EFFECT OF INORGANIC SALTS ON LIQUID-LIQUID EQUILIBRIUM IN EXTRACTION OF LACTIC ACID USING 1-BUTANOL

Kanungnit Chawong

มหาวิทยาลัยเทคโนโลยีสุรนารี

A Thesis Submitted in Partial Fulfillment of the Requirements for the

Degree of Master of Engineering in Chemical Engineering

Suranaree University of Technology

Academic Year 2013

ผลของเกลืออนินทรีย์ต่อสมดุลของเหลว – ของเหลว ในการสกัดกรดแล็คติกด้วย 1-บิวทานอล

นางสาวคนึงนิจ ชาวงษ์

มหาวิทยาลัยเทคโนโลยีสุรนารี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี
มหาวิทยาลัยเทคโนโลยีสุรนารี
ปีการศึกษา 2556

EFFECT OF INORGANIC SALTS ON LIQUID-LIQUID EQUILIBRIUM IN EXTRACTION OF LACTIC ACID USING 1-BUTANOL

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master’s Degree.

Thesis Examining Committee

(Dr. Terasut Sookkumnerd)
Chairperson

(Asst. Prof. Dr. Panarat Rattanaphanee)
Member (Thesis Advisor)

(Prof. Dr. Adrian E. Flood)
Member

(Asst. Prof. Dr. Atichat Wongkoblap)
Member

(Prof. Dr. Sukit Limpijumnong)
Vice Rector for Academic Affairs
and Innovation

(Assoc. Prof. Flt. Lt. Dr. Kontorn Chamniprasart)
Dean of Institute of Engineering

มหาวิทยาลัยเทคโนโลยีสุรนารี

คนึงนิจ ชาวงษ์ : ผลของเกลืออนินทรีย์ต่อสมดุลของเหลว-ของเหลวในการสกัดกรดแล็คติกด้วย 1-บิวทานอล (EFFECT OF INORGANIC SALTS ON LIQUID-LIQUID EQUILIBRIUM IN EXTRACTION OF LACTIC ACID USING 1-BUTANOL)
อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.พนารัตน์ รัตนพานี, 178 หน้า.

วิทยานิพนธ์นี้มีวัตถุประสงค์เพื่อศึกษาผลของเกลืออนินทรีย์ต่างชนิดต่อสมดุลของเหลว-ของเหลวของน้ำ 1-บิวทานอล และกรดแล็คติก และประยุกต์ใช้ผลการศึกษาที่ได้ในการสกัดแยกกรดแล็คติกจากสารละลายเอเควียสด้วย 1-บิวทานอล การศึกษาวิจัยในวิทยานิพนธ์แบ่งเป็น 3 ส่วน ส่วนแรกคือการศึกษาสมดุลของเหลว-ของเหลวของระบบผสมตัวทำละลายอิเล็กโทรไลต์ที่ประกอบด้วยน้ำ, 1-บิวทานอล และเกลืออนินทรีย์ต่างชนิด ได้แก่ โซเดียมคลอไรด์, โซเดียมซัลเฟต, แอมโมเนียมคลอไรด์และแอมโมเนียมซัลเฟตที่อุณหภูมิระหว่าง 303.15 ถึง 323.15 เคลวิน ภายใต้ความดันบรรยากาศ ผลการทดลองแสดงให้เห็นว่า ความสามารถในการละลายระหว่างน้ำและ 1- บิวทานอลลดลงเมื่อความเข้มข้นของเกลืออนินทรีย์ในระบบเพิ่มขึ้น และอุณหภูมิในช่วงที่ทำการศึกษามีผลต่อสมดุลของระบบดังกล่าวเพียงเล็กน้อย เมื่อหาค่าสหสัมพันธ์ของผลการทดลองที่ได้ด้วยแบบจำลอง Modified extended UNIQUAC พบว่า แบบจำลองนี้มีความสอดคล้องกับผลการทดลองอย่างน่าพอใจ มีค่าเบี่ยงเบนกำลังสองสัมบูรณ์เฉลี่ยต่ำกว่า 1%

การศึกษาวิจัยส่วนที่สองเป็นการศึกษาสมดุลของเหลว-ของเหลวของระบบน้ำ, 1-บิวทานอลและกรดแล็คติกภายใต้สภาวะความดันบรรยากาศ ที่อุณหภูมิ 303.15 เคลวิน และประเมินความเป็นไปได้ในการสกัดกรดแล็กติกด้วย 1-บิวทานอลจากค่าสัมประสิทธิ์การกระจายตัวของกรดแล็กติกระหว่างวัฏภาคเอเควียสและวัฏภาคสารอินทรีย์ ผลการศึกษาพบว่าค่าสัมประสิทธิ์การกระจายและประสิทธิภาพในการสกัดกรดแล็คติกเพิ่มขึ้นตามความเข้มข้นของกรดแล็คติกในสารละลายเริ่มต้น ผลการหาค่าสหสัมพันธ์ของสมดุลของเหลว-ของเหลวของระบบดังกล่าวด้วยแบบจำลอง UNIQUAC และ NRTL พบว่า แบบจำลอง UNIQUAC มีความสอดคล้องกับผลการทดลองดีกว่า โดยมีค่าเบี่ยงเบนกำลังสองสัมบูรณ์เฉลี่ยต่ำกว่า 0.5%

การศึกษาวิจัยส่วนสุดท้ายเป็นการประยุกต์ใช้ผลของเกลืออนินทรีย์ต่อพฤติกรรมสมดุลของเหลว - ของเหลวของระบบของผสมสององค์ประกอบน้ำ และ 1-บิวทานอล ในการสกัดกรดแล็กติก ผลการศึกษาพบว่าเกลือแต่ละชนิดส่งผลกระทบอย่างมีนัยสำคัญต่อการกระจายตัวของกรดแล็คติกระหว่างวัฏภาคเอเควียสและวัฏภาคสารอินทรีย์ โดยในระบบที่เติมโซเดียมคลอไรด์และแอมโมเนียมคลอไรด์ สัมประสิทธิ์การกระจายตัวและประสิทธิภาพการสกัดกรดแล็กติกมีค่า

ลดลงเมื่อความเข้มข้นของเกลือในระบบเพิ่มขึ้น เรียกปรากฏการณ์นี้ว่า Salting in ส่วนระบบที่เติมโซเดียมซัลเฟตและแอมโมเนียมซัลเฟตนั้น สัมประสิทธิ์การกระจายตัวและประสิทธิภาพการสกัดจะเพิ่มขึ้นตามความเข้มข้นของเกลือในระบบ เรียกปรากฏการณ์นี้ว่า Salting out เมื่อพิจารณาความสามารถของเกลือแต่ละชนิดในการเพิ่มค่าสัมประสิทธิ์การกระจายตัวของกรดแล็คติกและเรียงลำดับความสามารถดังกล่าวจากมากไปน้อยจะได้ว่าโซเดียมซัลเฟตมีความสามารถมากกว่าแอมโมเนียมซัลเฟส โซเดียมคลอไรด์ และแอมโมเนียมคลอไรด์ ตามลำดับ ผลการศึกษาของวิทยานิพนธ์ฉบับนี้สรุปได้ว่า เกลืออนินทรีย์ทั้ง 4 ชนิดมีผลต่อสมดุลของเหลว-ของเหลวน้ำ 1-บิวทานอล และน้ำ 1-บิวทานอล กรดแล็กติก โดยโซเดียมซัลเฟต และแอมโมเนียมซัลเฟตทำให้ประสิทธิภาพการสกัดกรดแล็กติกจากน้ำด้วย 1-บิวทานอลมีประสิทธิภาพดีขึ้น แต่โซเดียมคลอไรด์และแอมโมเนียมคลอไรด์ทำให้กระบวนการสกัดนี้มีประสิทธิภาพลดลง

มหาวิทยาลัยเทคโนโลยีสุรนารี

สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2556

ลายมือชื่อนักศึกษา ____________________
ลายมือชื่ออาจารย์ที่ปรึกษา ______________

KANUNGNIT CHAWONG : EFFECT OF INORGANIC SALTS ON LIQUID-LIQUID EQUILIBRIUM IN EXTRACTION OF LACTIC ACID USING 1-BUTANOL. THESIS ADVISOR : ASST. PROF. PANARAT RATTANAPHANEE, Ph.D., 178 PP.

LACTIC ACID/ LIQUID-LIQUID EXTRACTION/ 1-BUTANOL/ INORGANIC SALTS/ UNIQUAC MODEL/ MODIFIED EXTENDED UNIQUAC MODEL

This thesis aims to study effect of inorganic salts on liquid-liquid equilibrium (LLE) of water, 1-butanol and lactic acid, and its application in extraction of the acid from aqueous solution using 1-butanol. There are three parts of study in this thesis. The first part is a study of liquid-liquid equilibrium of electrolyte mixture system containing water, 1-butanol, and different inorganic salt i.e., NaCl, Na_2SO_4, NH_4Cl and $((NH_4)_2SO_4$ at temperatures in range of 303.15 to 323.15 K under atmospheric pressure. Experimental results showed that solubility between water and 1-butanol decreased with increasing inorganic salt concentration and the temperature in the range studied here was found to have a minor effect on this system. Correlation of experimental data by modified extended UNIQUAC model gave a satisfactory agreement, with an average absolute root mean square deviation of less than 1%.

The second part studied liquid-liquid equilibrium of water, 1-butanol and lactic acid system under atmospheric pressure at 303.15 K. Possibility of lactic acid extraction using 1-butanol was evaluated from distribution coefficient of the acid between aqueous and organic phases. The results showed that the distribution coefficient and degree of lactic acid extraction increased with increasing lactic acid concentration in the starting solution. The correlation of experimental LLE data was determined by UNIQUAC and NRTL models. It was found that the UNIQUAC model was more consistent with experimental LLE data, with an average absolute root mean square deviation less than 0.5%.

In the final part, the inorganic salt-modified LLE behavior of binary water and 1-butanol mixture was applied in the extraction of lactic acid. The results showed that each salts have a significant effect on the distribution of lactic acid between aqueous and organic phases. Upon addition of NaCl and NH_4Cl, the distribution coefficient and degree of lactic acid extraction were decreased with increasing salt concentration. This effect is called salting in. Addition of Na_2SO_4 and $(NH_4)_2SO_4$, on the other hand, led to increasing of the distribution coefficient and degree of lactic acid extraction. This effect is called salting out. Ability of these salts in increasing the distribution coefficient of lactic acid can be arranged as $Na_2SO_4 > (NH_4)_2SO_4 > NaCl > NH_4Cl$. All results from this thesis lead to the conclusion that the four inorganic salts could liquid-liquid equilibrium of water, 1-butanol and water, 1-butanol, lactic acid. Na_2SO_4 and $(NH_4)_2SO_4$ could increase of efficiency of lactic acid extraction from water using 1-butanol, while NaCl and NH_4Cl could decrease the efficiency of this process.

School of <u>Chemical Engineering</u>	Student's Signature__________________
Academic Year 2013	Advisor's Signature__________________

ACKNOWLEDGEMENTS

I would like to express my sincere thanks and gratitude to Asst. Prof. Dr. Panarat Rattanaphanee, my graduate advisor for her guidance and support throughout this work. Her guiding light, motivation, and patience was the most important source of my accomplishment.

I also would like to thank my thesis committee; Dr Terasut Sookkumnerd, Prof. Dr. Adrian E. Flood and Asst. Prof. Dr. Atichat Wongkoblap for their valuable time to serve as my committee member, and for their unconditional help and advice on the conduction of this work. I would like to thank all of lecturers at School of Chemical Engineering, Suranaree University of Technology, who led me to the world of Chemical Engineering.

I am thankful to Mr. Saran Dokmajkun for helping me with the laboratory facilities and for the valuable recommendations.

Finally, I would also like to express my deep sense of gratitude to my parents for their support and encouragement me throughout the course of this study at the Suranaree University of Technology.

Kanungnit Chawong

TABLE OF CONTENTS

Page

CHAPTER

TABLE OF CONTENTS (Continued)

Page

TABLE OF CONTENTS (Continued)

Page

มหาวิทยาลัยเทคโนโลยีสุรนารี

TABLE OF CONTENTS (Continued)

Page

TABLE OF CONTENTS (Continued)

Page

APPENDICES

มหาวิทยาลัยเทคโนโลยีสุรนารี

TABLE OF CONTENTS (Continued)

Page

มหาวิทยาลัยเทคโนโลยีสุรนารี

LIST OF TABLES

Table **Page**

มหาวิทยาลัยเทคโนโลยีสุรนารี

LIST OF TABLES (Continued)

Table **Page**

มหาวิทยาลัยเทคโนโลยีสุรนารี

LIST OF TABLES (Continued)

Table **Page**

มหาวิทยาลัยเทคโนโลยีสุรนารี

LIST OF FIGURES

LIST OF FIGURES (Continued)

Figure **Page**

LIST OF FIGURES (Continued)

มหาวิทยาลัยเทคโนโลยีสุรนารี

LIST OF FIGURES (Continued)

มหาวิทยาลัยเทคโนโลยีสุรนารี

SYMBOLS AND ABBREVIATIONS

A_x = Debye-Hückel parameter

A^- = dissociated acid

a = binary interaction parameter

b = Debye-Hückel parameter

C = molar concentration (mol/L)

D = dielectric constant

D = distribution coefficient

d = density (kg/m^3)

E = efficiency of acid extraction

e = electronic charge (c)

G = dimensionless interaction energy parameter

G^E = excess Gibbs energy

g = interaction energy parameter (J/mol)

HA = carboxylic acid

H^+ = hydrogen ion

I = ionic strength (mol/L)

I_x = mole fraction ionic strength

K_D = dimerization coefficient

K_{HA} = ionization coefficient

k = Boltzmann’s constant (J/K)

มหาวิทยาลัยเทคโนโลยีสุรนารี

SYMBOLS AND ABBREVIATIONS (Continued)

LA = lactic acid

M = molar mass of (kg/mol)

N_A = Avogadro’s number (mol^{-1})

n = number of ions

OF = objective function

q = surface area parameter

R = gas constant (J·mol^{-1}·K^{-1})

r = volume parameter

S = separation factor

T = temperature (K)

u = interaction energy parameter

V = volume (m^3)

w = mass fraction

x = mole fraction

z = charge number

Greek Symbols

ρ = closest approach parameter

ψ = UNIQUAC parameter

θ = surface fraction

ϕ = volume fraction

มหาวิทยาลัยเทคโนโลยีสุรนารี

SYMBOLS AND ABBREVIATIONS (Continued)

σ = Born radius (m)

ε_0 = vacuum permittivity

γ = activity coefficient for component

α = non dimensionless parameter in NRTL equation

τ = dimensionless interaction parameter

Δw = root mean square absolute deviation

Subscripts

i, j, k, l = component i, j, k, l

s = mixed solvent

w = water

0 = initial

aq = aqueous phase

org = organic phase

Superscripts

PDH = Debye-Hückel equation

UNIQUAC = UNIversal QUAsi Chemical equation

Born = Born equation

NRTL = Non-Random Two-Liquid

Comb = combinatorial part

Res = residual part

มหาวิทยาลัยเทคโนโลยีสุรนารี

SYMBOLS AND ABBREVIATIONS (Continued)

I = equilibrium aqueous phase

II = equilibrium organic phase

M = number of tie lines

N = number of components

exp = experimental

$calc$ = calculated

$*$ = ion term

∞ = infinite dilution term

มหาวิทยาลัยเทคโนโลยีสุรนารี

CHAPTER 1

INTRODUCTION

1.1 Background and Significance of the Problem

Lactic acid or 2-hydroxypropanoic acid is an organic acid that contains both hydroxyl and carboxylic groups in its molecule. The acid is commonly used as biologically produced acidulates and preservatives in food industry. It is also widely used as a starting material for chemical synthesis due to its optical activity and its hydroxyl and carboxyl moieties. In addition, the acid has a potential of becoming a very large volume chemical, produced from renewable resources for use as a feedstock for biodegradable plastics and other environmental-friendly green compounds. But until now, the extensive use of lactic acid in chemical industry is hampered by the high production costs of optically pure lactic acid (Borgardts et al, 1998), which is strictly required in the production of the biodegradable poly (lactic acid) polymers, especially those to be used in biomedical applications and drug delivery

The demand for lactic acid is increasing due to the expansion of its application areas. Fermentation processes for the organic acid production generate multi-component aqueous solutions with low concentration of the desired acid. Consequently, separation methods for recovery of lactic acid from aqueous solutions are receiving increasing attention. Recovery of these acids by purification and concentration is challenging since the organic acids have a high affinity for water. The classical method for recovery of lactic acid from fermentation broth is based on the precipitation of lactic acid in form of calcium lactate by adding calcium hydroxide to the aqueous fermentation broth. The solid is filtered off and treated with sulphuric acid, which leads to precipitation of calcium sulphate. After filtration to separate the precipitate, lactic acid is purified using activated carbon, evaporation and crystallization to yield crystals of the lactic acid. These separation and final purification stages account for approximately 50% of the production costs (Chaudhuri and Pyle, 1992). Consequently, they are undesirable and also environmental unfriendly due to consumption of lime and sulphuric acid and the production of calcium sulphate sludge as a solid waste in large quantity (Kertes and King, 1986; Wasewar et al, 2002).

Liquid-liquid extraction is a promising alternative to conventional methods for the recovery of lactic acid from fermentation broth. The method provides high selectivity and enhanced product recovery by utilizing a combination of an extractant (also known as carrier) and diluents. In recent years, liquid-liquid extraction for recovery lactic acid have been reported by several researchers. Amine extractants have been extensively studied because of their high efficiency and selectivity. The extraction mechanism of amine extractants is by competing with water available to interact with the solute and transfer it into the organic phase. Examples of amine extractants include tertiary amines, such as tri-*n*-octylamine (TOA), which forms a water-insoluble complex with lactic acid and selective extract the acid from the aqueous to the organic phase (Choudhury and Swaminathan, 1998). It has been reported that aliphatic amines are capable of extracting organic acids from aqueous solutions (Kertes and King, 1986). The strong interaction between the acid and the amine creates acid-amine complexes and provides high equilibrium distribution ratios. High acid-amine affinity also gives higher selectivity for the acid over other non-acidic components in the fermentation medium. Other extractants that have been reportedly used include alkyl phosphate esters, such as tributyl phosphate (TBP) and trioctyl phosphine oxide (TOPO) as well as neutral extractants with oxygen-containing polar groups such as ketones (e.g. methyl isobutyl ketone), alkyl sulfoxides, or esters (e.g., tri-*n*-butyl phosphate and trioctylphosphine oxide) (Labbaci et al, 2010). In addition, the extractants that is function as the ion exchangers. Examples are quaternary ammonium salts such as the commercial extractant Aliquat 336 or tri-(C_8C_{10}) methylammonium chloride, where chloride anion is replaced by anion of the acid during the extraction (Kyuchoukov et al, 2004). However, such extractants usually have problem of physical properties and expensive extractant. Different diuents were used to modifiy the properties of extractants (viscosity, specipic gravity and surface tension). In order to overcome problems connected with low solubility of the complexes formed in the organic phase. The frequently applied diluents are octanol, decanol, oleyl alcohol, ketone and hexane.

Despite the high distribution coefficient obtained from extraction with specified solvents, some of the extractants are expensive and might inherit some toxicity. As a result, recovery of lactic acid by extraction with more economical and environmental friendly solvents is still needed. Extraction of lactic acid from aqueous solution using 1-butanol was reported by Chawong and Rattanaphanee (2011). It was found that using 1-butanol as a single solvent was significantly on extraction efficiency. The distribution coefficient increased considerably with increasing concentration of lactic acid in aqueous solution. However, disadvantage of lactic acid extraction with 1-butanol is the fact that this alcohol is partially miscible in water, which, consequently, leads to incomplete solvent recovery after the operation.

Inorganic salts have been reported to affect the solubility of organic component in an aqueous-organic solvent mixture. The distribution of the solute between the two liquid phases mainly depends upon the concentration of salt. Specifically, adding salt to an aqueous solution of an organic acid can result in either decrease or increase in solubility of the solute in the solution (Khuntia and Swain, 2006). Several researchers in the past have worked on liquid-liquid extraction system but few of them have worked on the salt effect on liquid-liquid extraction system. Tan and Aravinth (1999) studied effects of sodium chloride (NaCl) and potassium chloride (KCl) on liquid-liquid equilibrium (LLE) of water + acetic acid + 1-butanol system at different temperatures. NaCl and KCl were experimentally shown to be effective in modifying the liquid–liquid equilibrium in favour of the solvent extraction of acetic acid from an aqueous solution with 1-butanol, particularly at high salt concentrations. Both the salts marginally decreased the concentrations of 1-butanol and acetic acid in the aqueous phase while significantly increased the concentrations of the same components in the organic phase as well as in the result of LLE of propionic acid and organic solvents (isopropyl methyl ketone and isobutyl methyl ketone) containing with salt (NaCl and KCl) have been investigated by Vakili-Nezhaad et al. (2004). It is observed that the use of salt has proven to be advantageous, although a relative few significant advances and developments in this field are reported at the experimental level. Therefore, the application of salt is interested to improve the extraction of acid.

