag{C20}$$

$$\ln \varphi_1^s = \frac{B_{11}P_1^s}{RT} \tag{C22}$$

$$\ln \varphi_1 = \frac{P}{RT}\left[B_{11} + \delta_{12} y_2^2\right] \tag{C23}$$

$$\ln \frac{\varphi_1^s}{\varphi_1} = \frac{B_{11}P_1^s}{RT} - \frac{P}{RT}\left[B_{11} + \delta_{12} y_2^2\right] \tag{C24}$$

$$\ln \frac{P_1^{s'}}{P_1^s} = \frac{B_{11}P_1^s}{RT} - \frac{P}{RT}\left[B_{11} + \delta_{12} y_2^2\right] + \frac{V_1^L\left(P-P_1^s\right)}{RT} \tag{C25}$$

$$= \frac{V_1^L\left(P-P_1^s\right) - B_{11}\left(P-P_1^s\right) - \delta_{12} P y_2^2}{RT} \tag{C26}$$

$$= \frac{\left(V_1^L - B_{11}\right)\left(P-P_1^s\right) - \delta_{12} P y_2^2}{RT} \tag{C27}$$

$$\therefore P_1^{s/} = P_1^{s}\exp\left[\frac{\left(V_1^L - B_{11}\right)\left(P - P_1^{s}\right) - P\delta_{12}y_2^2}{RT}\right] \tag{C28}$$

similarly

$$\therefore P_2^{s/} = P_2^{s}\exp\left[\frac{\left(V_2^L - B_{22}\right)\left(P - P_2^{s}\right) - P\delta_{12}y_1^2}{RT}\right] \tag{C29}$$

Proof of equation (C5) and (C6)

$$f_i^v = f_i^L \tag{C30}$$

$$=> Py_1\varphi_1 = x_1\gamma_1 P_1^{sat}\varphi_i^{sat}\exp\left[\frac{V_1^L\left(P - P_1^{sat}\right)}{RT}\right] \tag{C31}$$

$$=> \frac{Py_1}{x_1P_1^{sat}} = \frac{\varphi_1^{sat}}{\varphi_1}\exp\left[\frac{V_1^L\left(P - P_2^{sat}\right)}{RT}\right] \tag{C32}$$

$$=> \ln\left(\frac{Py_1}{x_1P_1^{sat}}\right) = \ln\gamma_1 + \ln\left\{\frac{\varphi_1^{sat}}{\varphi_1}\exp\left[\frac{V_1^L\left(P - P_2^{sat}\right)}{RT}\right]\right\} \tag{C33}$$

$$\ln\varphi_1 = \frac{P}{RT}\left(B_{11} + y_2^2\delta_{12}\right) \tag{C34}$$

$$\ln\varphi_1^{sat} = \frac{B_{11}P}{RT} \tag{C35}$$

$$\therefore \ln\left(\frac{Py_1}{x_1P_1^{sat}}\right) = \ln\gamma_1 + \frac{V_1^L\left(P - P_1^{sat}\right)}{RT} + \frac{B_{11}P_1^{sat}}{RT} - \frac{P_1}{RT}\left(B_{11} + y_2^2\delta_{12}\right) \tag{C36}$$

$$\therefore \ln\left(\frac{Py_1}{x_1P_1^{sat}}\right) = \ln\gamma_1 + \frac{V_1^L\left(P - P_1^{sat}\right)}{RT} + \frac{B_{11}(P - P_1^{sat})}{RT} - \frac{P_1y_2^2\delta_{12}}{RT} \tag{C37}$$

$$\therefore \ln\gamma_1 = \ln\left(\frac{Py_1}{x_1P_1^{sat}}\right) - \frac{(B_{11} - V_1^L)\left(P - P_1^{sat}\right)}{RT} + \frac{P_1y_2^2\delta_{12}}{RT} \tag{C38}$$

$$\therefore \ln\gamma_2 = \ln\left(\frac{Py_2}{x_2P_2^{sat}}\right) - \frac{(B_{22} - V_2^L)\left(P - P_2^{sat}\right)}{RT} + \frac{P_2y_1^2\delta_{12}}{RT} \tag{C39}$$