Theoretical knowledge about phase equilibrium of mixed solvent electrolytes systems is a prerequisite for process design in equilibrium system. An accurate thermodynamic model is required to calculate the liquid-liquid equilibria and the distribution of the solute between the liquid phases. Many thermodynamic models are available that is able to give an accurate description of the distribution of product between two liquid phases. It knows that presence of an electrolyte in a solvent mixture can significantly change its equilibrium and salt effect has been advantageously used in extraction. Hence, the separation by liquid-liquid extraction becomes increasingly more difficult as the tie lines become parallel to the solvent axis. By adding a suitable salt the tie lines of a liquid-liquid equilibrium mixture can be significantly changed. As a result, the several thermodynamic models have been developed to represent the liquid-liquid equilibrium in mixed solvent electrolyte systems.

มหาวิทยาลัยเทคโนโลยีสุรนารี

1.2 Research Objectives

The main objectives of this research are as below:

1.2.1 To study LLE of binary water + 1-butanol system and solubility of inorganic salt in water and in 1-butanol.

1.2.2 To study LLE of ternary water + 1-butanol + salt and LLE of water + 1-butanol + lactic acid system and correlate experimental LLE data with thermodynamic model.

1.2.3 To study effect of inorganic salts on extraction of lactic acid with 1-butanol.

1.3 Scope and limitation of the research

In this research, liquid-liquid equilibrium of water + 1-butanol and solubility of inorganic salts in water and in 1-butanol were investigated. The variables to be studied include equilibrium temperatures range of 303.15-323.15 K and salt types, i. e, NaCl, Na_2SO_4, NH_4Cl, and $(NH_4)_2SO_4$. Liquid-liquid equilibrium of water + 1-butanol + salt system under atmospheric pressure will be studied effect of salts type, salt concentration and temperatures. The salts type studied in this work are NaCl, Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$ with the concentration range of 0.1 to 3 g. The temperature studied at 303.15, 313.15 and 323.15 K. The modified extended UNIQUAC model will be used to correlate the experimental tie lines data and binary interaction parameters can be evaluated by this model. The liquid-liquid equilibrium of ternary water + 1-butanol + lactic acid system at 303.15 K under atmospheric pressure will be studied effect of lactic acid concentration in range of 0.1 to 3 M. The UNIQUAC model will be used to correlate the experimental tie lines data and binary interaction parameters can be evaluated by this model. In addition, effect of four inorganic salt type will be studied on extraction of lactic acid using 1-butanol at 303.15 K under atmospheric pressure. The salt concentration in range of 1 to 3 g will be studied in this work.

มหาวิทยาลัยเทคโนโลยีสุรนารี

1.4 Output of the research

1.4.1 LLE data of water + 1-butanol and solubility data of inorganic salt in water and in 1-butanol at temperature range of 303.15-323.15 K.

1.4.2 LLE data of water + 1-butanol + inorganic salt system at 303.15, 313.15 and 323.15 K and correlation of experimental tie lines data with modified extended UNIQUAC model.

1.4.3 LLE data of water + 1-butanol + lactic acid with varies of lactic acid concentration at 303.15 K and correlation of experimental tie lines data with UNIQUAC model.

1.4.4 The distribution coefficient and degree of lactic acid extraction with 1-butanol containing inorganic salt in aqueous solution at 303.15 K.

1.5 References

Borgardts, P., Krischke, W., Trosch, W., and Brunner, H. (1998). Integrated bioprocess for the simultaneous production of lactic acid and dairy sewage treatment. **Bioprocess Eng.** 19: 321-329.

Chaudhuri, J. B., and Pyle, D. L. (1992). Emulsion liquid membrane extraction of organic acids—I. A theoretical model for lactic acid extraction with emulsion swelling. **Chem. Eng. Sci.** 47: 41-48.

Kertes, A. S. and King, C. J. (1986). Extraction chemistry of fermentation product carboxylic acids. **Biotechnology and Bioengineering.** 28: 269-282.

Choudhury, B. and Swaminathan, T. (1998). Lactic acid extraction with trioctyl amine. **Biopro. Eng.** 19: 317-320.

Wasewar, K. L., Bert, A., Heesink, M., Versteeg, G. F., and Pangarkar, V. G. (2002). Reactive extraction of lactic acid using Alamine 336 in MIBK: Equilibria and Kinetics. **Journal of Biotechnology.** 97: 59-68.

Labbaci, A., Kyuchoukov, G., Albet, J., and Molinier, J. (2010). Detailed investigation of lactic acid extraction with tributylphosphate dissolved in dodecane. **J. Chem. Eng. Data.** 55: 228-233.

Kyuchoukov, G., Marinova, M., Albet, A., and Molinier, J. (2004). New method for the extraction of lactic acid by means of a modified extractant (Aliquat 336). **Ind. Eng. Chem. Res.** 43: 1179-1184.

Chawong, K., and Rattanaphanee, P. (2011). n-Butanol as an extractant for lactic acid recovery. **World Acad. Sci. Eng. Tech.** 56: 1437-1440.

Khuntia, M. K. and Swain, J. R. (2006). Salt effect on liquid-liquid equilibrium for ternaty system water+1-propanol+ethyl acetate. Department of Chemical Engineering National Institute of Technology Rourkela.

Tan, T. C. and Aravinth, S. (1999). Liquid-liquid equilibria of water/acetic acid/1-butanol system-effect of sodium (potassium) chloride and correlations. **J. Fluid Phase Equilibria.** 163: 243-257.

Vakili-Nezhaad, G. R., Mohsen-Nia, M., Taghikhani, V., Behpoor, M., and Aghahosseini, M. (2004). Salting-Out effect of NaCl and KCl on the ternay LLE data for the systems of (water+propionic acid+isopropyl methyl ketone) and of (water+propionic acid+isobuthyl methyl ketone). **J. Chem. Thermodymamics.** 36: 341-348.

มหาวิทยาลัยเทคโนโลยีสุรนารี

CHAPTER II

LIQUID-LIQUID EQUILIBRIUM OF WATER + 1-BUTANOL + INORGANIC SALT SYSTEM

2.1 Abstract

Liquid-liquid equilibrium (LLE) of mixed solvent electrolyte systems containing 1-butanol, water and salt at temperatures of 303.15, 313.15 and 323.15 K under atmospheric pressure have been studied experimentally and theoretically. The Effect of different inorganic salts on the LLE data for the ternary systems was also investigated. The results showed that the inorganic salts studies in this work, i. e., Na_2SO_4, $(NH_4)_2SO_4$, NaCl and NH_4Cl appeared to decrease mutual solubility between water and 1-butanol and enlarge the area of two-phase region of the phase diagram, particularly at high salt concentration. The temperature in the range studied here was found to have a minor effect on the LLE behavior of this system. Experimental LLE data were correlated by a modified extended UNIQUAC model, which is generally used to describe phase behavior of water and organic solvent mixtures containing inorganic salts. The model, which consists of the original UNIQUAC term, the Pizer-Debye-Hückel term and the Born term, for contribution of the excess Gibbs free energy, was found to satisfactory agree with the LLE data. The average absolute deviation between the calculated and measured mass fractions of the mixture components was less than 0.91%.

มหาวิทยาลัยเทคโนโลยีสุรนารี

2.2 Introduction

Modeling of electrolyte systems and more specifically, mixed solvent-electrolyte systems is important in chemical engineering because this type of mixture is found in many processes such as extractive crystallization and liquid-liquid extraction for mixtures containing of salt (Thomsen et al., 2004). The presence of dissolved salt changes the phase equilibrium behavior of the mixture significantly. The addition of non-volatile solute to a solvent mixture modifies the interaction among the various solvent solute molecules resulting in shifting their phase equilibrium even to the extent of eliminating the solute in liquid-liquid equilibrium. Salt mainly affects the solubility of organic component in an aqueous-organic solvent mixture. The distribution of the solute between the two liquid phases mainly depends upon the concentration of electrolyte. Specifically, adding salt to an aqueous solution of an organic acid can result in either decrease or increase in solubility of the solute in the solution (Ghalami-Choobar et al., 2011). If the solute solubility is increased upon addition of salt, the effect is called “salting in”. On the other hand, if its solubility is diminished when the salt is added, the effect is called “salting out”. It can be used in separation process such as extraction to alter the miscibility gabs to change the distribution coefficient of the solute.

Addition of the salt to an aqueous solution of LLE mixture solvent system increases its heterogeneity significantly. The area of heterogeneity is more as compared to no salt condition. Salt mainly affects the solubility of solute and water and the distribution coefficient of solute. Process selectivity, which is a ratio of distribution coefficient of solute to that of water, is also changed significantly upon salt addition. Experimental as well as theoretical knowledge about phase equilibrium of mixed solvent electrolyte systems is a prerequisite for process design in such systems. Several thermodynamic theories have been developed to represent in LLE of mixed solvent containing electrolytes systems such as electrolyte NRTL model (Santos et al., 2001; Vakili-Nezhaad et al., 2004 and Bhupesh et al., 2007) and extended UNIQUAC model (Thomsen et al., 2004).

Pirahmadi et al. (2010) presented a modified extended UNIQUAC model by explicitly taking into account the effect of mixed solvent on the liquid-liquid equilibrium of 1-butanol/water/sodium nitrate system at temperature of 25 and 30°C. The extended UNIQUAC model has previously been used for correlation of liquid-liquid equilibrium in aqueous salt systems containing alcohols. In that model the excess Gibbs energy consists of two terms, the original UNIQUAC term and Debye–Hückel term which considers the alcohol as a nonelectrolyte solute. In this work, a modified extended UNIQUAC model is used by taking into account mixed solvent theories. The model consists of three terms, the original UNIQUAC term, Pitzer–Debye–Hückel term and Born term. The model has been found to give a satisfactory description of LLE data obtained in this work.

This Chapter studied salting-out agents from the "Hofmeister series" (Hofmeister, 1888) for separating 1-butanol from aqueous solution. The LLE behavior of 1-butanol-water system presence of Na_2SO_4, $(NH_4)_2SO_4$, NaCl and NH_4Cl are measured. The LLE behavior is elucidated by correlating experimental data with modified extended UNIQUAC model.

2.3 Theory

2.3.1 Hofmeister Series

The empirical Hofmeister series (Hofmeister, 1888) relates to the minimal concentrations of various salts required to precipitate a given protein from aqueous solution. There emerged an ordering of the ions depending on their effectiveness, measured by concentration required to precipitate the protein. For a given anions, the series is generally written as (Nostro and Ninham, 2012):

$$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^{-} > F^{-} > Cl^{-} > Br^{-} \approx NO_3^{-} > I^{-} > ClO_4^{-} > SCN^{-}$$

A less well developed series exists among cations is shown as following (Pegram and Record, 2007 and Cacace et al., 1997):

$$(CH_3)_4N^{+} > (CH_3)_2NH_2^{+} > K^{+} \approx Na^{+} > Cs^{+} > Li^{+} > NH_4^{+} > Mg^{+} >> C(NH_2)_3^{+}$$

The effect of addition of salt into solutions of non-electrolytes is very complex, due to the different types of intermolecular interactions that involve the ions, the solvent, and the solute molecules. The salt effect theories are generally concerned with salting in and salting out effect, and is used to indicate the degree of the salt effect. The causes and effects of polar attraction of a dissolved salt for one component of a water non-electrolyte solution have been explained by various theories. These theories can be explained with respect to hydration, water dipole, electrostatic interaction, van der Waals forces and internal pressure.

มหาวิทยาลัยเทคโนโลยีสุรนารี

2.3.2 Mechanisms of the Salt Effect

2.3.2.1 Hydration Theory

This theory, salt ions attract and order surrounding a constant number of water molecules forming hydration shell, thereby decreasing the activity of the water. This bound water is then unavailable as solvent for the non-electrolyte. The number of water molecules so bound by each salt ion is called the hydration number of the ion. The hydration number is the number of solvating immobilized water molecules per single ion, depends on the type of hydration. The water molecules confined in the hydration shell are strongly influenced by ionic field. Generally, cations have a higher degree of hydration than anions. The cations and anions are responsible for salting out and salting in, respectively, and that the net salting effect of an electrolyte depends on the balance of these two opposing forces. The major part of the hydration theory explains the differences in effects due to solutes and ions by assuming that each ion orients water molecules in a definite direction, and has no effect on the solvent properties. Most importantly, the hydration theory is not explained in the salting in effect.

In the system of liquid-liquid equilibrium containing salt, when the salt ions are solvated, then water molecule become unavailable for the solutions. As a result, the solutes are salted out from the aqueous phase. This salt effect can be used for removing organic compounds from water. On the other hand, when a polar solvent is added to an aqueous salt solution, it captures the water molecules that were solvating the ions in a salting in affect. This effect may be used for recovering salt from concentrated aqueous solutions.

2.3.2.2 Water Dipole Theory

This theory considers that the solvent dipole molecules in the hydration shell around an ion are oriented. Cations attract the partially negative oxygen atom, whereas anions attract the partially positive hydrogen side. Therefore, ions play a significant role in enhancing or disfavoring the orientation of the water molecules toward the non-electrolyte solute, depending on the ionic charge. Thus, if there is a preferred orientation of water molecules toward a polar solute, then the ions of one sign should have a tendency to increase its solubility (salting-in), while those of opposite sign should have a tendency to decrease its solubility (salting-out). It has been suggested that, if the structure of the electrolyte is such that it affects the field beyond its hydration shell, then it will affect the water dipoles, which will determine whether salting out or salting in will occur (Grover and Ryall, 2004).

2.3.2.3 Electrostatic Theory

Electrostatic theory was developed by Debye and McAuley in 1925. This theory considers the difference in work necessary to discharge the ions in pure solvent from that required in a solution when the salt is dissolved in a solution containing non-electrolyte, due to a change in the dielectric constant produced by presence of the polar solute. This theory therefore related both salting in and salting out to influence of the solute on dielectric constant of the solvent. On that basis, if the saturated solution of solute has a dielectric constant less than water, the salting out occurs, and if the saturated solution has a dielectric constant more than water, then salting in occurs.

2.3.2.4 Van der Waals Forces Theory

The basis of this theory is that short-range electrostatic interactions occur between ions and neutral molecules. They depend on properties such as polarizability and ionizability of salt, solvent molecules, and non-electrolyte solute molecules. The concept of van der Waals forces is supported by the fact the predicted salting in of large ions. In the presence of the large ions having weak electrostatic fields or in the presence of rather undissociated salt, the highly polar water molecule may tend to associate much more strongly with each other than with the solvent forcing the salt into the vicinity of the less polar non-electrolyte molecules with which the salt is associated.

2.3.2.5 Internal Pressure Theory

According to the internal pressure concept proposed by Tammann (1926) and applied by McDavit and Long (1952), the concentration in total solution volume upon the addition of salt to water can be thought of as a compression of the solvent. This compression makes the introduction of a molecule of nonelectrolyte more difficult, and this result in salting out. An increase in total volume upon the addition of a salt would produce the counter effect known as salting in. McDavit and Long (1952), applied the internal pressure concept of Tammann (1926) to non-polar and non-electrolytes, calculated the free energy of the transfer of the latter from pure water to the salt solution.

2.3.3 Salting-In and Salting-Out Effect

Addition of salt to a solvent mixture can significantly change the interaction between the solvent and solute molecules resulting in shifting of the phase equilibrium. The salt mainly affects the solubility of organic component in an aqueous-organic solvent mixture. When the ions are solvated, some of the water becomes unavailable for solute which is then salted out from the aqueous phase. This can be exploited to remove organic compounds from water. This is known as salting-out effect which means the solubility of the solutr decreases with increasing salt concentration in the system. The water molecules which surround the ions are not available for the solution of non-electrolytes. The reason given for the greater effectiveness of the smaller ions is that these have a greater charge density for a given volume of ion and that it is this property which dictates the degree of hydration of the ion, and hence it is salting-out power. The rule that the salting-out power of an ion decreases as its size increases are, however, only roughly true and there are exceptions, particularly in the case of the small cations.

On the other hand, salting in occur when a polar solvent is added to an aqueous salt solution and is preferentially solvents the water and hence breaks the hydration cages previously formed around the salt ions. The concept of ion hydration, used to explain salting out, does not explain why very large ions can enhance the solubility. This effect may be due in part to the large attractive forces, which will exist between the non-polar part of these ions and the solute molecules. These ion-solute interactions would be expected to increase with the size of the ion and would tend to produce a congregation of non-electrolyte molecules around the ions at the expense of the water molecules. A large ion with an unsymmetrical charge distribution and a prominent non-polar region might be expected to show this effect particularly strong, and such ions do in fact cause salting-in in many cases.

2.3.4 Thermodynamics Model

A very important part of the modeling of separation processes is the modeling of phase equilibrium. The most relevant phase equilibrium for the work in this thesis is liquid-liquid equilibrium (LLE). This type of equilibrium has in common that the overall mixture has to split up into two liquid phases to reach a stable state, called equilibrium. This equilibrium can be represented by thermodynamic equations. Excellent descriptions on this subject can be found in the books by Smith and Van Ness (1987) and the book by Prausnitz et al. (1999).

2.3.4.1 Liquid-Liquid Equilibrium

At liquid-liquid equilibrium, the composition of the two phases (aqueous phase & organic phase) can be determined from the following equations:

$$(x_i\gamma_i)_I = (x_i\gamma_i)_{II} \tag{2.1}$$

$$\sum x_{i_I} = \sum x_{i_{II}} = 1 \tag{2.2}$$

x_i and γ_i are mole fraction and activity coefficient for component *i* and subscripts *I*, *II* represent the equilibrium aqueous and organic phase. This method of calculation gives a single tie line.

2.3.4.2 Modified Extended UNIQUAC Model

The modified extended UNIQUAC model (Modified Extended Universal Quasi-Chemical Model) for the excess Gibbs energy which is used in this research consists of three contributions; the first contribution is an original UNIQUAC term as given by Abrams and Prausnitz (1975) accounting for short-range

มหาวิทยาลัยเทคโนโลยีสุรนารี

entropic and energetic effects in the mixture. A Pitzer–Debye–Hückel (PDH) contribution (Pitzer, 1980) is contributed to long-range interaction effects. Finally, The Born term is added to the model in order to explain energy associated with the transfer of ionic species from an infinite dilution state in the mixed solvent to an infinitively dilute aqueous phase (Marcus, 1985). The excess Gibbs free energy is therefore given as:

$$\frac{G^{E}}{RT}=\frac{G^{E,UNIQUAC}}{RT}+\frac{G^{E,PDH}}{RT}+\frac{G^{E,Born}}{RT} \tag{2.3}$$

The UNIQUAC contribution for excess Gibbs energy is given as follows (Abrams and Prausnitz, 1975):

$$\frac{G^{E,UNIQUAC}}{RT}=\frac{G^{E,Comb}}{RT}+\frac{G^{E,\mathrm{Res}}}{RT} \tag{2.4}$$

The combinatorial and the residual terms are identical to the terms used in the traditional UNIQUAC equation. The combinatorial, entropic term is

$$\frac{G^{E,Comb}}{RT}=\sum_{j}x_{j}\ln\frac{\phi_{j}}{x_{j}}+5\sum_{j}q_{j}x_{j}\ln\frac{\theta_{j}}{\phi_{j}} \tag{2.5}$$

The parameters ϕ and θ are the surface and volume fractions, respectively. They depend on the volume and surface area parameters r_i and q_i:

มหาวิทยาลัยเทคโนโลยีสุรนารี

$$\phi_i = \frac{x_i r_i}{\sum_i x_i r_i} \tag{2.6}$$

$$\theta_i = \frac{x_i q_i}{\sum_i x_i q_i} \tag{2.7}$$

The residual, enthalpic term is

$$\frac{G^{E,\mathrm{Res}}}{RT} = \sum_j q_j x_j \ln \sum_k \theta_k \psi_{jk} \tag{2.8}$$

The parameter ψ_{kj} is defined in terms of the binary energy interaction parameter a_{kl}:

$$\psi_{kl} = \exp\left(-\frac{u_{kl} - u_{ll}}{RT}\right) = \exp\left(-\frac{a_{kl}}{T}\right) \tag{2.9}$$

Where $a_{kl} \neq a_{lk}$ and $a_{kk} = a_{ll} = 0$, u_{kl} and u_{ll} are characteristic parameters of the energy of the *k*–*l* interactions, and are dependents of temperature. With the residual term, short-range interactions of a centre molecule with its surrounding next neighbors are introduced using binary interaction parameters (*a*). Interaction parameters describe the sum of interactions between a nearest neighbor and a centre molecule over the various binary interactions occurring per compound pair. The interactions between identical and different molecule pairs are described by a number of binary interaction parameters (Sabine et. al., 1997).

มหาวิทยาลัยเทคโนโลยีสุรนารี

By partial molar differentiation of the combinatorial and the residual UNIQUAC terms, the combinatorial and the residual parts of the rational, symmetrical activity coefficients are obtained

$$\frac{G^{E,UNIQUAC}}{RT} = \sum_j x_j \ln\frac{\phi_j}{x_j} + 5\sum_j q_j x_j \ln\frac{\theta_j}{\phi_j} + \sum_j q_j x_j \ln\sum_k \theta_k \psi_{kj} \tag{2.10}$$

The PDH excess Gibbs energy is given as

$$\frac{G^{E,PDH}}{RT} = -\frac{4A_x I_x}{\rho}\ln(1+I_x^{1/2}) \tag{2.11}$$

The mole fraction ionic strength I_x is defined as

$$I_x = \frac{1}{2}\sum z_i^2 x_i \tag{2.12}$$

A_x is the Debye–Hückel parameter on a mole fraction basis and can be evaluated as

$$A_x = \frac{1}{3}\left(\frac{1000}{M_s}\right)^{1/2}\left(\frac{2\pi N_A d_s}{1000}\right)^{1/2}\left(\frac{e^2}{4\pi\varepsilon_0 D_s kT}\right)^{3/2} \tag{2.13}$$

e is electronic charge, N_A is Avogadro’s number, ε_0 is the vacuum permittivity and k is Boltzmann’s constant. M_s, d_s and D_s are the molar mass, density and dielectric constant of mixed solvent, respectively, which are defined as follows:

มหาวิทยาลัยเทคโนโลยีสุรนารี

$$M_s = \sum_j x_j^{'} M_j \tag{2.14}$$

$$d_s = \frac{M_s}{\sum_j (x_j^{'} M_j / d_j)} \tag{2.15}$$

$$D_s = \sum_j w_j^{'} D_j \tag{2.16}$$

where $w_j^{'}$ and $x_j^{'}$ are the salt free mass fraction and mole fraction of solvent *j*, respectively. M_j, d_j and D_j are the molar mass, density and dielectric constant of solvent *j*. The parameter ρ is related to a hard-core collision diameter or the distance of closest approach of ions in solution. The Born contribution to the excess Gibbs energy is given as (Marcus, 1985):

$$\frac{G^{E,Born}}{RT} = \frac{e^2}{2kT}\left(\frac{1}{4\pi\varepsilon_0 D_s} - \frac{1}{4\pi\varepsilon_0 D_w}\right)\sum_j \frac{x_i z_i^2}{\sigma_i} \tag{2.17}$$

าวิทยาลัยเทคโนโลยีสุรนาร

where D_w is dielectric constant of water, and σ is the Born radius of the ions. Based on Eq. (2.3), the activity coefficients of ions and solvents can be separated into terms arising from relevant contributions:

$$\ln \gamma_i^{*} = \ln \gamma_i^{*UNIQUAC} + \ln \gamma_i^{*PDH} + \ln \gamma_i^{*Born} \tag{2.18}$$

$$\ln \gamma_j = \ln \gamma_j^{UNIQUAC} + \ln \gamma_j^{PDH} + \ln \gamma_j^{Born} \tag{2.19}$$

j and *i* refer to solvent and ions respectively, and the asterisk shows that activity coefficients of the ions are defined using asymmetric convention. The activity coefficient of solvents and the asymmetrical activity coefficient of ions can be derived by straight-forward differentiation of excess Gibbs function:

$$\begin{aligned}\ln \gamma_j^{PDH} = & \frac{2A_x I_x^{3/2}}{1+\rho I_x^{1/2}} + \frac{4A_x I_x}{\rho}\ln(1+\rho I_x^{1/2})\left[\frac{1}{2M_s}\frac{\left(M_j - M_s\right)}{\sum\limits_{solvent} x_{solvent}}\right. \\ & \left. - \frac{1}{2d_s}\frac{\partial d_s}{\partial x_j} + \frac{3}{2D_s}\frac{\partial D_s}{\partial x_j}\right]\end{aligned} \tag{2.20}$$

$$\ln \gamma_j^{Born} = -\frac{e^2}{2kT}\frac{1}{4\pi\varepsilon_0 D_s^2}\frac{\partial D_s}{\partial x_j}\sum_i \frac{x_i z_i^2}{\sigma_i} \tag{2.21}$$

$$\begin{aligned}\ln \gamma_j^{UNIQUAC} = & 1 - \frac{\phi_j}{x_j} + \ln\left(\frac{\phi_j}{x_j}\right) - 5q_j\left[\ln\left(\frac{\phi_j}{\theta_j}\right) + 1 - \frac{\phi_j}{\theta_j}\right] \\ & + q_j\left[1 - \ln\left(\sum_k \theta_k \psi_{kj}\right) - \sum_k \frac{\theta_k \psi_{jk}}{\sum\limits_l \theta_l \psi_{lk}}\right]\end{aligned} \tag{2.22}$$

$$\ln \gamma_i^{*PDH} = -\frac{2A_x z_i^2}{\rho}\ln(1+\rho I_x^{1/2}) - \frac{2A_x I_x^{1/2} z_i^2}{1+\rho I_x^{1/2}} \tag{2.23}$$

$$\ln \gamma_i^{*Born} = -\frac{e^2}{2kT}\left(\frac{1}{4\pi\varepsilon_0 D_s} - \frac{1}{4\pi\varepsilon_0 D_w}\right)\frac{z_i^2}{\sigma_i} \tag{2.24}$$

$$\ln \gamma_i^{*UNIQUAC} = \ln \gamma_i^{UNIQUAC} - \ln \gamma_i^{\infty UNIQUAC} \tag{2.25}$$

The infinite dilution terms are obtained by setting x_w=1 in Eq. (2.8)

$$\begin{aligned} \ln \gamma_i^{\infty UNIQUAC} = {} & \ln\left(\frac{r_i}{r_w}\right) + 1 - \frac{r_i}{r_w} - 5q_i\left[\ln\left(\frac{r_i q_w}{r_w q_i}\right) + 1 - \frac{r_i q_w}{r_w q_i}\right] \\ & + q_i\left[1 - \ln \psi_{wi} - \psi_{iw}\right] \end{aligned} \tag{2.26}$$

The values of volume and surface area parameters (*r* and *q*) for lactic acid have been taken from Paticia et al. (2007), while the values of water, 1-butanol and ions have been extracted from Mascus (1997) and Pirahmadi et al. (2010 and 2012). In Table 2.1, the value of r and q are given for all components.

Table 2.1 The volume (*r*) and surface area (*q*) parameters for UNIQUAC model

	Water	**1-Butanol**	**NH_4^+**	**Na^+**	**Cl^-**	**SO_4^{2-}**
r	0.9200	3.9243	0.5570	0.1820	1.0200	2.0920
q	1.4000	3.6600	0.6860	0.3260	1.0250	1.6560

2.3.4.3 Estimation of Parameters

From the above description of the modified extended UNIQUAC model, it can be seen that the parameters in the model are the binary interaction parameter a_{ij} for the interaction between species *i* and *j*. The water-1-butanol, water-ion, 1-butanol-ion and ion-ion interaction parameters have been correlated using experimental data. Due to the limited experimental data sets in this research, all adjustable parameters have been determined by minimizing the differences between the experimental and calculated mass fractions for each of the components over all tie lines, using following objective function (*OF*) from Pirahmadi et al. (2012):

$$OF = \sum_{j=1}^{M}\sum_{i=1}^{N}\left[\left(w_{ij}^{calc} - w_{ij}^{\exp}\right)_{I}^{2} + \left(w_{ij}^{calc} - w_{ij}^{\exp}\right)_{II}^{2}\right] \tag{2.27}$$

The quality of this correlation is measured by the average root mean square absolute deviation of component mass fraction in both phases:

$$\%\Delta w = 100\left[\frac{\sum_{j=1}^{M}\sum_{i=1}^{N}\left[\left(w_{ij}^{I,\exp} - w_{ij}^{I,calc}\right)^{2} + \left(w_{ij}^{II,\exp} - w_{ij}^{II,calc}\right)^{2}\right]}{2MN}\right]^{1/2} \tag{2.28}$$

where *j* and *i* refer to solvent and ions, *M* and *N* are the number of tie-lines and the number of components, w^{calc} and w^{exp} signify mass fraction calculated by model and experimental data, *I* and *II* represent the equilibrium phase.

In this work, The binary interaction parameter is defined in equation 2.9, and these parameters were fitted to experimental data. It can be calculated the binary interaction parameters from the experimental LLE data under atmospheric pressure by step as follows the diagram in Figure C.1 on Appendix C.

2.4 Experimental Procedures

2.4.1 Chemicals

1-Butanol with 99.9% purity was purchased from Acros. Ammonium sulfate ($(NH_4)_2SO_4$), sodium sulfate (Na_2SO_4), ammonium Chloride (NH_4Cl) and sodium chloride ($NaCl$) were obtain from CARLO ERBA and deionized water was used in the experiments.

2.4.2 Procedure for Liquid-Liquid Equilibrium of Water and 1-Butanol

Equal volumes (10 ml) of deionized water and 1-butanol were added into Erlenmeyer flask and shaken with 90 rpm at desired temperature (30-80°C) in temperature-controlled shaking bath for 12 h and settling for 12 h for a complete phase separation, the mixture would split into two immiscible phases; the top phase was the 1-butanol rich phase (organic phase) and bottom phase was the water rich phase (aqueous phase). Samples of the top and bottom phase were taken for analysis of 1-butanol and water.

2.4.3 Procedure for Solubility of Inorganic Salt in Water and 1-Butanol

Solid-liquid equilibrium was obtained by using an excess amount of inorganic salt in 75 ml of the solvents. The solution was mixed in a 125 ml Erlenmeyer flask and shaken at 90 rpm at the desired temperature (30-80°C) in a temperature-controlled shaking bath for 24 h. The solution was kept still for 12 h to allow the undissolved solids to settle down in the lower portion of the solution. After enough time of solid-liquid mixing and gravitational settling, around 15 ml of clear solution was quickly taken out to another weighted measuring tube, and the compositions of saturated solutions were determined using the drying method.

2.4.4 Procedure for Liquid-Liquid Equilibrium of Water + 1-Butanol + Inorganic Salt System

The inorganic salts with quantities between 0.1 to 3 g were added into 10 ml deionized water. Equal volume of 1-butanol was then mixed with the prepared solution in 125 ml Erlenmeyer flask and shaken at 90 rpm at the desired temperature (30, 40 and 50°C) in the temperature-controlled shaking bath for 12 h and settling for 12 h. In each system, the mixture would split into two immiscible phases; the top phase was the organic phase with a small amount of dissolved salt, and the bottom phase was aqueous phase, which is rich in salt due to the higher solubility of salt in water than in 1-butanol. Samples of the top and bottom phase were taken for analysis of all components.

2.4.5 Methods of Analysis

The compositions of the top and bottom phase obtained from the liquid-liquid extraction are analyzed by the following methods:

2.4.5.1 Gas Chromatography Analysis of 1-Butanol

Concentrations of 1-butanol are analyzed by a Shimadzu Gas chromatography (GC)-14B equipped with flame ionization detector (FID) using helium (99.999 % purity) as the carrier gas. A TR-FFAP with 30m × 0.53 mm × 0.5 μm capillary column is used to separate the sample. The samples are diluted with deionized water before analysis. The oven is operated at variable-programmed temperature. Initially, the temperature of the oven is held at 50^{o}C for 3 minutes before increased to 230^{o}C at a rate of 10^{o}C/min and held for 4 minutes. Temperature of injector and detector are at 250^{o}C.

มหาวิทยาลัยเทคโนโลยีสุรนารี

2.4.5.2 Gas Chromatography Analysis of Water

Water contents are analyzed by a Varian Chrompack CP-3380 gas chromatography (GC) equipped with thermal conductivity detector using helium (99.999 % purity) as the carrier gas at a flow rate 6.5 ml/min. A 2m x 1/8 in. stainless steel column packed with Chromosorb 102 80/100 is used to separate the components. The injection temperature is 100^{o}C and the detector temperature is 250^{o}C. All samples are diluted with absolute ethanol before the analysis and the injection volume is 1 μL.

2.4.5.3 Drying of Salt

The sample of 5 ml was taken into tube for analysis of salt. Salt contents are analyzed by drying the samples at 120°C for 12 h to completely remove all the liquid.

มหาวิทยาลัยเทคโนโลยีสุรนารี

2.5 Results and Discussion

2.5.1 Liquid-Liquid Equilibrium of Binary System of 1-Butanol and Water

Equilibrium data of the binary mixtures obtained from LLE experiments of 1-butanol and water at temperature ranged from 303.15 to 353.15 K are listed in Table 2.2. Solubility of each component in the binary mixtures is represented by their mole fraction in the organic and aqueous phases. It can be seen that water and 1-butanol have some degree of mutual solubility. Each measured solubility data are very similar to the solubility data from references. It means that, these results show a good agreement with previous results. Alcohol molecule contains hydroxyl group (OH) connecting a hydrocarbon chain. The solubility of the alcohol in water depends on the balance between strength of hydrogen bonds formed between water and -OH group and the strength of the van der Waals forces between the hydrocarbon chains of the alcohol. In aqueous phase, 1-butanol molecules also make hydrogen bonds at the -OH group, 1-butanol has four numbers of carbon atoms in chain, so the hydrocarbon chain attracts one other by van der Waal's forces and water is more stable H-bonding with itself. This is a sufficient force to make 1-butanol less soluble in water.

The solubility curve of 1-butanol in water is shown in Figure 2.1. It can be seen that solubility of 1-butanol decrease with increasing of temperature until the solubility is the minimum where the temperature increases to 323.15 K. After that, the solubility is increased when the temperature increases. It should be noted that, the solubility of 1-butanol in water changes significantly with temperature. This could be due to the balance between strength of hydrogen bonds and strength of the van der Waals forces.

In addition, Table 2.2 and Figure 2.2 present measured solubility of water in 1-butanol. It can be seen that water dissolves in 1-butanol quite well. This could be that, the organic phase has more -OH group for hydrogen bonding with water molecules. In addition, the water solubility also increases with increasing of temperature; it may be because, when the temperature increases, 1-butanol molecules have more energy to break the van der Waals forces between its molecules. As a result, water molecules are likely to bind with 1-butanol molecules.

Table 2.2 Liquid-liquid equilibrium of binary water (1) and 1-butanol (2) system

Temperature (K)	**Aqueous phase**		**Organic phase**	
	$x_{2,\mathrm{Ref}}$	$x_{2,\mathrm{exp}}$	$x_{1,\mathrm{Ref}}$	$x_{1,\mathrm{exp}}$
303.15	0.0181	0.0180	0.5160	0.5182
313.15	0.0170	0.0173	-	0.5427
323.15	0.0165	0.0167	0.5440	0.5562
333.15	0.0166	0.0165	0.5620	0.5681
343.15	-	0.0171	0.5830	0.5774
353.15	0.0180	0.0177	-	0.5857

Remark: $x_{1,\mathrm{Ref}}$ and $x_{2,\mathrm{Ref}}$ are the mole fraction of water in organic phase and mole fraction of 1-butanol in aqueous phase from the references (Marian et al., 2006)

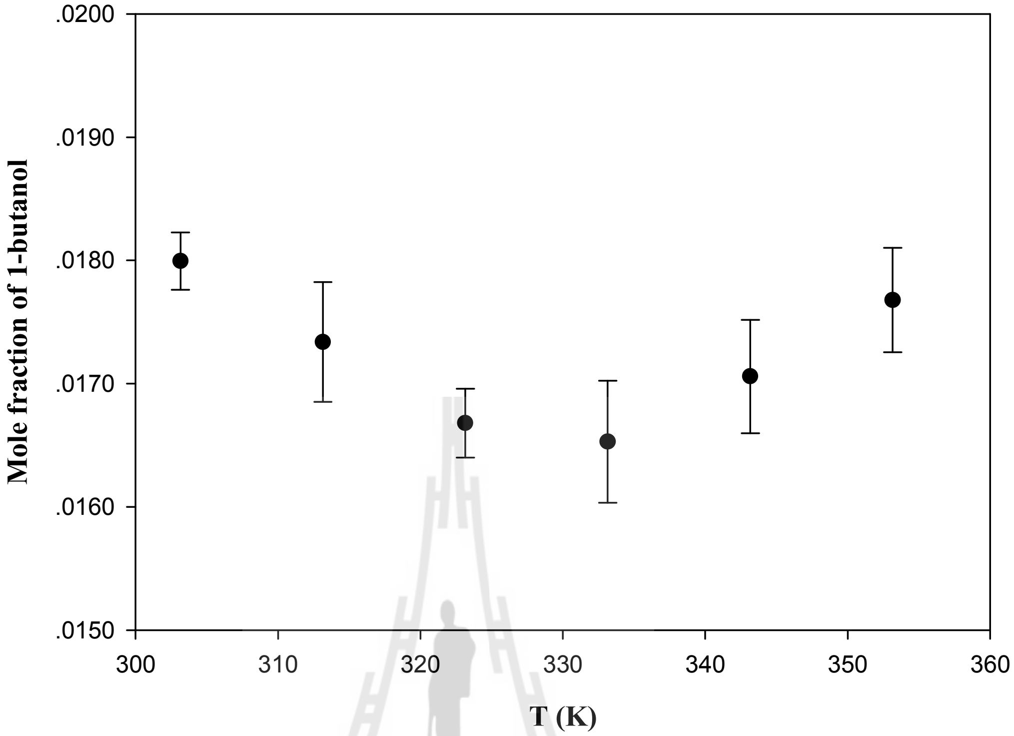


Figure 2.1 Mole fraction of 1-butanol in water at different temperature

มหาวิทยาลัยเทคโนโลยีสุรนารี

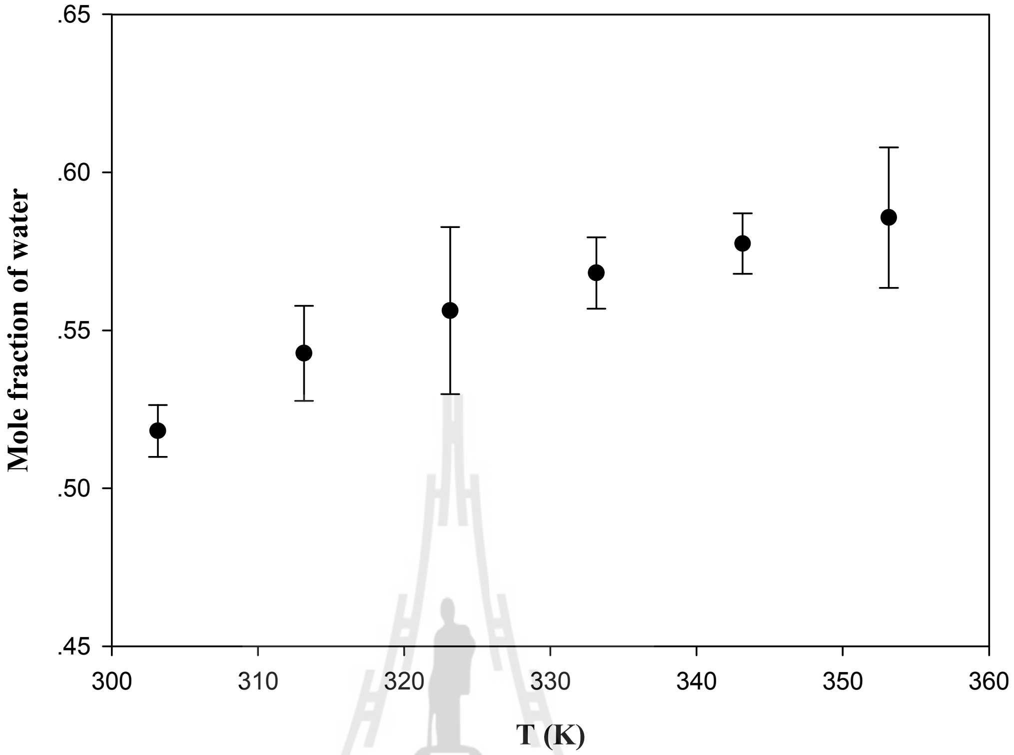


Figure 2.2 Mole fraction of water in 1-butanol at different temperature

2.5.2 Solubility of Inorganic Salt in Water and 1-Butanol

The measured solubility of NaCl, Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$, in water and 1-butanol at different temperatures range 303.15 to 353.15 K is summarized in Table 2.3 and 2.4 respectively. The measurements show that water exhibits the highest solubility to these salts at most temperatures, while 1-butanol always shows the lowest solubility. The quality of the measurement was investigated by comparing it with the values reported in the literature as shown in Table 2.3 for the systems of inorganic salt in water. It is possible to observe the good agreement of the measured data. The result observed showed that all the salts are less soluble in 1-butanol than in water. It is known that water is a polar solvent. Polar solvents are liquids whose molecules display a permanent dipole. The molecule of inorganic salt is polar because the two ions in it cause it to have different charges on each side. When dissolved in water, the water takes more energy to separate the lattice of salt. The inorganic salt framework disintegrates as the cations and anions become surrounded by the polar water molecules. Water forms layers of hydration around the ions of salt. The cations side is attracted to the oxygen side of the water molecules, while the anions side is attracted to the hydrogen side of the water molecule. This is the reason why the salt prefers to dissolve in water. On the other hand, 1-butanol is an organic compound that contains a polar -OH group; it is maybe attracted the anions of salt. It is well known that most salts are insoluble or less soluble in 1-butanol than in water.