Here, MATLAB code is given which will regress the coefficients A_0, A_1, A_2, and B_1 and will generate x-γ values.

```
% hebut22 is P-x data of Hexane-Butanol
load hebut22.m

for i=1:13
   xx(i,:)=1-hebut22(i,2);
   p(i,:)=hebut22(i,1)/760;
   an(i,1)=0;
end

X(1)=0;
X(2)=0;
X(3)=0;
X(4)=0;

%para=nlinfit(xx,p,@press,X);

para1=lsqcurvefit(@press,X,xx,p);

clc

for j=2:1000

      z=1-2*xx;

      A0=para1(1);

      A1=para1(2);

      A2=para1(3);

      B1=para1(4);

      R=82.0578;
      T=298.11;
      A=A0+z.*A1+A2*z.^2;
      AP=A1+z.*A2*2;
      B=1+z.*B1;
      BP=B1;
      c=1-z;
      d=1+z;
```

```
    for i=1:13

      lngm1(i,:)=(c(i,:)^2*(A(i,:)*B(i,:)+d(i,:)*(AP(i,:)*B(i,:)-A(i,:)*BP)))/4/(B(i,:)^2);
      lngm2(i,:)=(d(i,:)^2*(A(i,:)*B(i,:)-c(i,:)*(AP(i,:)*B(i,:)-A(i,:)*BP)))/4/(B(i,:)^2);
      gm1(i,:)=exp(lngm1(i,:));
      gm2(i,:)=exp(lngm2(i,:));

    end


     for i=1:13
      y=real(fsolve(@(y)
chh(y,gm1(i,:),gm2(i,:),hebut22(i,1),hebut22(i,2)),[hebut22(i,5);1-hebut22(i,5)]));
      a(i,:)=y(1);
      an(i,j)=y(1);
      b(i,:)=y(2);
      c(i,:)=y(1)+y(2);
      d(i,:)=an(i,j)-an(i,j-1);
      diff(i,j)=d(i,:);
    end

    d=abs(d);
    d=sort(d);

    if d(13,1)<.0001

        jj=j;
        break

    end


para1=lsqcurvefit(@(para1,xx) press1(para1,xx,a),para1,xx,p);

end


function PP=press(X,xx)

     p(1,:)=20.506/760;
     p(2,:)=51.221/760;
     p(3,:)=70.093/760;
     p(4,:)=99.668/760;
```

```
 p(5,:)=119.319/760;
 p(6,:)=129.820/760;
 p(7,:)=133.458/760;
 p(8,:)=140.831/760;
 p(9,:)=146.839/760;
 p(10,:)=149.622/760;
 p(11,:)=151.047/760;
 p(12,:)=151.887/760;
 p(13,:)=151.729/760;

 z=1-2*xx;

 A0=X(1);

 A1=X(2);

 A2=X(3);

 B1=X(4);

R=82.0578;
T=298.11;
B11=-1918;
B22=-6495;
B12=((B11^(.333)+B22^(.333))^3)/8;
d12=2*B12-B11-B22;
v1=131.66;
v2=92.02;
psat1=151.0324/760;
psat2=6.7881/760;
q1=(B11-v1)*(p-psat1)./R/T;
q2=(B22-v2)*(p-psat2)./R/T;
A=A0+z.*A1+A2*z.^2;
AP=A1+z.*A2*2;
B=1+z.*B1;
BP=B1;
c=1-z;
d=1+z;

for i=1:13

  lngm1(i,:)=(c(i,:)^2*(A(i,:)*B(i,:)+d(i,:)*(AP(i,:)*B(i,:)-A(i,:)*BP)))/4/(B(i,:)^2);
  lngm2(i,:)=(d(i,:)^2*(A(i,:)*B(i,:)-c(i,:)*(AP(i,:)*B(i,:)-A(i,:)*BP)))/4/(B(i,:)^2);
  gm1(i,:)=exp(lngm1(i,:));
```

```
  gm2(i,:)=exp(lngm2(i,:));
  p1(i,:)=(1-xx(i,:))*psat1*exp(-q1(i,:)+lngm1(i,:));
  p2(i,:)=xx(i,:)*psat2*exp(-q2(i,:)+lngm2(i,:));


end

PP=(p1+p2);
```

APPENDIX D
FORTRAN CODE

Here a sample calculation for Water-Butanol is shown which includes regression calculation using LLE,VLE,γ^{∞} and H^E data.

```
PROGRAM REGRESSION
INTEGER LDFJAC,M,N
PARAMETER (LDFJAC=183, M=183, N=4)
INTEGER IPARAM(6),NOUT,IR
REAL FJAC(LDFJAC,N),FSCALE(M),FVEC(M),RPARAM(7),
& X(N),XGUESS(N),XSCALE(N),F(M)
REAL GAMC(150,150),HE(1000),SOL(1000,1000)
EXTERNAL ROSBCK,UMACH,UNLSF,U4LSF
COMMON/INITIAL/COMP(1000,1000),EXPT(1000,1000),FEED(20,20)
DATA XGUESS/0.,0.,0.,0./
DATA XSCALE/4*1.0E0/,FSCALE/183*1E0/
C READING EXPERIMENTAL DATA TO EXPT(I,J)
OPEN(UNIT=6,FILE='25wabut.dat',STATUS='OLD')
OPEN(UNIT=7,FILE='35wabut.dat',STATUS='OLD')
OPEN(UNIT=8,FILE='50wabut.dat',STATUS='OLD')
OPEN(UNIT=9,FILE='60wabut.dat',STATUS='OLD')
OPEN(UNIT=10,FILE='70wabut.dat',STATUS='OLD')
OPEN(UNIT=11,FILE='90wabut.dat',STATUS='OLD')
OPEN(UNIT=12,FILE='30wabhe.dat',STATUS='OLD')
OPEN(UNIT=13,FILE='30_wabhe.dat',STATUS='OLD')
OPEN(UNIT=15,FILE='20wabutg.dat',STATUS='OLD')
OPEN(UNIT=16,FILE='25wabutg.dat',STATUS='OLD')
OPEN(UNIT=17,FILE='30wabutg.dat',STATUS='OLD')
OPEN(UNIT=18,FILE='35wabutg.dat',STATUS='OLD')
OPEN(UNIT=19,FILE='40wabutg.dat',STATUS='OLD')
OPEN(UNIT=20,FILE='45wabutg.dat',STATUS='OLD')
OPEN(UNIT=21,FILE='50wabutg.dat',STATUS='OLD')
OPEN(UNIT=22,FILE='55wabutg.dat',STATUS='OLD')
OPEN(UNIT=23,FILE='60wabutg.dat',STATUS='OLD')
OPEN(UNIT=24,FILE='70wabutg.dat',STATUS='OLD')
OPEN(UNIT=25,FILE='80wabutg.dat',STATUS='OLD')
OPEN(UNIT=26,FILE='90wabutg.dat',STATUS='OLD')
OPEN(UNIT=27,FILE='99wabutg.dat',STATUS='OLD')
OPEN(UNIT=101,FILE='wabutrf4.dat',STATUS='NEW')
OPEN(UNIT=102,FILE='wabutgrf4.dat',STATUS='NEW')
```

```
OPEN(UNIT=103,FILE='wabherf4.dat',STATUS='NEW')
OPEN(UNIT=104,FILE='solnrf4.dat',STATUS='NEW')
DO 103 I=1,6
READ(6,906) (COMP(I,J),J=1,5)
906 FORMAT (5F9.5)
103 CONTINUE
DO 104 I=7,13
READ(7,907) (COMP(I,J),J=1,3)
907 FORMAT (3F7.4)
104 CONTINUE
DO 105 I=14,42
READ(8,908) (COMP(I,J),J=1,3)
908 FORMAT (3F7.4)
105 CONTINUE
DO 106 I=43,47
READ(9,909) (COMP(I,J),J=1,3)
909 FORMAT (3F7.4)
106 CONTINUE
DO 107 I=48,53
READ(10,910) (COMP(I,J),J=1,3)
910 FORMAT (3F7.4)
107 CONTINUE
DO 108 I=54,59
READ(11,911) (COMP(I,J),J=1,3)
911 FORMAT (3F7.4)
108 CONTINUE
DO 109 I=60,68
READ(12,912) (COMP(I,J),J=1,2)
912 FORMAT (2F7.4)
109 CONTINUE
DO 110 I=69,80
READ(13,913) (COMP(I,J),J=1,2)
913 FORMAT (2F7.4)
110 CONTINUE
FEED(1,1)=.8
FEED(1,2)=.2
c T=15
EXPT(81,1)=.5048
EXPT(81,2)=.0213
c T=20
c EXPT(82,1)=.508
c EXPT(82,2)=.0202
c T=25
EXPT(82,1)=.5056
```

```
EXPT(82,2)=.0187
c T=30
EXPT(83,1)=.516
EXPT(83,2)=.0182
c T=35
EXPT(84,1)=.523
EXPT(84,2)=.0175
c T=40
EXPT(85,1)=.528
EXPT(85,2)=.0168
c T=50
EXPT(86,1)=.543
EXPT(86,2)=.0165
c T=60
EXPT(87,1)=.5599
EXPT(87,2)=.0162
c T=70
EXPT(88,1)=.58
c EXPT(89,2)=.0167
c T=80
EXPT(89,1)=.597
c EXPT(90,2)=.017
c T=92
EXPT(90,1)=.646
DO 112 I=91,91
READ(15,915) (COMP(I,J),J=1,3)
915 FORMAT (3F7.4)
112 CONTINUE
DO 113 I=92,93
READ(16,916) (COMP(I,J),J=1,3)
916 FORMAT (3F7.4)
113 CONTINUE
DO 114 I=94,94
READ(17,917) (COMP(I,J),J=1,3)
917 FORMAT (3F7.4)
114 CONTINUE
DO 115 I=95,95
READ(18,918) (COMP(I,J),J=1,3)
918 FORMAT (3F7.4)
115 CONTINUE
DO 116 I=96,96
READ(19,919) (COMP(I,J),J=1,3)
919 FORMAT (3F7.4)
116 CONTINUE
```

```
DO 117 I=97,97
READ(20,920) (COMP(I,J),J=1,3)
920 FORMAT (3F7.4)
117 CONTINUE
DO 118 I=98,98
READ(21,921) (COMP(I,J),J=1,3)
921 FORMAT (3F7.4)
118 CONTINUE
DO 119 I=99,99
READ(22,922) (COMP(I,J),J=1,3)
922 FORMAT (3F7.4)
119 CONTINUE
DO 120 I=100,100
READ(23,923) (COMP(I,J),J=1,3)
923 FORMAT (3F7.4)
120 CONTINUE
DO 121 I=101,102
READ(24,924) (COMP(I,J),J=1,3)
924 FORMAT (3F7.4)
121 CONTINUE
DO 122 I=103,103
READ(25,925) (COMP(I,J),J=1,3)
925 FORMAT (3F7.4)
122 CONTINUE
DO 123 I=104,104
READ(26,926) (COMP(I,J),J=1,3)
926 FORMAT (3F7.4)
123 CONTINUE
DO 124 I=105,105
READ(27,927) (COMP(I,J),J=1,3)
927 FORMAT (3F7.4)
124 CONTINUE
C READING FEED COMPOSITIONS
C STARTING REGRESSION
CALL U4LSF(IPARAM,RPARAM)
RPARAM(4) = 10.0E0*RPARAM(4)
CALL UNLSF(ROSBCK,M,N,XGUESS,XSCALE,FSCALE,IPARAM,RPARAM,
&X,FVEC,FJAC,LDFJAC)
CALL UMACH (2,NOUT)
WRITE(*,*) 'SOL',X
c WRITE(*,*) 'THE FUNCTION EVALUATED AT THE SOLUTION', FVEC