Table 2.3 Solubility of inorganic salts in water at different temperatures

Temperature (K)	**Solubility of salt in water (g / 100 g of water)**							
	NaCl		**Na_2SO_4**		**NH_4Cl**		**$(NH_4)_2SO_4$**	
	Ref.	***Exp.***	***Ref.***	***Exp.***	***Ref.***	***Exp.***	***Ref.***	***Exp.***
303.15	36.30	36.05	40.80	39.62	41.40	39.15	78.00	78.39
313.15	36.60	36.54	48.80	48.71	45.80	44.33	81.10	80.66
323.15	37.00	36.82	46.70	46.65	50.40	48.29	84.30	83.96
333.15	37.30	37.43	45.30	45.31	55.20	53.24	88.00	87.11
343.15	37.80	37.71	-	44.38	60.20	59.08	-	90.57
353.15	38.40	38.25	47.30	43.63	65.60	62.02	95.30	94.26

Remark: *Exp.* and *Ref.* are the experimental solubility data from this work and the solubility data from Perry's Chemical Engineering Handbook.

Table 2.4 Solubility of inorganic salts in 1-butanol at different temperatures

Temperature	**Solubility of salt in 1-butanol (g / 100 g of 1-butanol)**			
(K)	**NaCl**	**Na_2SO_4**	**NH_4Cl**	**$(NH_4)_2SO_4$**
303.15	0.0025	0.0732	0.0013	0.0161
313.15	0.0073	insoluble	0.0788	insoluble
323.15	0.0102	insoluble	0.0994	insoluble
333.15	0.0071	insoluble	0.1084	insoluble
343.15	0.0045	insoluble	0.1101	insoluble
353.15	insoluble	insoluble	0.1121	insoluble

The result in Figure 2.3 shows that the solubility of inorganic salt in water is in order $(NH_4)_2SO_4$ > NH_4Cl > Na_2SO_4 > NaCl. The solubility of $(NH_4)_2SO_4$ and NH_4Cl in water considerably increases with temperature, while the solubility of Na_2SO_4 and NaCl is nearly constant with the increasing temperature. It can be explained that each salt acts differently when dissolved in water, and this is due to the physical properties of the ions in each salt. Polyatomic ions, the ions that are made of multiple atoms like NH_4^+ and SO_4^{2-} ion, will act much differently than a monatomic ion like Na^+ and Cl^- ion. When a salt crystal dissolves, the solubility of an ionic compound, therefore, depends on the strength of its ionic bonds: the stronger the bonds, the lower the solubility. The strength of the ionic bond depends on the charge density of the cation and the anion. An ion with lower charge density will form weaker ionic bonds than the ion with higher charge density (Collin, 1997). In general, polyatomic ions have large diameter and thus have lower charge densities than monatomic ions with the same charge. For this reason, the salt with polyatomic ions will be more soluble in water than the salt with monatomic ions.

Solubility in water of salt studied here was found to depend on temperature. $(NH_4)_2SO_4$ and NH_4Cl exhibit a dramatic increase in solubility with increasing of temperature. On the other hand, Na_2SO_4 and NaCl exhibit little variation. Generally, the solubility of salt in water increases with increasing of temperature. It is because, when the temperature increases, the water molecules have more energy to move around and break the chemical bonds of salt. The salt molecule is easier to split for attracted with the oppositely charged end of the dipole in the water molecule. However, there is no simple relationship between the structure of substance and temperature dependence of its solubility. There is generally no good way to predict how the solubility will vary with temperature.

The solubility of inorganic salts in 1-butanol is shown in Figure 2.4. The result showed that the chloride salts can soluble in 1-butanol, while the sulfate salts are insoluble. It should be noted that 1-butanol contains OH group, which can attracted the salt ion. However, oxygen atom is slightly negative because the eletron closer to it. Thus, there will be one side that is capable of binding with the salt ions. It is likely that the solubility of salt in 1-butanol most likely occurs significantly with ion dipole interaction between positive pole of 1-butanol and anion of salt. In addition, it is known that the salt with the polyatomic ions will be better soluble in solvent than that the monoatomic ions. This reason is clearly why NH_4Cl can soluble in 1-butanol more than NaCl.

มหาวิทยาลัยเทคโนโลยีสุรนารี

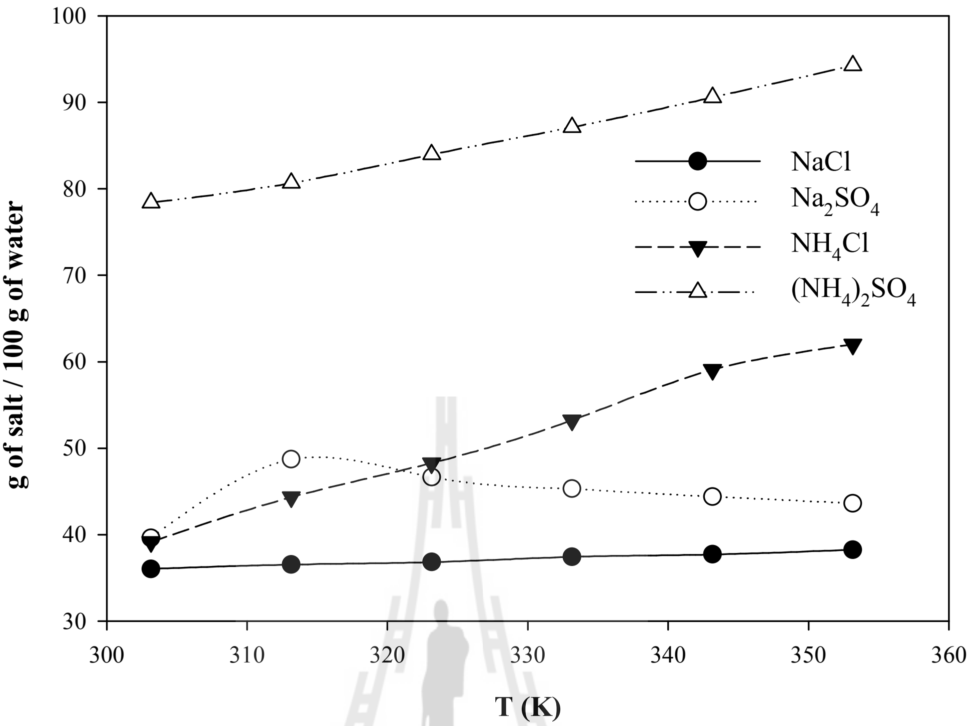


Figure 2.3 Solubility of inorganic salts in water at different temperatures

มหาวิทยาลัยเทคโนโลยีสุรนารี

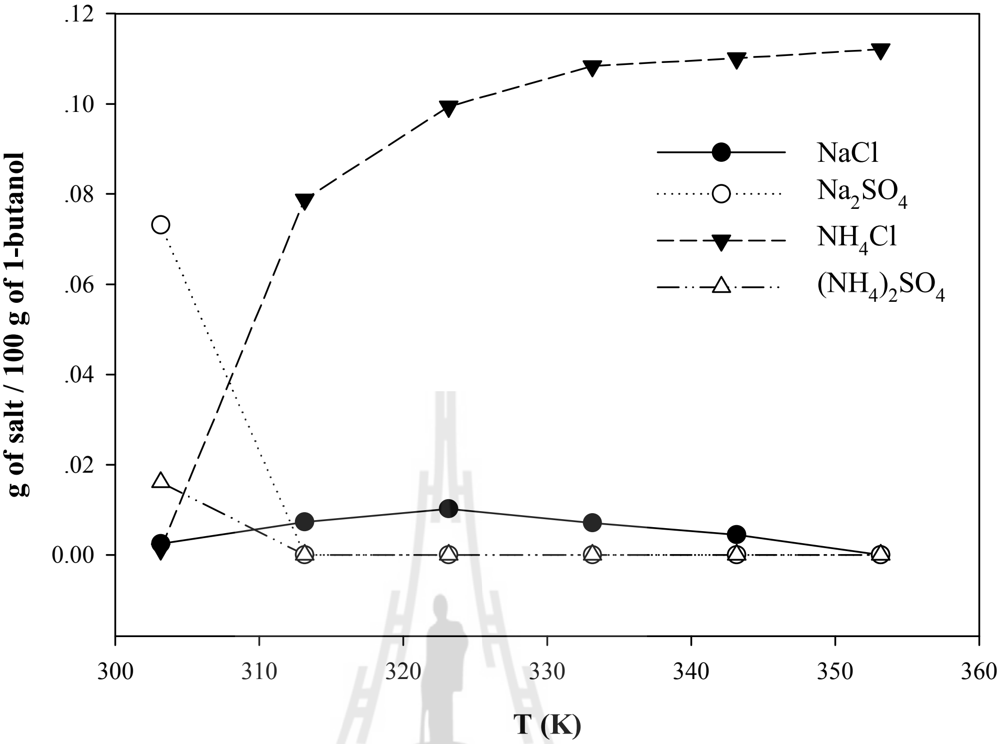


Figure 2.4 Solubility of inorganic salts in 1-butanol at different temperatures

มหาวิทยาลัยเทคโนโลยีสุรนารี

2.5.3 Liquid-liquid Equilibrium of Water + 1-Butanol + Salt System

2.5.3.1 Effect of Inorganic Salt on Liquid-Liquid Equilibrium

Experiments are conducted on the system of water + 1-butanol + inorganic salt with varying salt concentrations and varying temperatures. Four types of inorganic salts: NaCl, Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$ were investigated under the system temperatures of 303.15, 313.15 and 323.15 K. The measured LLE data of the system with; NaCl, Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$ are presented in Table 2.5-2.8 and are also depicted by the ternary diagrams in Figure 2.8-2.19, respectively. The composition are presented in terms of mass percents ($\%w_i$) and mass fraction (w_i).

It was found that, water and 1-butanol are partially miscible and the salt more soluble in water than 1-butanol, which is consistent with the results from 2.5.1 and 2.5.2. However, the presence of the salt decreases the concentration of 1-butanol in aqueous phase, especially at higher salt concentration. It means that, the presence of salt decreases the mutual solubility of the system and increasing the heterogeneous zone. Heterogeneous area is an important characteristic. It is evident from the Figure 2.8-2.19 that the area of heterogeneity for all systems with salts are larger than that the systems of without salts and this effect is observed higher in the higher concentration of salts. In addition, similar LLE behaviors are observed at all the temperature studied here. It can be observed that the temperature has a minor effect of LLE conditions which cause of the measured data were obtained over a relatively small temperature interval.

In addition, it was found that the mass percents of salt in the system of Na_2SO_4, $(NH_4)_2SO_4$ and NaCl are quite a small value while in the system of NH_4Cl is quite high. It can be observed that these results depend on the solubility of salt in 1-butanol, which NH_4Cl has the ability soluble in 1-butanol than other salts. It is explained in 2.5.2. The measured LLE data of NH_4Cl system at 298.15, 308.15 and 318.15 K from reference (Pirahmadi et. al., 2010) are shown in Table 2.9. It was observed the trend of NH_4Cl mass percents in the organic phase likely the same with experimental data here.

Table 2.5 Experimental liquid-liquid equilibrium data of water (1) + 1-butanol (2) + NaCl (3) system under atmospheric pressure

Temperature (K)	**Aqueous phase**			**Organic phase**		
	%w_1	**%w_2**	**%w_3**	**%w_1**	**%w_2**	**%w_3**
303.15	92.98	7.02	0	20.71	79.29	0
	91.84	7.12	1.04	14.68	85.30	0.02
	91.11	6.18	2.71	13.21	86.75	0.04
	90.00	4.80	5.20	10.15	89.77	0.08
	86.93	3.20	9.87	8.51	91.37	0.12
	80.58	1.69	17.73	6.89	92.95	0.16
	74.59	1.13	24.28	6.56	93.26	0.18
313.15	93.23	6.77	0	22.47	77.53	0
	92.41	6.46	1.13	14.22	85.76	0.02
	91.48	5.76	2.75	12.22	87.74	0.04
	90.04	4.62	5.34	11.97	87.95	0.08
	86.60	3.42	9.98	8.77	91.10	0.13
	80.10	1.93	17.97	7.43	92.39	0.18
	74.30	1.15	24.55	6.41	93.35	0.24
323.15	93.41	6.59	0	23.87	76.13	0
	91.19	7.67	1.13	22.60	77.36	0.04
	90.62	6.59	2.79	16.76	83.20	0.04
	89.28	5.43	5.29	14.44	85.49	0.07
	86.41	3.63	9.96	12.16	87.71	0.13
	79.98	2.10	17.92	8.06	91.75	0.18
	74.94	1.07	23.99	7.87	91.91	0.22

มหาวิทยาลัยเทคโนโลยีสุรนารี

Table 2.6 Experimental liquid-liquid equilibrium data of water (1) + 1-butanol (2) + Na_2SO_4 (3) system under atmospheric pressure

Temperature (K)	Aqueous phase			Organic phase		
	$\%w_1$	$\%w_2$	$\%w_3$	$\%w_1$	$\%w_2$	$\%w_3$
303.15	92.98	7.02	0	20.71	79.29	0
	92.44	6.38	1.18	12.82	87.17	0.01
	91.93	5.23	2.84	10.09	89.90	0.01
	90.81	3.96	5.24	9.89	90.03	0.08
	87.26	2.29	10.45	8.67	91.27	0.06
	80.83	0.82	18.36	8.23	91.76	0.02
	93.47	6.53	25.21	6.45	93.53	0.01
313.15	93.23	6.77	0	22.47	77.53	0
	92.66	6.14	1.20	16.71	83.28	0.01
	92.09	4.94	2.97	13.44	86.54	0.03
	91.11	3.41	5.48	10.65	89.33	0.01
	87.42	2.11	10.47	9.97	90.01	0.02
	81.20	0.78	18.02	8.47	91.51	0.02
	75.59	0.28	24.13	7.26	92.71	0.03
323.15	93.47	6.53	0	23.87	76.13	0
	92.85	5.96	1.19	15.16	84.80	0.04
	91.52	5.55	2.93	14.14	85.85	0.02
	90.48	3.81	5.71	12.00	88.00	0.01
	87.02	2.45	10.53	9.72	90.27	0.01
	80.83	0.93	18.24	8.95	91.04	0.01
	73.64	0.35	26.01	7.86	92.01	0.12

มหาวิทยาลัยเทคโนโลยีสุรนารี

Table 2.7 Experimental liquid-liquid equilibrium data of water (1) + 1-butanol (2) + $(NH_4)_2SO_4$ (3) system under atmospheric pressure

Temperature (K)	Aqueous phase			Organic phase		
	$\%w_1$	$\%w_2$	$\%w_3$	$\%w_1$	$\%w_2$	$\%w_3$
303.15	92.98	7.02	0	20.71	79.29	0
	93.93	5.14	0.93	8.24	91.76	0.01
	93.50	4.31	2.19	7.87	92.12	0.01
	92.25	3.62	4.13	7.73	92.25	0.02
	88.66	2.33	9.01	6.34	93.65	0.01
	83.53	0.94	15.53	5.85	94.14	0.01
	76.92	0.58	22.50	5.36	94.62	0.01
313.15	93.23	6.77	0	22.47	77.53	0
	92.41	6.35	1.24	14.24	85.76	0.00
	92.19	5.02	2.79	14.25	85.75	0.01
	90.09	3.96	5.94	9.18	90.80	0.01
	86.14	2.76	11.10	9.21	90.78	0.01
	80.22	1.17	18.61	7.08	92.92	0.01
	75.55	0.87	23.58	6.17	93.81	0.01
323.15	93.47	6.53	0	23.87	76.13	0
	92.14	6.65	1.21	11.02	88.98	0.00
	91.39	5.57	3.04	10.27	89.72	0.01
	90.19	4.23	5.58	9.94	90.05	0.01
	86.53	2.78	10.70	8.55	91.43	0.02
	79.96	1.24	18.80	7.56	92.42	0.02
	74.49	0.35	25.16	6.81	93.17	0.02

มหาวิทยาลัยเทคโนโลยีสุรนารี

Table 2.8 Experimental liquid-liquid equilibrium data of water (1) + 1-butanol (2) + NH_4Cl (3) system under atmospheric pressure

Temperature	Aqueous phase			Organic phase		
(K)	%w_1	%w_2	%w_3	%w_1	%w_2	%w_3
303.15	92.98	7.02	0	20.71	79.29	0
	92.21	6.69	1.10	15.20	84.75	0.05
	90.68	6.42	2.90	12.71	87.21	0.07
	89.10	5.63	5.27	11.11	88.72	0.17
	87.24	4.35	8.40	9.87	89.78	0.35
	82.29	2.68	15.03	7.72	91.74	0.54
	73.77	2.53	23.70	6.47	92.80	0.73
313.15	93.23	6.77	0	22.47	77.53	0
	91.88	7.01	1.11	15.30	84.66	0.04
	91.01	6.31	2.69	12.69	87.21	0.10
	89.35	5.47	5.19	11.61	88.19	0.20
	86.25	4.09	9.67	9.29	90.36	0.35
	79.63	3.04	17.33	8.28	91.13	0.59
	73.46	2.71	23.83	7.02	92.17	0.80
323.15	93.47	6.53	0	23.87	76.13	0
	90.93	8.15	0.92	11.55	88.43	0.019
	89.71	7.86	2.43	9.57	90.41	0.022
	87.90	7.25	4.85	9.03	90.90	0.069
	84.56	6.10	9.33	8.16	91.60	0.234
	78.48	4.60	16.91	5.93	93.59	0.472
	72.51	3.80	23.69	5.25	94.05	0.701

มหาวิทยาลัยเทคโนโลยีสุรนารี

Table 2.9 Experimental liquid-liquid equilibrium data of water (1) + 1-butanol (2) + NH_4Cl (3) system under atmospheric pressure (Pirahmadi et. al., 2010)

Temperature	Aqueous phase			Organic phase		
(K)	$\%w_1$	$\%w_2$	$\%w_3$	$\%w_1$	$\%w_2$	$\%w_3$
298.15	92.97	7.03	0	20.68	79.32	0
	89.79	5.95	4.26	17.87	81.97	0.16
	87.64	5.04	7.32	15.26	84.66	0.08
	84.75	4.76	10.49	14.31	85.46	0.23
	84.85	3.88	11.27	13.31	86.47	0.22
	77.47	3.76	18.77	11.78	87.71	0.51
	76.54	3.46	20.00	11.21	88.32	0.47
	74.77	3.08	22.15	9.34	89.96	0.70
308.15	93.97	6.30	0	21.52	78.48	0
	91.47	5.18	3.35	21.39	78.53	0.08
	86.37	4.52	9.11	16.51	83.06	0.43
	83.88	3.98	12.14	15.65	84.18	0.17
	81.05	3.64	15.31	17.74	84.85	0.41
	77.20	3.56	19.24	14.48	84.96	0.56
	76.21	3.35	20.44	13.65	85.61	0.74
	74.19	3.20	22.60	13.01	86.13	0.86
	72.54	3.01	24.45	12.69	86.75	0.56
318.15	93.95	6.05	0	22.77	77.23	0.00
	89.51	5.13	5.36	21.13	78.64	0.23
	87.18	4.92	7.90	18.75	80.96	0.29
	81.47	4.35	14.18	16.20	82.84	0.96
	80.91	3.77	15.32	15.55	83.83	0.62
	78.46	3.44	18.1	14.34	85.01	0.65
	75.84	3.03	21.13	13.86	85.40	0.74
	73.12	2.95	23.93	13.11	85.98	0.91
	71.67	2.56	25.77	12.85	86.23	0.92

มหาวิทยาลัยเทคโนโลยีสุรนารี

It is known that the presence of salt can significantly change the equilibrium composition. When the ions are solvated, each salt ion attracts and order surrounding water molecules forming hydration shells. The water dipole molecules in the hydration shell around an ion are oriented; cations attract the partially negative oxygen atom, whereas anions attract the partially positive hydrogen side, thereby decreasing the activity of the water. The effect is called “salting-out”. This effect can be used for removing organic compounds from water. It means that the solubility of organic compounds is decreased when the salt is added. On the other hand, if organic compounds solubility is increased upon addition of salt, the effect is called “salting-in”.