c WRITE(*,*) 'NO. OF ITERATIONS',IPARAM(3)
c WRITE(*,*) 'NO. OF FUNCTION EVALUATIONS',IPARAM(4)
CALL GAMA(N,X,GAMC)
```

```
CALL LLEQ(N,X,SOL)
CALL EXCS(N,X,HE)
err1=0.
err2=0.
DO 155 I=1,59
IF(I.LT.7)THEN
err1=err1+(abs(comp(I,4)-gamc(I,1)))*100./comp(I,4)
err2=err2+(abs(comp(I,5)-gamc(I,2)))*100./comp(I,5)
WRITE(101,928)comp(I,2),comp(I,4),gamc(I,1),comp(I,5),gamc(I,2),
1 (abs(comp(I,4)-gamc(I,1)))*100./comp(I,4),
2 (abs(comp(I,5)-gamc(I,2)))*100./comp(I,5)
ELSE
err1=err1+(abs(comp(I,2)-gamc(I,1)))*100./comp(I,2)
err2=err2+(abs(comp(I,3)-gamc(I,2)))*100./comp(I,3)
WRITE(101,928)comp(I,1),comp(I,2),gamc(I,1),comp(I,3),gamc(I,2),
1 (abs(comp(I,2)-gamc(I,1)))*100./comp(I,2),
2 (abs(comp(I,3)-gamc(I,2)))*100./comp(I,3)
ENDIF
928 FORMAT (7F9.5)
155 continue
write(101,929) err1/59,err2/59,X
929 FORMAT (9F12.5)
err1=0.
err2=0.
DO 156 I=91,105
err1=err1+(abs(comp(I,2)-gamc(I,1)))*100./comp(I,2)
err2=err2+(abs(comp(I,3)-gamc(I,2)))*100./comp(I,3)
WRITE(102,930)comp(I,1),comp(I,2),gamc(I,1),comp(I,3),gamc(I,2),
1 (abs(comp(I,2)-gamc(I,1)))*100./comp(I,2),
2 (abs(comp(I,3)-gamc(I,2)))*100./comp(I,3)
930 FORMAT (7F9.5)
156 continue
write(102,934) err1/11, err2/11,X
934 FORMAT (9F12.5)
err=0.
DO 157 I=60,80
err=err+abs((comp(I,2)-HE(I))*100./comp(I,2))
WRITE(103,935)comp(I,1),comp(I,2),HE(I),
1 abs((comp(I,2)-HE(I))*100./comp(I,2))
935 FORMAT (4F9.3)
157 continue
write(103,936) err/21,X
936 FORMAT (8F12.5)
er1=0.
```

```
er2=0.
DO 158 I=81,90
IF(I.GT.87) THEN
WRITE(104,977)expt(i,1),sol(I,1),
1 abs(expt(i,1)-sol(I,1))*100./expt(i,1)
er1=er1+abs(expt(i,1)-sol(I,1))*100./expt(i,1)
977 FORMAT(4F9.5)
ELSE
WRITE(104,937)expt(i,1),sol(I,1),expt(i,2),sol(I,2),
1 abs(expt(i,1)-sol(I,1))*100./expt(i,1),
2 abs(expt(i,2)-sol(I,2))*100./expt(i,2)
er1=er1+abs(expt(i,1)-sol(I,1))*100./expt(i,1)
er2=er2+abs(expt(i,2)-sol(I,2))*100./expt(i,2)
ENDIF
937 FORMAT(6F9.5)
158 CONTINUE
WRITE(104,938)er1/10.,er2/7.,X
938 FORMAT(9F12.5)
END
SUBROUTINE ROSBCK(M,N,X,F)
INTEGER M,N
COMMON/INITIAL/COMP(1000,1000),EXPT(1000,1000),FEED(20,20)
REAL X(N),F(M),REG(7),FIR(6),GAMC(150,150),HE(1000),
1 SOL(1000,1000)
CALL GAMA(N,X,GAMC)
CALL LLEQ(N,X,SOL)
CALL EXCS(N,X,HE)
IR=1
DO 9 I=1,6
F(IR)=(COMP(I,4) - GAMC(I,1)) / COMP(I,4)
F(IR)=F(IR)*1.
IR=IR+1
F(IR)=(COMP(I,5) - GAMC(I,2)) / COMP(I,5)
F(IR)=F(IR)*1.
IR=IR+1
9 CONTINUE
DO 10 I=7,59
F(IR) = (COMP(I,2) - GAMC(I,1)) / COMP(I,2)
IR=IR+1
F(IR) = (COMP(I,3) - GAMC(I,2)) / COMP(I,3)
IR=IR+1
10 CONTINUE
DO 11 I=60,80
F(IR)=(COMP(I,2) - HE(I)) / COMP(I,2)
```

```
F(IR)=F(IR)*1.
IR=IR+1
11 CONTINUE
DO 12 I = 81,90
DO 14 J=1,2
F(IR) = (EXPT(I,J) - SOL(I,J)) / EXPT(I,J)
IF(I.EQ.81.AND.J.EQ.2) F(IR)=F(IR)*4.5
IF(I.GT.87)GOTO 12
IR=IR+1
14 CONTINUE
12 CONTINUE
DO 13 I=91,105
F(IR) = (COMP(I,2) - GAMC(I,1)) / COMP(I,2)
F(IR)=F(IR)*1.
IF(I.EQ.92)F(IR)=F(IR)*1.
IR=IR+1
F(IR) = (COMP(I,3) - GAMC(I,2)) / COMP(I,3)
F(IR)=F(IR)*1.
IF(I.EQ.93)F(IR)=F(IR)*1.
IR=IR+1
13 CONTINUE
RETURN
END
SUBROUTINE GAMA(N,X,GAMC)
COMMON/BINARY/A(100,100),B(100,100),C(100,100),AL(100,100)
COMMON/INITIAL/COMP(1000,1000),EXPT(1000,1000),FEED(20,20)
REAL Z(20),GAM(20),tau(20,20)
INTEGER NC,ID(20),ERR,N
DIMENSION GAMC(150,150),X(N)
NC = 2
A(1,1)=0.
A(1,2)= 1031.46
A(2,1)= 229.43
A(2,2)=0.
B(1,1)=0.
B(1,2)=X(1)
B(2,1)=X(3)
B(2,2)=0.
C(1,1)=0.
C(1,2)=X(2)
C(2,1)=X(4)
C(2,2)=0.
AL(1,2)=.4081
AL(2,1)=AL(1,2)
```

```
ID(1)=1
ID(2)=2
KEY=1
C COMP(1,1)=0.
C COMP(2,1)=1.
C N,ID,KEY,X,T,GAM,ERG
DO 103 I=1,6
Z(1)=COMP(I,2)
Z(2)=1.-Z(1)
T = 273.15+25
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
103 CONTINUE
DO 104 I=7,13
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+35
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
c print*,GAMC(I,1),GAMC(I,2)
104 CONTINUE
DO 105 I=14,42
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+50
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
105 CONTINUE
DO 106 I=43,47
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+60
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
106 CONTINUE
DO 107 I=48,53
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
```

```
T = 273.15+70
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
107 CONTINUE
DO 108 I=54,59
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+90
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
108 CONTINUE
DO 112 I=91,91
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+20
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
112 CONTINUE
DO 113 I=92,93
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+25
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
113 CONTINUE
DO 114 I=94,94
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+30
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
114 CONTINUE
DO 115 I=95,95
Z(1)=COMP(I,1)
```

```
Z(2)=1.-Z(1)
T = 273.15+35
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
115 CONTINUE
DO 116 I=96,96
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+40
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
116 CONTINUE
DO 117 I=97,97
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+45
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
117 CONTINUE
DO 118 I=98,98
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+50
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
118 CONTINUE
DO 119 I=99,99
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+55
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
119 CONTINUE
DO 120 I=100,100
```

```
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+60
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
120 CONTINUE
DO 121 I=101,102
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+70
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
121 CONTINUE
DO 122 I=103,103
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+80
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
122 CONTINUE
DO 123 I=104,104
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+90
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
123 CONTINUE
DO 124 I=105,105
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+99
CALL nrtl(NC,ID,KEY,Z,T,GAM,ERR)
GAMC(I,1) = GAM(1)
GAMC(I,2) = GAM(2)
C print*, GAMC(I,1),GAMC(I,2)
124 CONTINUE
```

```
RETURN
END
SUBROUTINE EXCS(N,X,HE)
COMMON/BINARY/A(100,100),B(100,100),C(100,100),AL(100,100)
COMMON/INITIAL/COMP(1000,1000),EXPT(1000,1000),FEED(20,20)
REAL HE(1000),HEE,Z(20)
INTEGER N
DIMENSION X(N)
A(1,1)=0.
A(1,2)= 1031.46
A(2,1)= 229.43
A(2,2)=0.
B(1,1)=0.
B(1,2)=X(1)
B(2,1)=X(3)
B(2,2)=0.
C(1,1)=0.
C(1,2)=X(2)
C(2,1)=X(4)
C(2,2)=0.
AL(1,2)=.4081
AL(2,1)=AL(1,2)
DO 109 I=60,68
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T = 273.15+30
CALL ENTH(Z,T,HEE)
HE(I)=HEE
C print*, HE
109 CONTINUE
DO 110 I=69,80
Z(1)=COMP(I,1)
Z(2)=1.-Z(1)
T=273.15+30
CALL ENTH(Z,T,HEE)
HE(I)=HEE
C print*, HE
110 CONTINUE
RETURN
END
SUBROUTINE LLEQ(N,X,SOL)
COMMON/BINARY/A(100,100),B(100,100),C(100,100),AL(100,100)
COMMON/INITIAL/COMP(1000,1000),EXPT(1000,1000),FEED(20,20)
REAL K(20),Z(20),GAE(20),GAR(20)
```

```
INTEGER ID(20),ERR,NC,N
DIMENSION XE(20), XR(20),SOL(1000,1000),X(N)
REAL GAME(20), GAMR(20)
NC = 2
ID(1) = 1
ID(2) = 2
A(1,1)=0.
A(1,2)= 1031.46
A(2,1)= 229.43
A(2,2)=0.
B(1,1)=0.
B(1,2)=X(1)
B(2,1)=X(3)
B(2,2)=0.
C(1,1)=0.
C(1,2)=X(2)
C(2,1)=X(4)
C(2,2)=0.
AL(1,2)=.4081
AL(2,1)=AL(1,2)
Z(1) = FEED(1,1)
Z(2) = FEED(1,2)
KEY = 1
IR=1
IE=2
T=273.15+15
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(81,1) = XE(1)
SOL(81,2) = XR(2)
c print*,sol(91,1),sol(91,2)
c T=273.15+20
c CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
c SOL(82,1) = XE(1)
c SOL(82,2) = XR(2)
T=273.15+25
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(82,1) = XE(1)
SOL(82,2) = XR(2)
T=273.15+30
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(83,1) = XE(1)
SOL(83,2) = XR(2)
T=273.15+35
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
```

```
SOL(84,1) = XE(1)
SOL(84,2) = XR(2)
T=273.15+40
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(85,1) = XE(1)
SOL(85,2) = XR(2)
T=273.15+50
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(86,1) = XE(1)
SOL(86,2) = XR(2)
T=273.15+60
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(87,1) = XE(1)
SOL(87,2) = XR(2)
T=273.15+70
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(88,1) = XE(1)
SOL(88,2) = XR(2)
T=273.15+80