Salting-in and salting-out effect of each salt are more apparent when the mass percent of 1-butanol in aqueous phase is plotted against the ionic strength of the aqueous solution in each system. Ionic strength (*I*) is a measure of the concentration of ions in the solution and can be calculated from

$$I = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 \tag{1}$$

วิทยาลัยเทคโนโลยีสุรนาร

where C_i is molar concentration of the i^{th} ion, Z_i is the charge of the ion and *n* is the number of ions presented in the solution. The plots, depicted in Figure 2.5-2.7 for the system at 303.15, 313.15 and 323.15 K, respectively, that all the salts pose similar effect on solubility of 1-butanol in aqueous phase as the concentration of 1-butanol in this phase decreases with ionic strength of aqueous solution. It can be note that, at increasing salt concentrations more 1-butanol is less soluble in aqueous phase. This is referred to as salting-out effect. Presence of salts, mainly increase the concentrations of 1-butanol in the organic phase and hence enlargement of the two-phase region occurred. These effects increase with salt concentrations. The influence of salts in this study on the salting-out effect in the following order:

$$Na_2SO_4 > (NH_4)_2SO_4 > NaCl > NH_4Cl$$

The greatest salting-out effect salts are obviously related to the properties of ions. It can be seen that the rank of effectiveness of anions in salting-out of 1-butanol from aqueous solution is $SO_4^{2-} > Cl^-$, and rank order of cations is $Na^+ > NH_4^+$. The salts with divalent anion (SO_4^{2-}) show stronger influence on partitioning 1-butanol from aqueous solution than the salts with monovalent anion (Cl^-). When the salt is added into water and 1-butanol mixture, the water molecules surrounding the ions are unavailable, so that 1-butanol is less soluble and enriched to the organic phase. This salting out effect may be significantly affected by hydration radii and hydration number of ions added. In general, divalent ions are more effective at salting-out than monovalent ions, and ions with small radii more effective than large ions (Collins and Washabaugh, 1985). It has been observed that SO_4^{2-} has larger radii than Cl^-. However, SO_4^{2-} has a higher hydration number (see Table A.3 on Appendix 3) to hold their hydration shells more strongly, whereas the Cl^- has a lower hydration number and weaker hydration shells (Tansel et al., 2006). For cations, both ions are monovalent cations, which is the Na^+ has smaller radii and higher hydration number than NH_4^+. It is clearly for cations effect on salting-out.

In addition, it was observed that the salting-in effect in the system with NaCl and NH_4Cl at 313.15 and 323.15 K in Figure 2.6 and 2.7 where the mass percent of 1-butanol increased with the ionic strength. However, these systems induces a salting-in effect with a magnitude dependent on the salt concentration. When small amounts of NaCl and NH_4Cl was added, mass percent of 1-butanol in aqueous phase were increased, which signified that 1-butanol preferred to be in aqueous phase rather than the organic phase. Then, the decreasing mass percent of 1-butanol is, the higher concentration of NaCl and NH_4Cl. The reason why salting-in is found in the system with chloride salts, while sulfate salts present only salting-out; it may be because, the chloride ion is monovalent anion and small hydration number. When small amounts of chloride salt dissolved in water, less the ionic charge attracted to the water molecule. Therefore, this result verifies the “salting-out” effect in the present system by adding suitable amount of NaCl and NH_4Cl.

มหาวิทยาลัยเทคโนโลยีสุรนารี

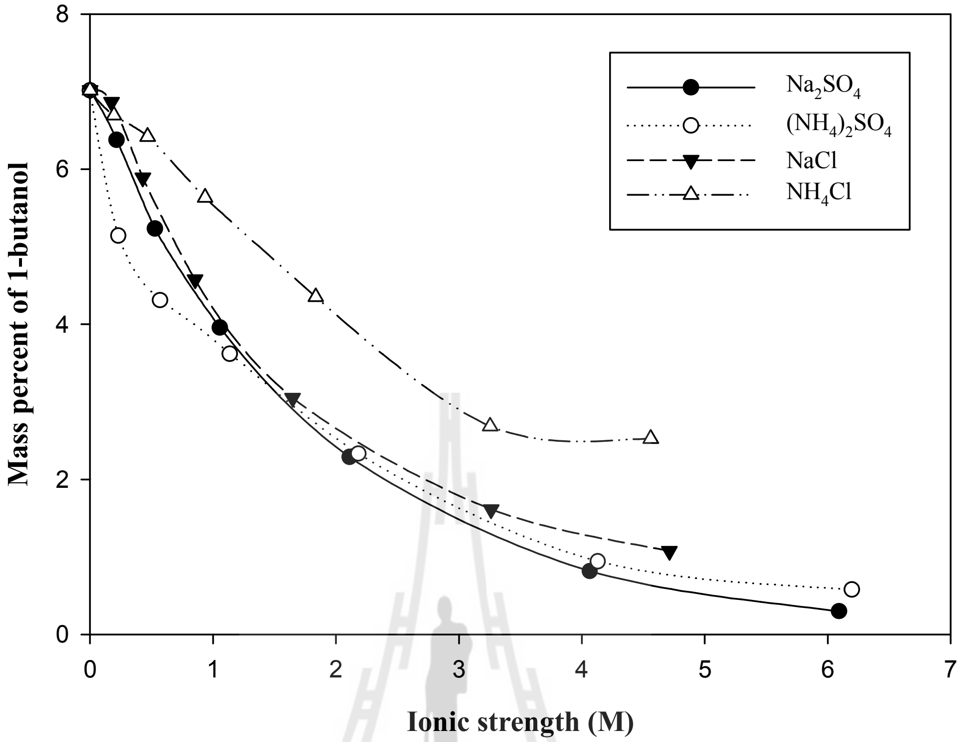


Figure 2.5 The relation between the concentration of 1-butanol and ionic strength in aqueous phase at 303.15 K

มหาวิทยาลัยเทคโนโลยีสุรนารี

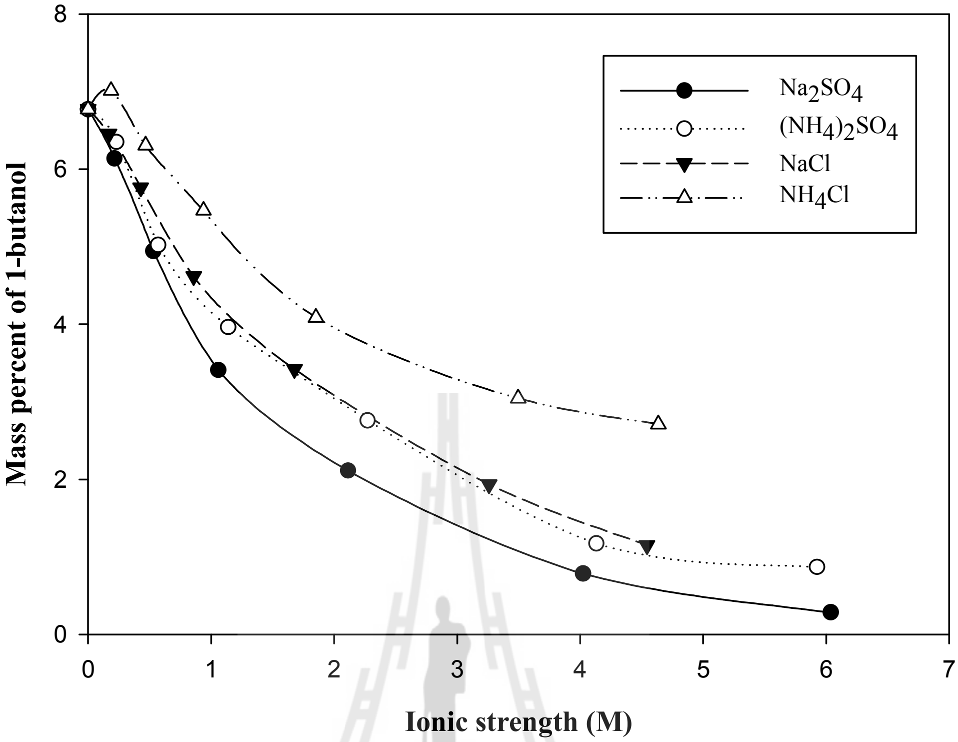


Figure 2.6 The relation between the concentration of 1-butanol and ionic strength in aqueous phase at 313.15 K

มหาวิทยาลัยเทคโนโลยีสุรนารี

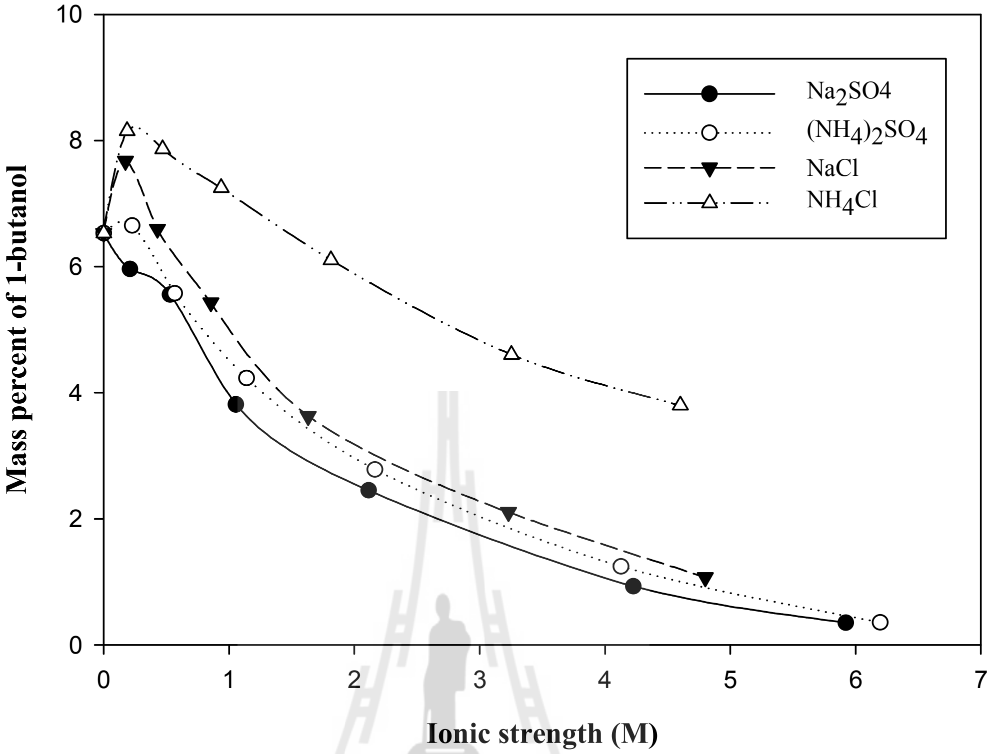


Figure 2.7 The relation between the concentration of 1-butanol and ionic strength in aqueous phase at 323.15 K

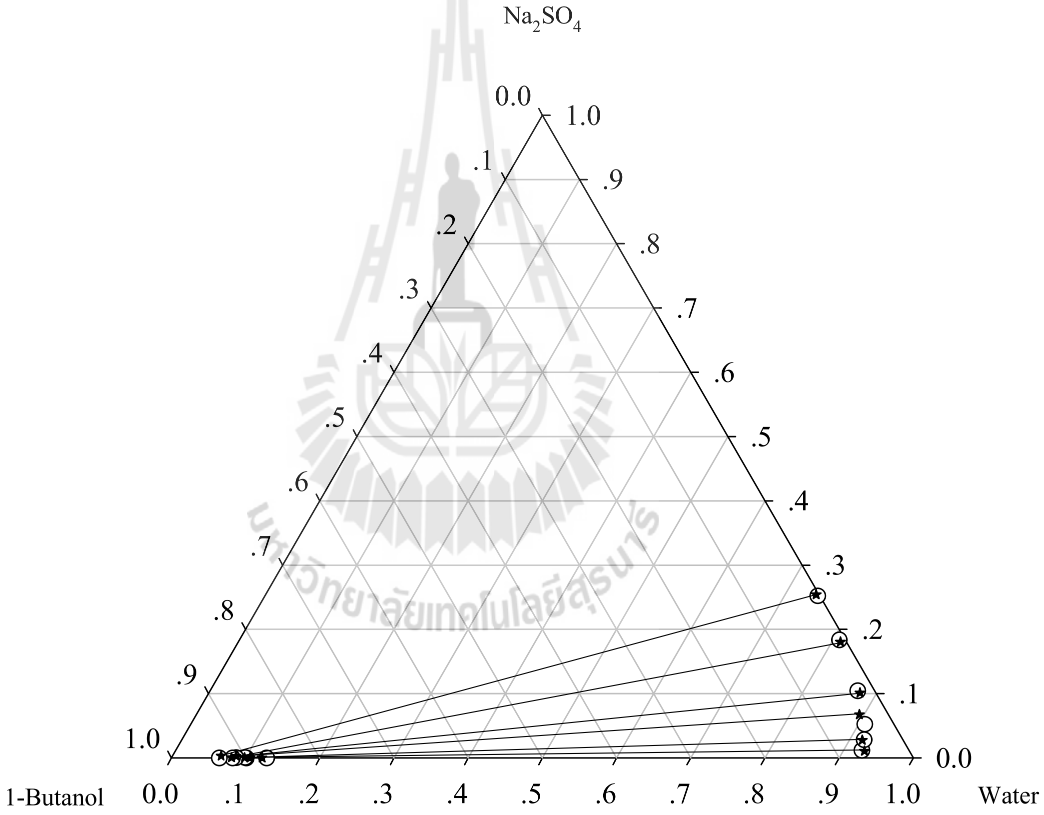
มหาวิทยาลัยเทคโนโลยีสุรนารี

2.5.3.2 Correlation Model and Evaluation of Parameters

The modified extended UNIQUAC model was used to correlate the experimental LLE data. Water and 1-butanol are considered as the solvent, where their activity coefficients are defined by symmetrical convention. The activity coefficients of cationic and anionic species from dissociation of the salt are defined using the asymmetric convention. The structure parameters r and q used in these systems are presented in Table 2.1. All adjustable interaction parameters have been determined by minimizing the differences between the experimental and calculated mass fractions for each of the components over all tie lines, using the objective function in Eq. 2-27. The quality of the correlation is measured by the root mean square absolute deviation of component mass fraction in both phases following Eq. (2.28).

The correlated results together with the experimental data for each ternary system were plotted and are shown in Figure 2.8-2.19, the ternary phase diagrams have been depicted in terms of the component mass fraction at temperatures of 303.15, 313.15 and 323.15 K in the system of Na_2SO_4, $(NH_4)_2SO_4$, NaCl and NH_4Cl, respectively. Although the 1-butanol-water interaction parameters were reported by Pirahmadi, (2010) but these parameters are not used in this works because these parameters are obtained from binary system between water-1-butanol, which is different model and system. Therefore, all binary interaction parameters; ion-water, ion-ion, water-1-butanol and ion-1-butanol have been estimated using the experimental data measured in this work. Values of binary interaction parameters obtained after the model optimization are given in Table 2.9.

The results in Figure 2.8-2.19 show that the calculated mass fraction close to experimental data for all tie lines. It can be concluded that the modified extended UNIQUAC model, with binary interaction parameters estimated by the objective function was able to successfully correlate the LLE data, This is shown the absolute deviation in Table 2.9 were less than 0.91% for all tie-lines. These results are considered very satisfactory.



มหาวิทยาลัยเทคโนโลยีสุรนารี

Figure 2.8 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + Na_2SO_4 (3) at 303.15 K.

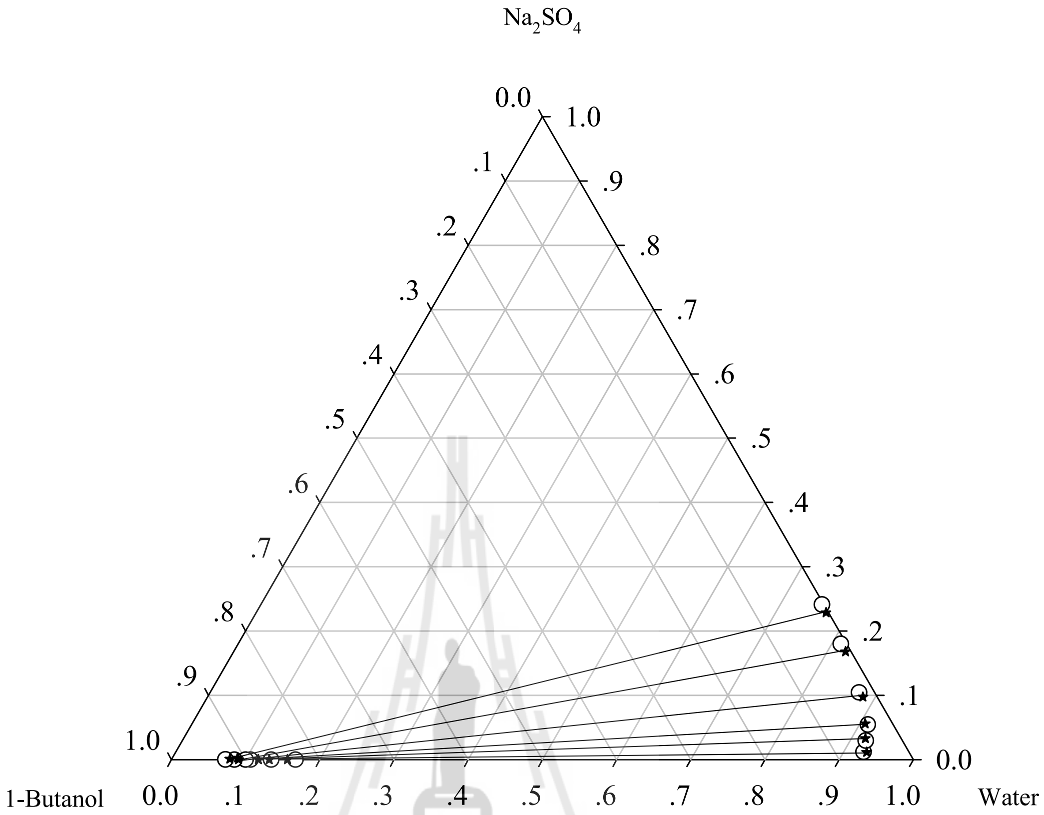


Figure 2.9 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + Na_2SO_4 (3) at 313.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

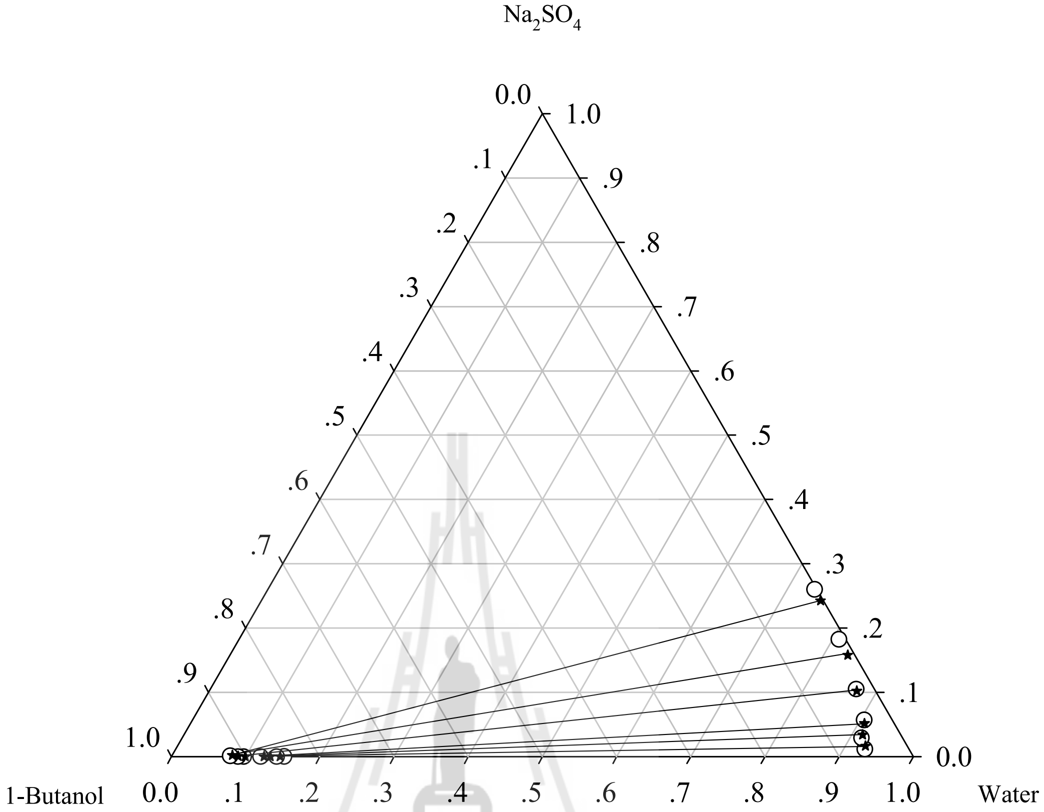


Figure 2.10 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + Na$_2$SO$_4$ (3) at 323.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