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(89,1) = XE(1)
SOL(89,2) = XR(2)
T=273.15+92
CALL ELIPS(NC,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
SOL(90,1) = XE(1)
SOL(90,2) = XR(2)
C print*,sol(1,1),sol(1,2)
RETURN
END
SUBROUTINE ELIPS(N,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
C ELIPS CALCULATES CONJUGATE PHASE COMPOSITIONS XR AND XE FOR
C PARTIALLY MISCIBLE N COMPONENT LIQUID SYSTEMS OF OVERALL
COMPOSTION
C Z AT GIVEN TEMPERATURE T(K). INDICES OF THE COMPONENTS
INVOLVED
C SHOULD BE IN THE VECTOR ID. IR AND IE ARE THE COMPONENT NRS OF
THE
C R AND E PHASE SOLVENTS (SHOULD BE ..................)
REAL Z(N),XR(N),XE(N),K(N),GAR(20),GAE(20),K1(20),KS,KP,K2,
1 RX(20),EX(20)
INTEGER ID(N),ERR,ERL
100 ERR = 0
KEE = KEY
IF (IR.EQ.0.OR.IE.EQ.0) GO TO 101
```

```
GO TO(101,130,130,130,130,130,130,130,101,130),KEY
C FOR NEW SYSTEMS WITHOUT IR, IE SPECIFIED, FIND IR, IE AS LEAST
SOLUBLE
C PAIR
101 KS = 1.
KP = 1.
110 DO 115 I=1,N
XR(I) = 0.
115 XE(I) = 0.
J1 = 1
IF (IR.NE.0) GO TO 120
IF (IE.NE.0) GO TO 121
116 DO 119 J=2,N
XR(J1) = 0.
XE(J1) = 0.
J1 = J-1
XR(J) = 0.98
XE(J) = 0.02
XR(J-1) = 0.
XE(J-1) = 0.
IF(Z(J).LT.0.10) GO TO 119
DO 118 I=1,J1
XE(I) = 0.98
XR(I) = 0.02
IF(I.GT.1) XE(I-1) = 0.
IF(I.GT.1) XR(I-1) = 0.
IF(Z(I).LT.0.10) GO TO 118
CALL LILIK(N,ID,KEE,XR,XE,T,K,GAR,GAE,ERL)
IF(ERL.GT.1) GO TO 900
KEE = 3
IF(K(I).LE.KS) GO TO 117
KS = K(I)
IS = I
117 IF(1./K(J).LE.KS) GO TO 118
KS = 1./K(J)
IS = J
118 CONTINUE
119 CONTINUE
XR(N) = 0.
XE(N) = 0.
XR(J1) = 0.
XE(J1) = 0.
GO TO 125
120 IF(IE.NE.0) GO TO 130
```

```
IS = IR
GO TO 125
121 IS = IE
125 XE(IS) = 0.98
XR(IS) = 0.02
126 DO 129 J=1,N
IF(J.EQ.IS) GO TO 129
XR(J) = 0.98
XE(J) = 0.02
IF(J.EQ.(IS+1)) GO TO 128
IF(J.GT.1) XR(J-1) = 0.
IF(J.GT.1) XE(J-1) = 0.
127 IF(Z(J).LT.0.10) GO TO 129
CALL LILIK(N,ID,KEE,XR,XE,T,K,GAR,GAE,ERL)
IF(ERL.GT.1) GO TO 900
KEE = 3
IF(K(J).GE.KP) GO TO 129
KP = K(J)
IP = J
GO TO 129
128 IF(J.GT.2) XR(J-2) = 0.
IF(J.GT.2) XE(J-2) = 0.
GO TO 127
129 CONTINUE
IE = IP
IF(IR.NE.IS) IE = IS
IF(IR.NE.IS) IR = IP
C INITIALIZE R AND E PHASE COMPOSITIONS
130 DO 131 I=1,N
XR(I) = 0.
131 XE(I) = 0.
XR(IR) = 0.98
XE(IR) = 0.02
XR(IE) = 0.02
XE(IE) = 0.98
C GET INITIAL ESTIMATES FOR K VALUES
135 CALL LILIK(N,ID,KEE,XR,XE,T,K,GAR,GAE,ERL)
IF(ERL.GT.1) GO TO 900
SZ = 0.
136 DO 137 I=1,N
SZ = SZ+Z(I)
137 K1(I) = K(I)-1
IF(ABS(SZ-1.).GT.0.01) GO TO 903
C GET INITIAL ESTIMATE FOR A
```

```
A = Z(IE)/(Z(IE)+Z(IR))
A = -A/K1(IR)+(A-1.)/K1(IE)
IF(A.LT.0.) A=0.
IF(A.GT.1.) A=1.
A0 = A
IT = 0
KAC = 0
C CONDUCT ITERATION OVER PHASE COMPOSTION (OUTER LOOP)
200 IT = IT+1
IF(IT.GT.50) GO TO 900
AA = A0
A0 = A
AN = A
C CONDUCT NEWTON-RAPHSON ITERATION FOR A AT FIXED K VALUES
300 DO 319 M=1,10
F = 0.
DF = 0.
301 DO 309 I = 1,N
K2 = A*K1(I)+1.
F = F+Z(I)*K1(I)/K2
309 DF = DF-Z(I)*(K1(I)/K2)**2
IF(ABS(F).LT.1.E-05) GO TO 210
DA = F/DF
310 AN = A-DA
C LIMIT A TO RANGE 0-1 IF IT FALLS OUTSIDE POLES OF F
IF(AN.LT.-1./K1(IR)) GO TO 312
AN = A+(1./K1(IR)+A)/2.
GO TO 319
312 IF(AN.GT.-1./K1(IE)) GO TO 319
AN=A+(1./K1(IE)+A)/2.
319 A = AN
GO TO 900
210 A = AN
SR = 0.
SE = 0.
C FIND NEW R AND E PHASE COMPOSITIONS
211 DO 215 I=1,N
XR(I) = Z(I)/(A*K1(I)+1.)
XE(I) = K(I)*XR(I)
SR = SR+XR(I)
215 SE = SE+XE(I)
220 DO 225 I=1,N
XR(I) = XR(I)/SR
225 XE(I) = XE(I)/SE
```

```
C AT ALTERNATE ITERATIONS AFTER 3 ACCELERATE PHASE
COMPOSITIONS BY
C WEGSTEIN METHOD BASED ON SUM OF DEVIATIONS OF COMPONENT
FUGACITITES
230 IF(IT.LT.3) GO TO 250
IF(IT.LE.5.AND.(A.LT.0..OR.A.GT.1.)) GO TO 250
IF(KAC.GE.1) GO TO 239
IF(SS.GT.SL) GO TO 250
IF(SS.GT.0.2) GO TO 250
KAC = 1
WG = SS/(SL-SS)
WK = 1.+WG
SR = 0.
SE = 0.
DO 235 I=1,N
XR(I) = WK*XR(I)-WG*RX(I)
C ALLOW NO NEGATIVE MOL FRACTIONS
IF(XR(I).LT.0.) XR(I) = 0.
XE(I) = WK*XE(I)-WG*EX(I)
IF(XE(I).LT.0.) XE(I) = 0.
SR = SR+XR(I)
235 SE = SE+XE(I)
C NORMALIZE ACCELERATED COMPOSITIONS (TO ALLOW FOR XR(I) OR
XE(I) SET
C TO 0)
236 DO 237 I=1,N
XR(I) = XR(I)/SR
237 XE(I) = XE(I)/SE
GO TO 250
239 KAC = 0
C NEW K AND GAMMA VALUES
250 CALL LILIK(N,ID,3,XR,XE,T,K,GAR,GAE,ERL)
IF(ERL.GT.1) GO TO 900
ESS = 1.E-03
IF(IT.LE.5) GO TO 252
C CHECK FOR VICINITY OF A PLAIT POINT
PPI = K(IR)/K(IE)+K(IE)/K(IR)