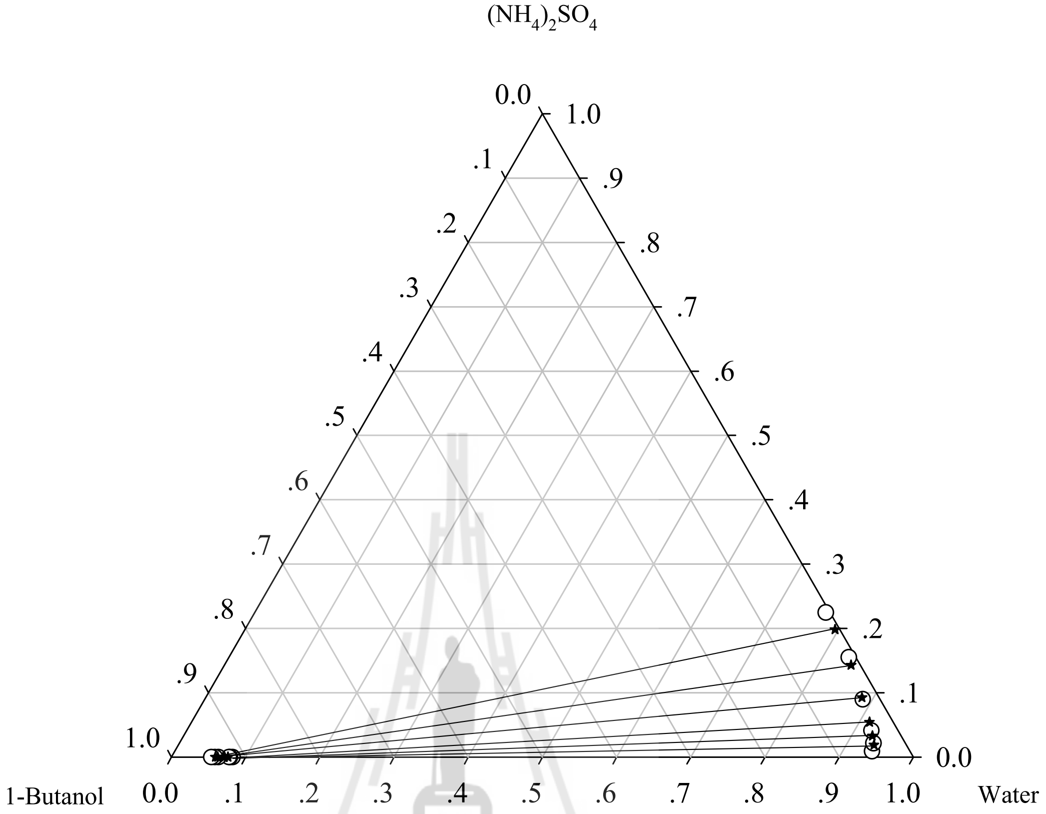


Figure 2.11 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + $(NH_4)_2SO_4$ (3) at 303.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

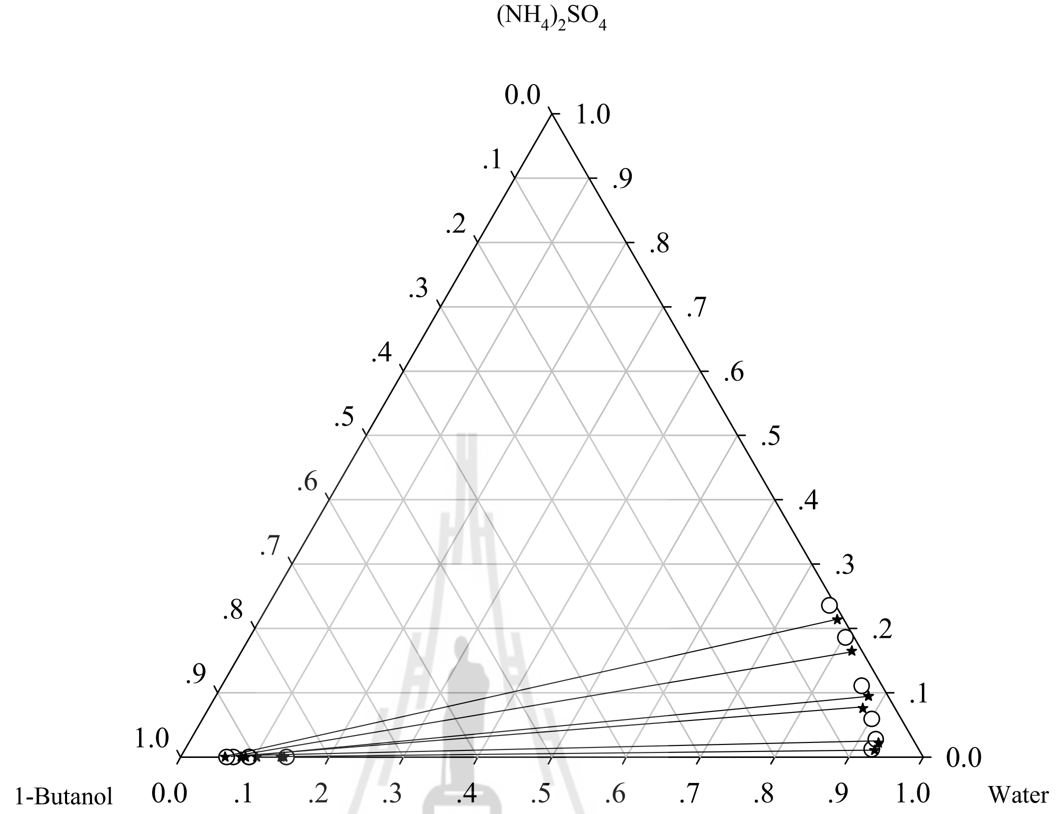


Figure 2.12 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + $(NH_4)_2SO_4$ (3) at 313.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

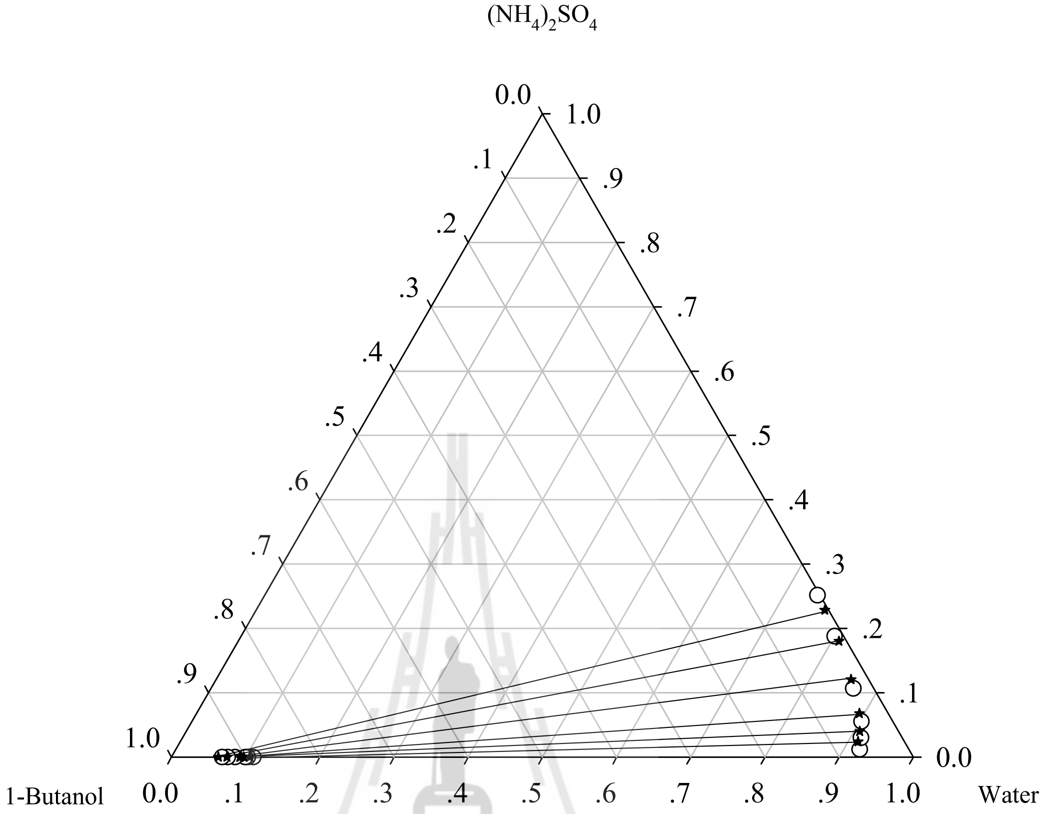


Figure 2.13 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + $(NH_4)_2SO_4$ (3) at 323.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

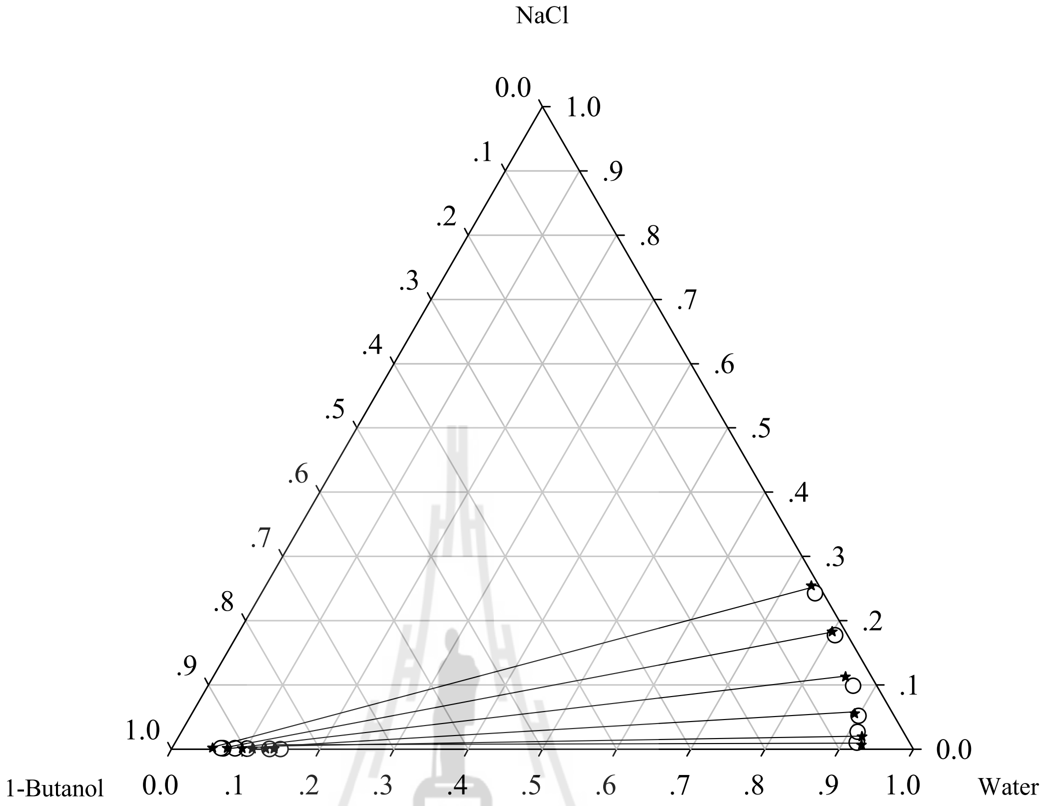


Figure 2.14 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + NaCl (3) at 303.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

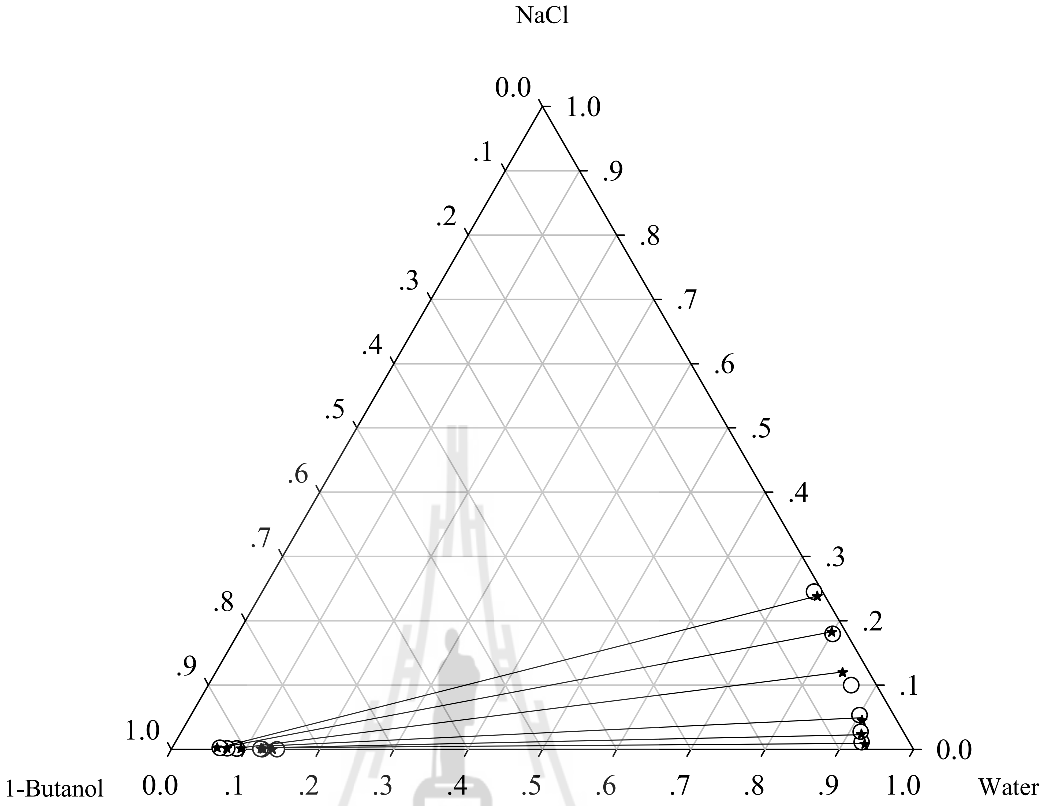


Figure 2.15 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + NaCl (3) at 313.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

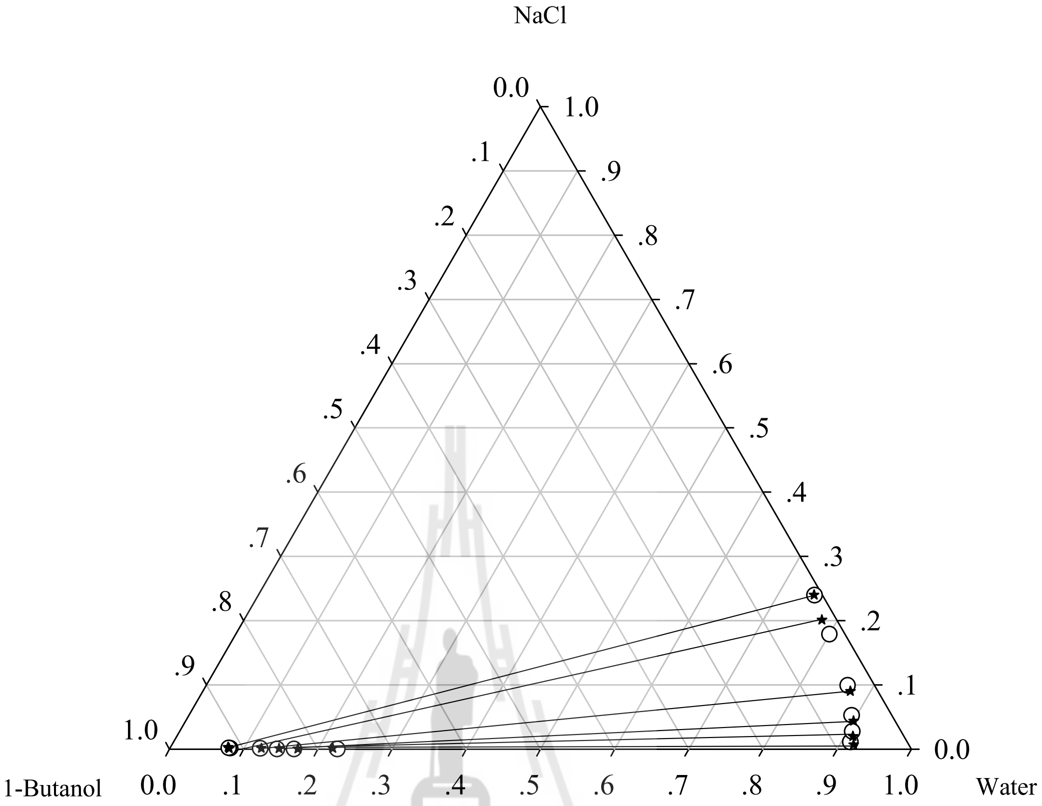


Figure 2.16 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + NaCl (3) at 323.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

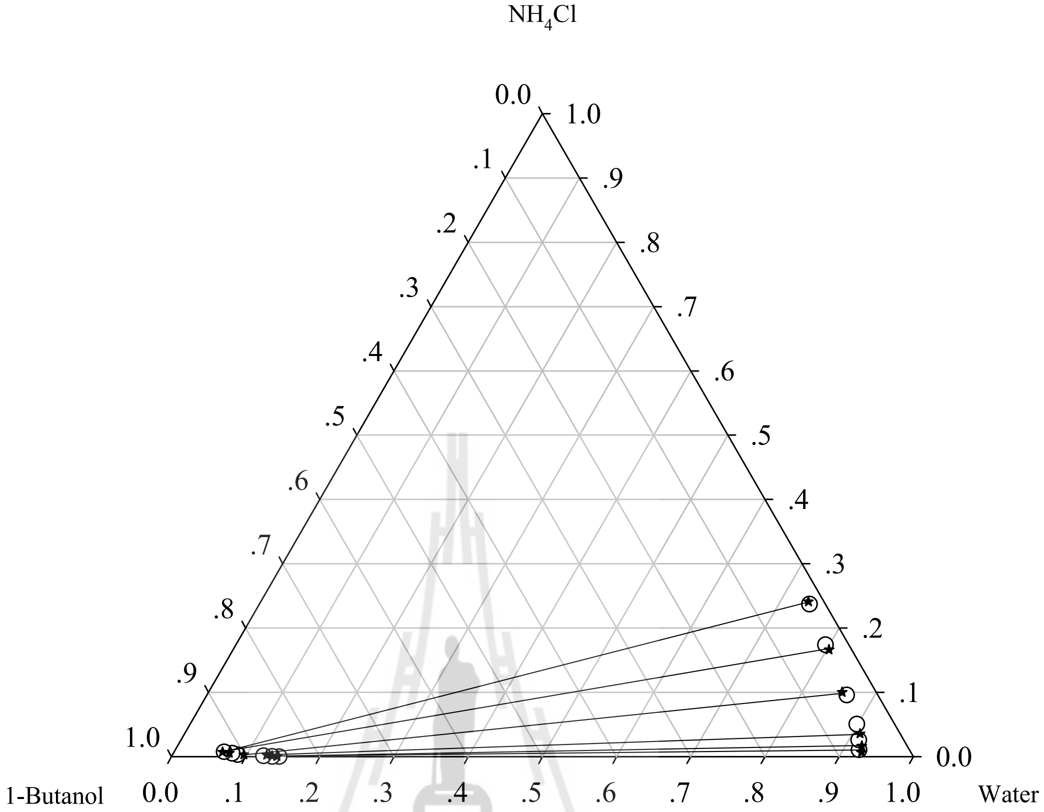


Figure 2.17 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + NH_4Cl (3) at 303.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนาร

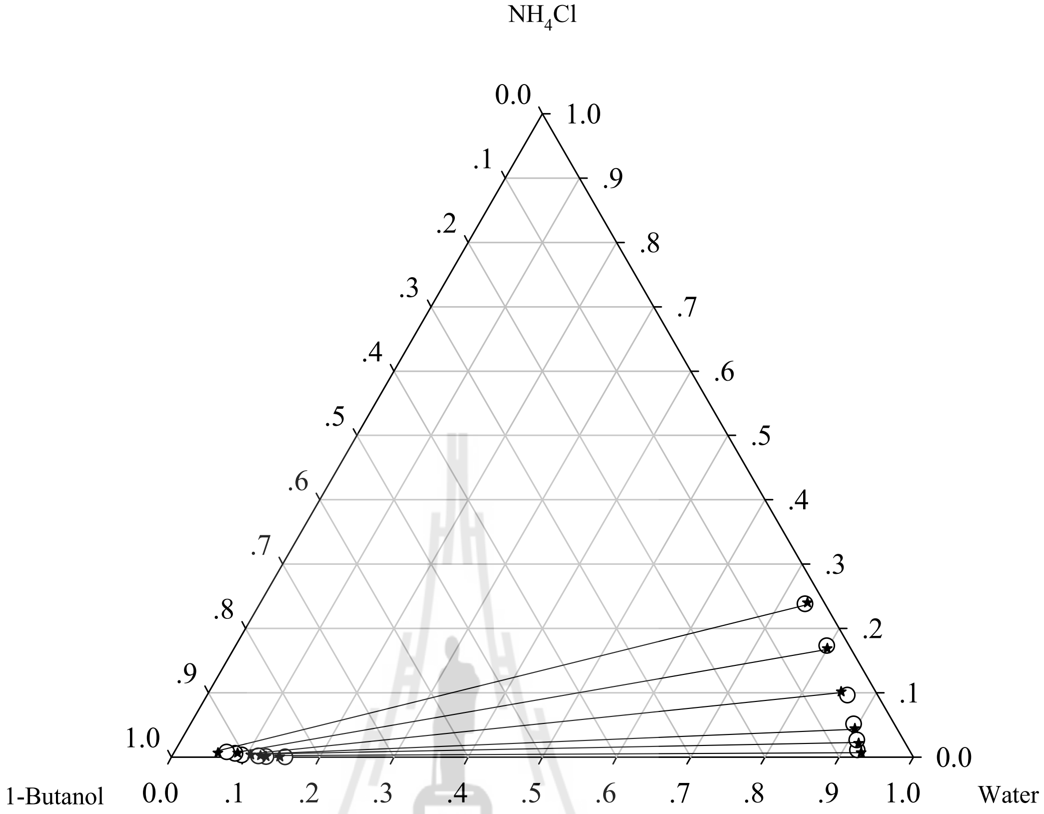


Figure 2.18 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + NH$_4$Cl (3) at 313.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

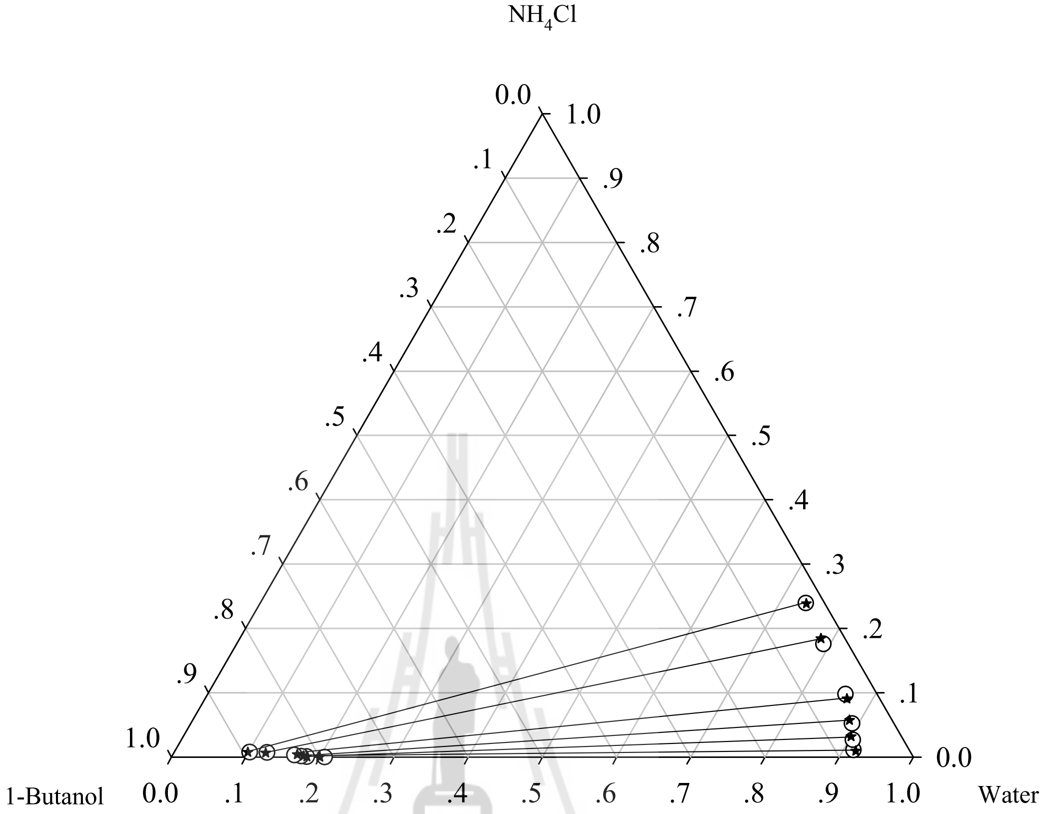


Figure 2.19 Experimental (○) and calculated (-★-) liquid-liquid equilibrium tie-lines for water (1) + 1-butanol (2) + NH_4Cl (3) at 323.15 K.

มหาวิทยาลัยเทคโนโลยีสุรนารี

Table 2.10 Binary interaction parameters and average absolute deviations in this work of the modified extended UNIQUAC model

		303.15 K		**313.15 K**		**323.15 K**	
i	***j***	a_{ij} **(K)**	a_{ji} **(K)**	a_{ij} **(K)**	a_{ji} **(K)**	a_{ij} **(K)**	a_{ji} **(K)**
		Water (1) + 1-butanol (2) + Na^+ (3) + SO_4^{2-} (4)					
1	2	183.48	123.61	236.27	55.80	254.80	63.37
1	3	-2429.86	-1026.68	-2296.12	-1154.79	-24629.97	-1196.87
1	4	-2598.08	-188.62	-2714.01	-350.04	8147.62	5338.71
2	3	2648.91	3555.56	2488.49	3454.68	26807.53	20154.17
2	4	2692.23	4478.23	2741.15	4673.07	-3809.61	20911.45
3	4	-236.58	-116.83	-229.25	-98.33	-4868.96	-1216.80
%Δ*w*		0.8785		0.9092		0.7967	
		Water (1) + 1-butanol (2) + NH_4^+ (3) + SO_4^{2-} (4)					
1	2	168.81	207.71	126.71	215.08	180.10	159.41
1	3	-18851.29	-763.87	-31691.33	-865.72	-9379.17	-891.55
1	4	-12327.69	4501.49	-4156.87	37038.94	-3670.75	9255.00
2	3	21150.88	24839.89	36754.21	34784.97	10831.30	11516.91
2	4	14521.12	23224.39	9754.03	17494.97	3583.56	10150.93
3	4	-2239.18	-870.54	-5643.68	-1980.42	-5221.33	-541.60
%Δ*w*		0.6815		0.7257		0.7476	
		Water (1) + 1-butanol (2) + Na^+ (3) + Cl^- (4)					
1	2	114.52	225.44	130.38	223.06	135.49	176.29
1	3	-88042.67	-745.83	-16482.80	-804.99	-30315.46	-908.40
1	4	28735.50	115156.63	7302.73	21082.52	11418.11	22933.90
2	3	104309.72	63558.87	19365.35	11876.38	36006.68	25918.87
2	4	-13266.97	2846.27	-3980.35	75.55	-3603.13	40.46
3	4	-14502.65	-7401.19	-5078.67	-1303.81	-4927.28	-2573.03
%Δ*w*		0.5705		0.3705		0.5390	
		Water (1) + 1-butanol (2) + NH_4^+ (3) + Cl^- (4)					
1	2	56.96	354.82	65.27	361.83	176.19	118.48
1	3	-3714.71	-692.56	-11249.20	-716.31	-5255.05	-906.99
1	4	-3214.82	3540.01	-5964.79	14034.72	-4085.22	3983.47
2	3	4469.58	4116.02	13428.39	11112.85	6322.80	6421.21
2	4	-2767.54	-118.33	-3318.93	-207.23	-4217.49	-410.39
3	4	-4419.82	-343.09	-4679.63	-995.56	-5431.75	-472.89
%Δ*w*		0.2646		0.2843		0.2163	

Table 2.11 Binary interaction parameters and average absolute deviations of the modified extended UNIQUAC model from Pirahmadi et. al. (2010).

		298.15 K		**308.15 K**		**318.15 K**	
i	***j***	***a*** a_{ij} **(K)**	a_{ji} **(K)**	a_{ij} **(K)**	a_{ji} **(K)**	a_{ij} **(K)**	a_{ji} **(K)**
		Water (1) + 1-butanol (2) + NH_4^+ (3) + Cl^- (4)					
1	2	180.88	89.40	204.29	73.72	227.57	57.17
1	3	-1930.51	28.83	-1957.05	85.99	-1983.77	143.19
1	4	-1870.92	-240.92	-1882.47	-193.24	-1894.34	-145.61
2	3	7893.61	10163.47	7954.23	10424.57	8014.58	10685.86
2	4	7462.10	13001.94	7684.29	13337.37	7907.03	13672.78
3	4	3396.24	947.74	3369.58	984.36	3342.28	102.58
$\%\Delta w$		1.3255		0.6944		0.6670	

In addition, the binary interaction parameters of water 1-butanol + NH_4Cl system at 298.15, 308.15 and 318.15 K was reported by Pirahmadi et. al. (2010). These parameters are shown in Table 2.11 where the binary interaction parameters in modified extended UNIQUAC model were obtained from binary LLE data of Winkelman et. al. (2009) for water and 1-butanol system. Fitted values of binary ion-water and ion-ion interaction parameters were used for obtaining the water + NH_4Cl system (Guedouzi et. al., (2001) and Korhonen et. al., 1997)). Hence, only the binary of 1-butanol - ion interaction parameter have been estimated in their work.

Of course, the binary interaction parameter of water +1-butanol + NH_4Cl system in Table 2.10 different from the reference values in Table 2.11. The reason is the difference of temperature and may be because of this work estimated all parameters, while the reference estimated only binary of 1-butanol - ion parameter. However, It can be observed that the objective function values of this system reported here are quite smaller than the values of reference. It can be explained that the fitting all binary interaction parameters obtained from experimental data may be better.

Because of the solubility behavior of each component in mixture has the effect on LLE behavior. Therefore, using the obtained experimental data for estimation of all parameters can be described this LLE behavior of water + 1-butanol + NH_4Cl system better than using some parameters from binary LLE system.

มหาวิทยาลัยเทคโนโลยีสุรนารี

2.6 Conclusion

The equilibrium solubility between water and 1-butanol, solubility data of inorganic salts in water and 1-butanol have been studied at temperatures range of 303.15-353.15 K and experimental liquid-liquid equilibrium data of mixed solvent electrolyte systems containing 1-butanol, water and inorganic salt has been measured at temperatures of 303.15, 313.15 and 323.15 K. The result of the solubility show that water and 1-butanol is partially miscible and salt is less soluble in 1-butanol as compared to the water. The experimental LLE data of water + 1-butanol + salt systems show that the presence of salt changed the mutual solubility of the solvent in the aqueous and organic phases. The salting-out effect is detected due to the addition of salt; it can be found that the addition of salt decreases the 1-butanol concentration in the aqueous phase as well as the water concentration in the organic phase. This effect was observed at all temperatures in the range studied. The result shows that Na_2SO_4 was most powerful in enhancing the salting-out. The influence of the salt in this study on the salting-out effect is in order of Na_2SO_4 > $(NH_4)_2SO_4$ > NaCl > NH_4Cl, which is the same arrangement as the Hofmeister series. However, the effect of temperature was minimal in the temperature range 303.15-323.15 K.

The modified extended UNIQUAC model was used to correlate the experimental LLE data. The corresponding optimized UNIQUAC binary interaction parameters were also reported here. The model gave good agreement between the experimental and the calculated data

2.7 References

Thomsen, K., Iliuta, M. C., and Rasmussen, P. (2004). Extended UNIQUAC model for correlation and prediction of vapor-liquid-liquid-solid equilibria in aqueous salt systems containing non-electrolytes. Part B. Alcohol (ethanol, propanols, butanols)-water-salt systems. **Chem. Eng. Sci.** 59: 3631-3647.

Ghalami-Choobar, B., Ghanadzadeh, A, and Kousarimehr, S. (2011). Salt effect on the liquid-liquid equilibrium of (water + propionic acid + cyclohexanol) system at T = (298.2, 303.2, and 305.2) K. **Chin. J. Chem. Eng.** 19(4): 565-569.

Santos, F. S., Saul, G. D., and Martin, A. (2001). Salt effect on liquid–liquid equilibrium ofwater + 1-butanol + acetone system: experimentaldetermination and thermodynamic modeling. **J. Fluid Phase Equilibria.** 187-188: 265-274.

Vakili-Nezhaad, G. R., Mohsen-Nia, M., Taghikhani, V., Behpoor, M., and Aghahosseini, M. (2004). Salting-Out effect of NaCl and KCl on the ternay LLE data for the systems of (water+propionic acid+isopropyl methyl ketone) and of (water+propionic acid+isobuthyl methyl ketone). **J. Chem. Thermodynamics.** 36: 341-348.

Bhupesh, C., Roy, M. R., Awual and Goto, M. (2007). Effect of in organic Salts on Ternary Equilibrium Data of Propionic Acid-Water-Solvents Systems. Journal of Applied Sciences. 7(7): 1053-1060, 2007.

Pirahmadi, F., Deghani, M. R., Behzadi, B., Seyedi, S. M., and Rabiee, H. (2010). Experimental and theoretical study on liquid-liquid equilibrium of 1-butanol+water+$NaNO_3$. **Fluid phase Equilibria.** 299: 122-126.

Pirahmadi, F., Deghani, M. R., and Behzadi, B. (2012). Experimental and theoretical study on liquid-liquid equilibrium of 1-butanol+water+NH_4Cl. **Fluid phase Equilibria.** 325: 1-5.

Hofmeister F. (1888). On the understanding of the effect of salts. Second report. On regularities in the precipitating effect of salts and their relationship to their physiological behavior. **Naunyn-Schmiedebergs Arch Exp Pathol Pharmakol (Leipzig)**. 24:247-260.

Nostro, P. L., and Ninham, B. W. (2012). Hofmeister phenomena: An update on ion specificity in biology. **Chem. Rev.** 112: 2286-2322.

Pegram, L. M., and Record, M. T., Jr. (2007). Hofmeister Salt Effects on Surface Tension Arise from Partitioning of Anions and Cations between Bulk Water and the Air−Water Interface. **J. Phys. Chem. B.** 111: 5411-5417.

Cacace, M. G.; Landau, E. M., and Ramsden, J. J. (1997). The Hofmeister series: salt and solvent effects on interfacial phenomena. **Q. ReV. Biophys.** 30: 241-277.

Grover, P. K., and Ryall. R. L. (2004). Critical appraisal of salting-out and its applications for chemical and biological sciences. **Chem. Rev.** 105: 1-9.

Long, F. A., and McDevit, W. F. (1952). Activity coefficients of nonelectrolyte solutes in aqueous salt solutions. **Chemical Reviews.** Washington, DC, United States. 51: 119-69.

Debye, P., and McAuley, J. (1925). The electric field of the ions and the neutral salt effect. **Physik. Z.** 26:2.

McDevit, W. F., and Long, F. A. (1952). The activity coefficient of benzene in aqueous salt solutions. **Journal of the American Chemical Society**. 74:1773-1777.

Tammann, G. Z. (1926). The molecular composition of water. **Anorg. Allg. Chem.** 158: 25.

Smith, J. M., and Van ness, H. C. (1987). **Introduction to Chemical Engineering Thermodynamics. 4th Edition.** Mcgraw-Hill Chemical Engineering Series. New York.

Prausnitz, J. M., Lichtenthaler, R. N., and Azevedo, E. G. d. (1999). **Molecular thermodynamics of fluid-phase equilibria.** Prentice Hall PTR. Upper Saddle River. N. J.

Abrams, D. S., and Prausnitz, J. M. (1975). Statistical thermodynamics of liquid mixtures. New expression for the excess Gibbs energy of partly or completely miscible systems. **AIChE Journal.** 21(1): 116-28.

Pitzer, K. S. (1980). Electrolytes. From dilute solutions to fused salts. **Journal of the American Chemical Society.** 102(9): 2902-2906.

Debye, P., and Huckel, E. (1923). The theory of electrolytes. I. Lowering of freezing point and related phenomena. **Physikalische Zeitschrift.** 24: 185-206.

Sabine, M., Agena, M. Sc., and Dipl.-Ing. (1997). **Modelling of protein solution properties.** Ph. D. Philosophy. University of London, London.

Marcus, Y. (1985). **Ion Solvation.** Weiley. New York.

Marcus, Y. (1997). **Ion Properties. 3rd ed.** Marcel Dekker. Ind. Eng. New York.

Patricia, D., Mar´ıa, T. S., and Sagrario, B. (2007). Isobaric vapor–liquid equilibria for the quaternary reactive system: Ethanol +water + ethyl lactate + lactic acid at 101.33 kPa. **Fluid Phase Equilibria.** 225:17-23.

Marian, G., Barbara, W. G., and Andrzej, M. (2006). Recommended Liquid-Liquid Equilibrium Data. Part 4.1-Alkanol-water Systems. **J. Phts. Chem. Ref. Data.** 35(3):1391-1414.

Collins, K. D. (1997). Charge density dependent strength of hydration and biological structure. **Biophysical Journal.** 72(1): 65-76.

Collins, K. D., and Washabaugh, M. W. (1985). The Hofmeister effect and the behaviour of water at interfaces. **Q. Rev. Biophys.** 18: 323-422.

Tansel, B., Sager, J., Rector, T., Garland, J., Strayer, R. F., Levine, L. F., Robert, M., Hummerick, M., and Bauer, J. (2006). Significance of hydrated radius and hydration shells on ionic permeability during nanofiltration in dead end and cross flow modes. **Sep. Purif. Technol.** 51(1): 40-47.

Winkelmam, J. G. M., Kraai, G. N., and Heeres, H. J. (2009). Binary, ternary and quaternary liquid–liquid equilibria in 1-butanol, oleic acid, water and n-heptane mixtures. **Fluid Phase Equilibria.** 284:71-79.

Guendouzi, M., Dinane, A., and Mounir, A. (2001). Water activities, osmotic and activity coefficients in aqueous chloride solutions atT = 298.15 K by the hygrometric method. **J. Chem. Thermodyn.** 33: 1059-1072.

Korhonen, P., Kulmala, M., and Viisanen, Y. (1997). **J. Aerosol. Sci.** 28: 901-999.

CHAPTER III

LIQUID-LIQUID EQUILIBRIUM FOR TERNARY SYSTEM OF WATER+1-BUTANOL+LACTIC ACID

3.1 Abstract

Liquid-liquid equilibrium data for water, 1-butanol and lactic acid were presented at 303.15 K under atmospheric pressure. The distribution coefficient of lactic acid between aqueous and organic phase was used to evaluate the possibility for its separation from its aqueous solution. Distribution coefficients and separation factors were evaluated over the immiscibility regions. The results showed that 1-butanol was partially miscible in the aqueous phase, and the areas of two-phase regions primarily were dependent on the mutual solubility of water and 1-butanol. In separation of lactic acid, it was found that 1-butanol was capable to extract lactic acid from its aqueous solution, with the separation factors greater than 1. The distribution coefficient and degree of lactic acid extraction were also enhanced by increasing lactic acid concentration in the aqueous phase. The experimental tie-lines of the ternary system were correlated using the UNIQUAC model. The results for the binary interaction parameters for UNIQUAC model are also reported in this chapter. It was concluded results that the UNIQUAC model provided a satisfactory description of LLE data obtained in this work.

3.2 Introduction

Lactic acid is one of the most widely used carboxylic acids, as it has many industrials applications. In recent years, the interest towards lactic acid recovery from fermentation broth has been increased. This interest is caused by increasing the demand for pure, naturally produced lactic acid, mainly for food industry, pharmaceutical industry or for production of biodrgradable polymers (Yankov et al., 2004). Recovery of lactic acid from aqueous solution is a growing requirement in fermentation based industries and recovery from waste streams. The traditional recovery process of lactic acid from fermentation broth is quite complicated. Separation of this acid from dilute wastewater or fermentation broth is an economic problem. The possibility to add value also causes interest in lactic acid removal from water (Duke et al., 2008 and Geanta et al., 2013).

With an increase in demand for environmentally friendly chemicals, an efficient separation of lactic acid from aqueous solution is an important method. Nowadays, several separation methods have been employed, such as liquid-liquid extraction, chromatographic method, reverse osmosis, evaporation, membrane separation, ion exchange, distillation, crystallization, and precipitation. Liquid-liquid extraction process is the most useful method for purification, enriching and separation of components. This process is a process in which a solution is brought into contact with a second liquid essentially immiscible or partially miscible with the first one in the order to bring about transfer of one or more components from solution into solvent. Separation of lactic acid by liquid-liquid extraction has been investigated by several investigators. Juang and Huang (1997) and Kahya et al. (2001) works on reactive extraction of lactic acid from aqueous solution with tri-n-octylamine (TOA) in solvent. They reported that distribution coefficient increased with increasing TOA concentration. Effect of temperature on extraction of lactic acid was explored by Kertes and King (1986). Extraction temperature in the range of 20 to 90°C was found to have a very slight effect on the distribution ratio of lactic acid into alcohols. However, in the amine based solvent extraction systems, it was known that the extractability of the single acid decreases with increasing temperature (Tamada et al, 1990). In addition, the effect of the pH on extraction of lactic acid was studied in previous works. Yang et al. (1991) directed their studies towards understanding the effects of pH on the extraction as well as on the fermentation before designing an optimum extractive fermentation process. They found out that lower pH values result in good separation of lactic acid by long chain tertiary amines. In the intermediate pH range (3-5), distribution coefficient decreased with increasing equilibrium pH of the aqueous phase. However, in the extremely high and low pH ranges, the distribution coefficient remained insensitive to pH values. The results from investigators have been summarized that the liquid-liquid extraction has the advantage that lactic acid can be removed easily from the fermentation broth, preventing the lowering of pH. Further, the lactic acid can be re-extracted and the extractant recycled to the fermentation process. Despite the high distribution coefficient obtained from the extraction, some of the solvents are expensive and might inherit some toxicity. Hence, selection of solvent for the separation of this acid is still needed to improve.