IF(PPI.GT.10..OR.SS.GT.0.05) GO TO 251
C EXIT IF TOO NEAR PLAIT POINT
IF(IT.GE.20) GO TO 290
IF(PPI.GT.7.) GO TO 251
C CHECK IF CALCULATION NEAR PLAIT POINT IS PROBABLY IN SINGLE
PHASE
C REGION--IF SO CONTINUE
```

```
DE=A0
IF(DE.GT.0.5) DE=A0-1.
DI = (AA-A)/DE
IF(DI.LT.0.1) GO TO 290
251 IF(PPI.LT.20) ESS = 2.E-04
252 SL = SS
SS = 0.
253 DO 255 I=1,N
K1(I) = K(I)-1.
C CALCULATE OBJECTIVE FUNCTION
255 SS = SS+ABS(GAE(I)*XE(I)-GAR(I)*XR(I))
C CHECK CONVERGENCE
IF(SS.LE.ESS) GO TO 190
IF(A.GE.0..AND.A.LE.1.) GO TO 260
IF(IT.LT.3.OR.SS.GT.0.20) GO TO 260
IF(IT.LT.5.AND.SS.GT.0.05) GO TO 260
C CHECK IF A MOVING AWAY FROM 0 - 1 REGION
WRITE(*,*) 'DONE',A,A0
IF((ABS(A)-ABS(A0)).GT.0.) GO TO 195
C SAVE LAST PHASE COMPOSITIONS FOR USE IN ACCELERATION
260 DO 265 I=1,N
RX(I) = XR(I)
265 EX(I) = XE(I)
GO TO 200
C FEED IN VICINITY OF PLAIT POINT -- CHECK IF IN TWO PHASE REGION
290 IF(A.GE.0..AND.A.LE.1.) GO TO 905
GO TO 195
C DO NOT ALLOW CONVERGENCE ON ACCELERATED ITERATION
190 IF(KAC.EQ.1) GO TO 260
C CONVERGED SOLUTION--CHECK IF IN TWO PHASE REGION
191 IF(A.LT.0..OR.A.GT.1.) GO TO 195
ERR = ERL
RETURN
C FEED OUTSIDE TWO PHASE REGION
195 DO 196 I=1,N
WRITE(*,*) 'JUNK'
XR(I) = Z(I)
196 XE(I) = Z(I)
IF(A.LT.0.) A=0.
IF(A.GT.1.) A=1.
ERR=ERL
RETURN
C ON FAILURE TO CONVERGE SET A TO -1 AND ERR TO 2
900 ERR = 2
```

```
GO TO 910
C FOR BAD INPUT DATA SET A TO -1 AND ERR TO 5
903 ERR = 5
GO TO 910
C FOR FEED TOO NEAR PLAIT POINT SET A TO -1 AND ERR TO 7
905 ERR = 7
910 DO 911 I=1,N
XR(I) = Z(I)
911 XE(I) = Z(I)
A = -1
RETURN
END
SUBROUTINE LILIK(N,ID,KEY,XR,XE,T,K,GAR,GAE,ERR)
REAL XR(N),XE(N),K(N),GAR(N),GAE(N),X(20),Y(20),GX(20),GY (20)
INTEGER ID(N),IDF(20),ERR,ERG
100 ERR = 0
C CONVERT COMPOSITION VECTORS TO DIMENSION 20 TO MATCH LOWER
LEVEL
C SUBROUTINES
101 DO 102 I=1,N
X(I) = XR(I)
Y(I) = XE(I)
102 IDF(I) = ID(I)
C GET R AND E PHASE ACTIVITY COEFFICIENT VECTORS TO DIMENSION N
CALL NRTL(N,IDF,KEY,X,T,GX,ERG)
CALL NRTL(N,IDF,3,Y,T,GY,ERG)
C CONVERT ACTIVITY COEFFICIENT VECTORS TO DIMENSION N
110 DO 119 I=1,N
GAR(I) = GX(I)
GAE(I) = GY(I)
K(I) = GAR(I)/GAE(I)
IF(K(I).LE.0..OR.K(I).GT.1.E+19) GO TO 900
119 CONTINUE
ERR = ERG
RETURN
C FOR A K VALUE OUT OF RANGE SET ERR TO 2
900 ERR = 2
DO 905 I=1,N
905 K(I)=0.
RETURN
END
SUBROUTINE NRTL(N,ID,KEY,X,T,GAM,ERG)
C STGX=SUMMATION OF PRODUCT TAU,G,X
C SGX=SUMMATION OF PRODUCT G,X
```

```
C XG=PRODUCT OF X,G
C SGX=SUMMATION OF PRODUCT G,X
C SXTG=SUMMATION OF PRODUCT X,TAU,G
C TAU=TAU(I,J)
C SG FOR 'g',AL FOR ALPHA
REAL X(20),GAM(20),STGX,SGX1,SGX2,SGX3,SXTG,ST2,
1 TAU(20,20),G(20,20),SG(20,20)
COMMON/BINARY/A(100,100),B(100,100),C(100,100),AL(100,100)
integer bb,cc,r
do 15 bb=1,n
do 25 cc=1,n
sg(bb,cc)=A(bb,cc)+B(bb,cc)*(T-298.15)+C(bb,cc)*(T-298.15)**2
tau(bb,cc)=sg(bb,cc)/T
G(bb,cc)=exp(-AL(bb,cc)*tau(bb,cc))
25 continue
15 continue
DO 120 I=1,N
SGX1=0.
ST2=0.
STGX=0.
DO 121 J=1,N
STGX=STGX+TAU(J,I)*G(J,I)*X(J)
121 CONTINUE
DO 122 L=1,N
SGX1=SGX1+G(L,I)*X(L)
122 CONTINUE
DO 123 J=1,N
sgx2=0.
sxtg=0.
sgx3=0.
DO 124 L=1,N
SGX2=SGX2+G(L,J)*X(L)
124 CONTINUE
DO 125 R=1,N
SXTG=SXTG+X(R)*TAU(R,J)*G(R,J)
125 CONTINUE
DO 126 L=1,N
SGX3=SGX3+G(L,J)*X(L)
126 CONTINUE
ST2=ST2+X(J)*G(I,J)/SGX2*(TAU(I,J)-SXTG/SGX3)
123 CONTINUE
GAM(I)=EXP(STGX/SGX1+ST2)
120 CONTINUE
RETURN
```

```
END
SUBROUTINE ENTH(X,T,HE)
C TAU=TAU(I,J)
C SG FOR 'g',AL FOR ALPHA
REAL X(20),TAU(20,20),G(20,20),SG(20,20),HE,T
COMMON/BINARY/A(100,100),B(100,100),C(100,100),AL(100,100)
integer bb,cc
do 15 bb=1,2
do 25 cc=1,2
sg(bb,cc)=A(bb,cc)+B(bb,cc)*(T-298.15)+C(bb,cc)*(T-298.15)**2
tau(bb,cc)=sg(bb,cc)/T
G(bb,cc)=exp(-AL(bb,cc)*tau(bb,cc))
25 continue
15 continue
A12=A(1,2)
A21=A(2,1)
B12=B(1,2)
B21=B(2,1)
C12=C(1,2)
C21=C(2,1)
G12=G(1,2)
G21=G(2,1)
sg12=sg(1,2)
sg21=sg(2,1)
TAU12=TAU(1,2)
TAU21=TAU(2,1)
ALP=AL(1,2)
x1=X(1)
x2=1.-x1
c HE=x1*x2*(G21*(A21-2*C21*T**2)/(x1+x2*G21)**2*(x1*(1.-ALP*
c 1 TAU21)+x2*G21)+G12*(A12-2*C12*T**2)/(x2+x1*G12)**2*(x2*(1.-ALP*
c 2 TAU12)+x1*G12))
HE=(x1*x2*G21/(x1+x2*G21))*(-1.+ALP*x1*TAU21/(x1+x2*G21))*
1 (B21*T+2*C21*T*(T-298.15)-sg21)+
2 (x1*x2*G12/(x2+x1*G12))*(-1.+ALP*x2*TAU12/(x2+x1*G12))*
3 (B12*T+2*C12*T*(T-298.15)-sg12)
HE=HE*8.314
RETURN
END
```

APPENDIX E
TERNARY DATA

Table E1. Experimental Ternary Data for Hexane – 1-Butanol – Water (in mole percent) [1]

Hexane – Rich Phase			Water – Rich Phase		
Hexane	**1-Butanol**	**Water**	**Hexane**	**1-Butanol**	**Water**
99.791	0.209	0.000	0	0.170	99.830
99.544	0.456	0.000	0	0.343	99.657
99.057	0.943	0.000	0	0.550	99.450
98.444	1.556	0.000	0	0.695	99.305
97.826	2.174	0.000	0	0.792	99.208
97.225	2.775	0.000	0	0.819	99.181
96.756	3.244	0.000	0	0.885	99.115
96.607	3.393	0.000	0	0.887	99.113
95.694	4.306	0.000	0	0.955	99.045
96.964	3.036	0.000	0	0.871	99.129
95.280	4.720	0.000	0	0.997	99.003
93.336	6.664	0.000	0	1.077	98.923
93.030	6.410	0.560	0	1.037	98.963
88.656	10.301	1.043	0	1.144	98.856
83.966	14.224	1.810	0	1.216	98.784
80.071	17.338	2.591	0	1.228	98.772
75.459	21.029	3.512	0	1.279	98.721
71.569	23.895	4.536	0	1.326	98.674
65.068	28.635	16.296	0	1.348	98.652
24.740	52.850	22.410	0	1.411	98.589
16.978	55.206	27.816	0	1.451	98.449
11.762	56.548	31.690	0	1.480	98.520

Table E2. Experimental Ternary Data for Hexane – 1-Butanol – Water (in mole percent) [22]

Hexane – Rich Phase			Water – Rich Phase		
Hexane	**1-Butanol**	**Water**	**Hexane**	**1-Butanol**	**Water**
83.28	15.40	01.32	0	00.66	99.34
76.01	21.18	02.81	0	00.71	99.29
55.71	35.47	08.82	0	00.80	99.20
44.60	42.07	13.33	0	00.90	99.10
29.83	49.42	20.75	0	01.02	98.98
19.89	53.11	27.00	0	01.20	98.80
06.69	54.13	39.18	0	01.29	98.71

APPENDIX F

TABLES OF DATA SELECTION OVER THE TEMPERATURE RANGE 10-100 °C

Table F1. Binary data selection over the temperature range 10-100 °C

Binary pair	Type of data	Temp(°C)	Data[Ref]
Hexane-Water	Solubility of Hexane in Water	25	2.57E-06 [from @25°C selection]
		35	2.69E-06 [20]
		93	5.73E-06 [20]
		100	6.21E-06 [20]
	Solubility of Water in Hexane	25	4.7E-04 [from @25°C selection]
		40	1.5E-03 [20]
		93	5.95E-03 [20]
		100	7.09E-03 [20]
Butanol-Water	Solubility of Butanol in Water	15	.5048 [36]
		25	.506 [from @25 °C selection]
		30	.511 [36]
		35	.516 [36]
		40	.523 [36]
		50	.528 [36]
		60	.543 [36]
		70	.559 [36]
		80	.581 [36]
		92	.597 [36]
	Solubility of Water in Butanol	15	.021 [36]
		25	.0187 [from @25 °C selection]
		30	.0181 [36]
		35	.0175 [36]
		40	.0168 [36]
		50	.0165 [36]
		60	.0162 [73]
	γ^{∞} of Butanol	20	48.4 [35]
		25	51.37 [from @25 °C selection]
		30	53.4 [35]
		35	57.2 [35]
		40	58.9 [35]
		45	60.2 [35]
		50	61.5 [35]
		55	62.8 [35]
		60	63.4 [35]
		70	63.8 [35]
	γ^{∞} of Water	25	5.06 [from @25 °C selection]
		70	3.27 [80]

		80	3.12 [80]
		90	3.07 [80]
		99	2.97 [80]
	VLE	25	[from @25 C selection]
		35	[71]
		50	[78]
		60	[43]
		70	[72]
		90	[72]
	H^E	30	[74]
		30	[74]
		30	[83]
Hexane-Butanol	γ^∞ of Hexane	25	5.12 [from @25 °C selection]
		50	5.6 [65]
		60	5.3 [65]
	γ^∞ of Butanol	25	38.6 [from @25 °C selection]
		42	22.5 [41]
		58	15.1 [41]
		67	12.2 [41]
	VLE	25	[from @25 °C selection]
		30	[48]
		35	[48]
		40	[48]
		45	[48]
		50	[48]
		59	[76]
		65	[76]
		75	[76]
	H^E	15	[89]
		25	[from @25 °C selection]
		35	[82]
		45	[82]