Weiser and Geankoplis (1955) and Petritis and Geankoplis (1959) have been investigated two solvents; 3-methyl-1-butanol and butyl alcohol for extraction of lactic acid from aqueous solution at 25 ˚C. They found that the butyl alcohol was also a good solvent for lactic acid extraction. Moreover, extraction of lactic acid with 1-

butanol was studied by Chawong and Rattanaphanee (2011). It was reported that the process efficiency was significantly dependent on pH of the aqueous solution. The pH effect was substantially pronounced at pH of the aqueous solution less than 1. Initial lactic acid concentration appeared to have a positive effect on the distribution coefficient and the degree of extraction.

Several thermodynamic theories have been developed to represent in LLE of water + carboxylic acid + alcohol systems such as NRTL and UNIQUAC model. Domingues et al. (2013) presented NRTL model on LLE of water + lactic acid + C_4-C_7 alcohol (1-butanol, 1-pentanol, 1-hexanol and 1-heptanol) at 298.2 K. The result indicated that the NRTL model gives a satisfactory description of LLE data of the long carbon chain of alcohol system. The LLE systems of water + formic acid + primary alcohol, i.e. 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol were studied by Gilani and Asan (2013). The experimental LLE data were correlated using the NRTL and the UNIQUAC models. It was found that UNIQUAC gives a better agreeable with the measured LLE data of the system containing 1-butanol than NRTL model.

Therefore, the purpose of this Chapter is to determine LLE data of water + 1-butanol + lactic acid and application of 1-butanol on extraction of lactic acid. The LLE data for the ternary systems was measured at 303.15 K and atmospheric pressure. In addition, the measured LLE data of this ternary system were correlated by UNIQUAC model in order to obtain the binary interaction parameters.

3.3 Theory

3.3.1 Physical Extraction of Carboxylic Acids

Carboxylic acids, mainly exist as dimmers in the organic phase owing to strong intermolecular hydrogen bonding. On the contrary, in the aqueous phase, they existed as monomers because of the intermolecular hydrogen bonding between the acid is destroyed owing to their preferential hydrogen bonding with the water molecules. At the pH less than the its pKa values, the acid can be assumed to be transferred into organic solvent by the following mechanism (Kailas et al., 2010):

(i) Ionization of the acid in aqueous phase:

$$HA_{aq} \leftrightarrow H^{+} + A^{-} \tag{3.1}$$

$$K_{HA} = \frac{[H^{+}][A^{-}]}{[HA]} \tag{3.2}$$

(ii) Distribution of undissociated molecular acid between the two phases, aqueous and organic:

$$HA_{aq} \leftrightarrow HA_{org} \tag{3.3}$$

$$D = \frac{[HA]_{org}}{[HA]_{aq}} \tag{3.4}$$

(iii) Dimerization of the acid in the organic phase:

$$2HA_{org} \leftrightarrow HA_{2,org} \tag{3.5}$$

$$K_{D} = \frac{[HA]_{2,org}}{[HA]_{org}} \tag{3.6}$$

Efficiency of acid extraction is represented by degree of extraction (*%E*).

$$\%E = \frac{[HA]_0 V_0 - [HA]_{aq} V_{aq}}{[HA]_0 V_0} \times 100 \tag{3.7}$$

where subscripts *aq* and *org* represent the equilibrium aqueous and organic phase.

$[HA]$ is the equilibrium concentration of acid

$[A^-]$ is the concentration of dissociated acid

$[H^+]$ is the concentration of hydrogen ion

V_0 is the volume of starting solution

V_{aq} is the volume of the aqueous phase after extraction

K_{HA} is ionization coefficient

D is distribution coefficient

K_D is dimerization coefficient

3.3.2 UNIQUAC model

The UNIQUAC model is an extension of the quasi-chemical theory for non-random mixtures containing components of different sizes. The UNIQUAC model for the excess Gibbs energy (G^E) consists of two parts: a combinatorial, entropic contribution, which accounts the molecules size and shape effects, and a residual, enthalpic contribution, that accounts for the energy. The UNIQUAC contribution for excess Gibbs energy is given as follows (Abrams and Prausnitz, 1975):

The UNIQUAC equation is applicable to a wide variety of non-electrolyte liquid mixtures containing nonpolar or polar fluids such as hydrocarbons, alcohols, nitriles, ketones, aldehydes, organic acids, etc. and water, including partially miscible mixtures.

$$\frac{G^{E,UNIQUAC}}{RT} = \frac{G^{E,Comb}}{RT} + \frac{G^{E,\mathrm{Res}}}{RT} \tag{3.8}$$

The combinatorial and the residual terms are identical to the terms used in the traditional UNIQUAC equation. The combinatorial, entropic term is

$$\frac{G^{E,Comb}}{RT} = \sum_j x_j \ln\frac{\phi_j}{x_j} + 5\sum_j q_j x_j \ln\frac{\theta_j}{\phi_j} \tag{3.9}$$

The parameters ϕ and θ are the surface and volume fractions, respectively. They depend on the volume and surface area parameters r_i and q_i:

$$\phi_i = \frac{x_i r_i}{\sum_i x_i r_i} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_i x_i q_i} \tag{3.10}$$

$$\frac{G^{E,\mathrm{Res}}}{RT} = \sum_j q_j x_j \ln\sum_k \theta_k \psi_{kj} \tag{3.11}$$

The parameter ψ_{kj} is defined in terms of the binary energy interaction parameter a_{kl}:

$$\psi_{kl} = \exp\left(-\frac{u_{kl} - u_{ll}}{T}\right) = \exp\left(-\frac{a_{kl}}{T}\right) \tag{3.12}$$

Where $a_{kl} \neq a_{lk}$ and $a_{kk} = a_{ll} = 0$. By partial molar differentiation of the combinatorial and the residual UNIQUAC terms, the combinatorial and the residual parts of the rational, symmetrical activity coefficients are obtained

$$\frac{G^{E,UNIQUAC}}{RT} = \sum_j x_j \ln\frac{\phi_j}{x_j} + 5\sum_j q_j x_j \ln\frac{\theta_j}{\phi_j} + \sum_j q_j x_j \ln\sum_k \theta_k \psi_{kj} \tag{3.13}$$

The values of the r_i and q_i used in this work are shown in Table 2.1 for water and 1-butanol, for lactic acid is used $r = 3.1648$ and $q = 2.8800$ (Patricia et al., 2007).

3.3.3 The Non-Random Two-Liquid Model (NRTL Model)

The non-random two-liquid equation is based on the concept of local compositions. Local compositions, different from overall compositions, are assumed to account for the short range order and nonrandom molecular orientations that result from differences in molecular size and intermolecular forces. The original NRTL model was proposed by Renon and Prausnitz (1968). It is applicable to partially miscible as well as completely miscible systems. The excess Gibb energy of the NRTL equation for multicomponent mixtures is as follows:

$$\frac{G^E}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=i}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} \tag{3.14}$$

where $\tau_{ji} = \dfrac{g_{ji} - g_{ii}}{RT}$ $\qquad (\tau_{ji} \neq \tau_{ij})$ (3.15)

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \qquad (\alpha_{ji} \neq \alpha_{ij}) \tag{3.16}$$

The activity coefficient expressions for the NRTL equation can be represented as follows:

$$\ln\gamma_i = \frac{\sum_{j=1}^{m}\tau_{ji}G_{ji}x_j}{\sum_{l=1}^{m}G_{li}x_l} + \sum_{j=1}^{m}\frac{x_jG_{ij}}{\sum_{l=1}^{m}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{k=l}^{m}x_k\tau_{kj}G_{kj}}{\sum_{l=1}^{m}G_{li}x_l}\right) \tag{3.17}$$

The significance of g_{ij} is an energy parameter characteristic of the *i-j* interaction. The randomness factor (α_{ij}) is a constant that the characteristic of the randomness of the system. Walas (1985) recommends the values of 0.3 for non-aqueous mixture and 0.4 for aqueous organic mixtures.

3.4 Experimental procedure

3.4.1 Chemicals

Lactic acid with concentration of 88 %wt and 1-butanol with 99.9% purity were purchased from Acros. The deionized water was used in the experiments.

3.4.2 Procedure for Liquid-Liquid Equilibrium of Water + 1-Butanol + Lactic Acid Ternary System

The aqueous solution containing 0.1 to 3 M of lactic acid was used for the LLE study. 1-Butanol was used as an organic phase. Equal volumes (10 ml each) of aqueous and organic phase were then mixed in 125 ml of Erlenmeyer flask and shaken with 90 rpm at a constant temperature of 30°C in temperature-controlled shaking bath for 12 h and settling for 12 h for a complete phase separation. After the phase separation, volumes of the aqueous and organic phase were measured. Samples of the top and bottom phase were taken for analysis. Water and 1-butanol concentration was analyzed by GC (detail descripted in Chapter II). Lactic acid concentration was determined by High performance liquid chromatography (HPLC).

3.4.3 High Performance Liquid Chromatography Analysis of Lactic Acid

Lactic acid concentration was determined by HPLC from Agilent Technologies using a Hypersil BDS-C18 column to separate the compounds and UV detector was set at 210 nm. 10% of sulfuric acid concentrations of 0.005 M and 90% of water were used as a mobile phase at a flow rate of 0.35 ml/min. The column oven temperature was maintained at 50 °C. All samples are diluted with deionized water and the injection volume was 10 μL.

มหาวิทยาลัยเทคโนโลยีสุรนารี

3.5 Results and Discussion

3.5.1 Experimental LLE data

The measured compositions of the LLE for water(1) + 1-butanol(2) + lactic acid(3) ternary system at 303.15 K under atmospheric pressure are shown in Table 3.1, in which w_i denotes that mass fraction of the i^{th} components. The experimental LLE data and the calculated tie-lines for this system were plotted in Figure 3.2 and 3.3. The organic solvent is one of most important factor which influence the equilibrium characteristics and the immiscible region of this investigated system. The area of two-phase region, primarily depend on the solubility of water and 1-butanol. As seen from the LLE phase diagram, the result shows that the 1-butanol is less soluble in the aqueous phase and solubility of water in the organic phase increase with increasing of the concentration of lactic acid.

Effect of initial concentration of lactic acid in the aqueous solution on distribution coefficient and degree of lactic acid extraction were investigated in the extraction where the pH was not controlled. The pH strongly affects the ionization of carboxylic acids. Most carboxylic acids are weak acids. The partially ionize in the aqueous solution according to Eq. 3.1. The concentrations of dissociated $[A^-]$ and undissociated acids $[HA]$ are affected by the concentration of hydrogen ions $[H^+]$ or pH. At extremely low pH values, the acid is mainly in undissociated form. Most organic solvent extract undissociated acids from the aqueous phase (Yang et al., 1991). The dissociation coefficient of the lactic acid is 1.38×10^{-4} (for pKa = 3.86). The results in Table 3.2 show that the pH depends on lactic acid concentration. The pH values decrease from 2.30 to 1.65 when the lactic acid concentration increases from 0.17 to 3.03 M. It can be seen that all the aqueous solution has the pH lower than the pKa of lactic acid, it means that the lactic acid is slightly dissociated in the aqueous phase. Hence, it can be assumed mechanism from (ii) to determine the efficiency of lactic acid extraction in this work.

Table 3.1 Experimental liquid-liquid equilibrium data of water (1) + 1-butanol (2) + lactic acid (3) at 303.15 K under atmospheric pressure

Aqueous phase			**Organic phase**		
%w_1	**%w_2**	**%w_3**	**%w_1**	**%w_2**	**%w_3**
92.24	6.73	1.03	23.12	76.14	0.74
91.29	6.51	2.21	22.00	76.36	1.64
90.53	6.48	2.99	23.62	74.04	2.34
89.78	6.02	4.20	22.85	73.39	3.76
88.11	5.65	6.24	22.31	72.41	5.27
85.91	6.41	7.68	25.58	63.50	10.92
82.17	7.19	10.65	33.55	51.97	14.48

Efficiency of lactic acid extraction was represented by the distribution coefficient (D) and the degree of extraction (%E) of lactic acid, shown in Table 3.2. A higher degree of extraction means that more lactic acid is transferred from the aqueous phase to the organic phase, which implies a successful forward extraction. As water and 1-butanol are partially miscible, volumes of aqueous and organic phase after extraction differed from initial volumes of aqueous solution and 1-butanol. The volumes of organic phase are increase at the expense that of aqueous phase in equilibrium and it increases with increase in acid concentration. For this reason, the distribution coefficient of lactic acid (D) in this study was defined as follows:

$$D = \frac{[LA]_{org} V_{org}}{[LA]_{aq} V_{aq}} \tag{3.18}$$

where $[LA]_{org}$ and $[LA]_{aq}$ are the equilibrium concentration of lactic acid in the organic and aqueous phase, respectively. V_{org} and V_{aq} are the volume of the organic and aqueous phase after extraction, respectively.

The effectiveness of extraction of lactic acid by 1-butanol is given by its separation factor, which is a measure of the ability of 1-butanol to separate the lactic acid from the water. The separation factors (*S*) were calculated as follows:

$$S = \frac{D}{D_w} \tag{3.18}$$

where D is the distribution coefficient of lactic acid and distribution coefficient of water (D_w) is defined as follows:

$$D_w = \frac{[H_2O]_{org} V_{org}}{[H_2O]_{aq} V_{aq}} \tag{3.19}$$

where $[H_2O]_{org}$ and $[H_2O]_{aq}$ are the equilibrium concentration of water in the organic and aqueous phase, respectively. The results show that the separation factor obtained in this is than 1 (varying from 2.84 to 7.77) for the system reported here, which means that extraction of lactic acid by 1-butanol is possible. In addition, it was found that the distribution coefficient of water values are small when compared to that of lactic acid, which means that the most of lactic acid is transferred from aqueous phase to 1-butanol phase while the water is slightly soluble in 1-butanol phase.

Table 3.2 Distribution coefficient, degree of extraction and separation factor as a function of initial lactic acid concentration in aqueous phase at 303.15 K

Concentration of lactic acid (M)			Volume (ml)		pH	D_w	D	%E	S
Initial	Aqouous	Organic	V_{aq}	V_{org}					
0.18	0.11	0.07	8.7	11.0	2.30	0.27	0.77	44.01	2.84
0.40	0.24	0.15	8.5	11.3	2.20	0.27	0.84	48.97	3.09
0.56	0.33	0.22	8.3	11.5	2.00	0.32	0.95	50.05	3.00
0.88	0.48	0.36	8.3	11.9	1.90	0.31	1.08	52.96	3.51
1.24	0.64	0.46	7.9	12.0	1.88	0.33	1.11	56.68	3.37
2.23	0.90	1.06	6.4	13.6	1.75	0.52	2.50	72.60	4.80
3.26	1.22	1.41	3.3	16.6	1.65	0.75	5.78	86.63	7.70

It should be noted that the distribution coefficient of lactic acid and degree of lactic acid extraction were enhanced with increasing initial lactic acid concentration in the aqueous solution. This result was expectable and was similar to the observation reported in the previous study (Chawong and Rattanaphanee, 2011). The reason of the behavior can be explained as follows. The extent of hydration of the acid and energy of the bond to water molecules are the two factors that affect extractability. 1-butanol has very low solubility in water, so it behaves close to ideality in term of volume changes when lactic acid at low concentration partitions between them. To obtain complete miscibility in the phases, very high concentration of lactic acid is required. At high acid, content, i.e. in water deficient situations, the solvation shell around lactic acid is composed of both water and solvent molecules, thus making the solute species prefer the organic solvent. Thus, appearance of the distribution coefficient and degree of lactic acid extraction was observed at a higher acid concentration.

มหาวิทยาลัยเทคโนโลยีสุรนารี

Equilibrium distribution compositions of lactic acid in aqueous and organic phase are shown in Figure 3.1. The graph indicates that the solubility of lactic acid in organic phase depends on concentration of lactic acid in aqueous phase, which confirmed that the acid extraction with 1-butanol was promoted when increasing of concentration of lactic acid.

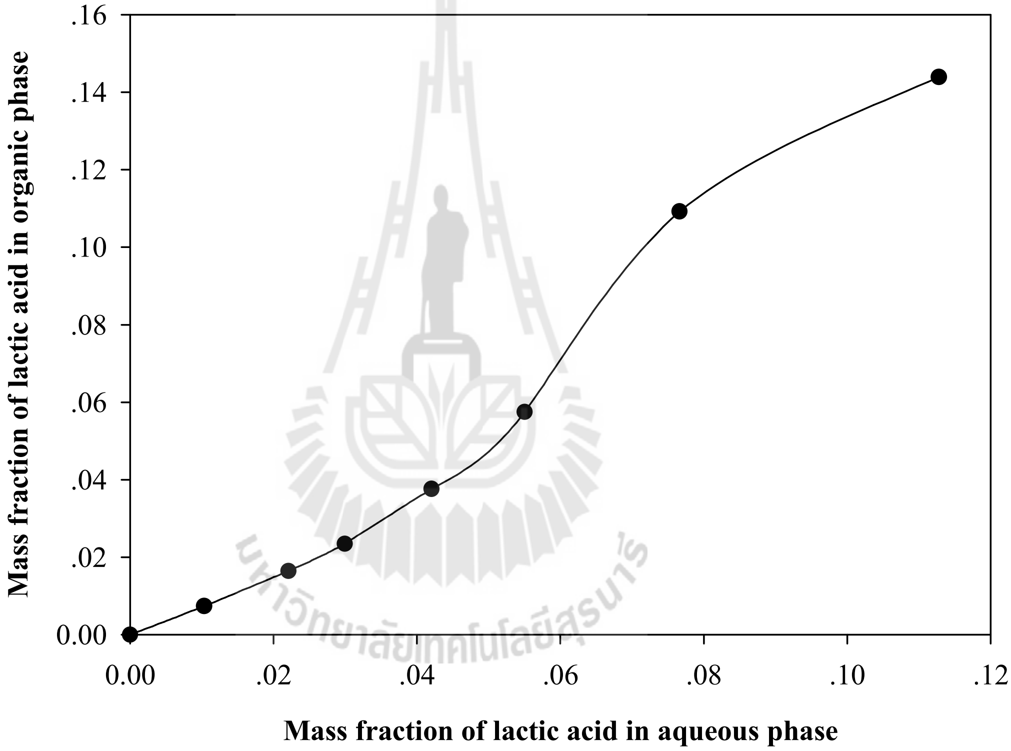


Figure 3.1 Equilibrium distribution diagram for the system water(1) + 1-butanol(2) + lactic acid(3) at 303.15 K

3.5.2 Correlation model

The UNIQUAC model was used to correlate the experimental LLE data of the system water(1) + 1-butanol(2) + lactic acid(3) at 303.15 K. The adjustable parameters have been estimated by minimizing the differences between the experimental and calculated mass fractions of the components for all tie-lines, using the objective function (*OF*) expressed in Eq. 2.28. In the present work, the binary interaction parameters in the UNIQUAC model for the binary water+1-butanol system was taken from Winkelman et al. (2009). These values are given in Table 3.3. Therefore, this work has been using the values of binary water-1-butanol parameters (a_{12} and a_{21}) to estimate the values of water-lactic acid and 1-butanol-lactic acid parameters. Fitted values of water-lactic acid and 1-butanol-lactic acid interaction parameters are listed in Table 3.3. The tie-lines have been presented in Figure 3.2. It can be seen that result is in good agreement between experimental and calculated data with the *OF* of 0.0024 and $\%\Delta w$ of about 0.40%.

In addition, all adjustable binary interaction parameters in the UNIQUAC model are investigated. The binary interaction parameters are shown in Table 3.4, the tie lines were plotted and are presented in Figure 3.3. It can be seen that the result is a good agreement between experimental and calculated data with the *OF* of 0.0014 and $\%\Delta w$ of about 0.34%. However, it should be noted that the *OF* and $\%\Delta w$ in this case are less than that the values with minimized by fixed a_{12} and a_{21} and the all binary interaction parameters are significantly different from the parameters in Table 3.3. Of course, the fact that these parameters are changed as a result of changing the a_{12} and a_{21}. In previous cases, both values are referred from the binary LLE system of water and 1-butanol. While both values in this case are calculated taking into account the effect of all components in the system. It is known that lactic acid is miscible in both aqueous and organic phases, which the miscibility of lactic acid may have a slight effect on the interaction between water and 1-butanol. This reason is confirmed as seen that the a_{12} and a_{21} was slightly changed. As a result, the other binary interaction parameters are changed.

Table 3.3 The binary interaction parameters and the objective function for water(1) + 1-butanol(2) + lactic acid(3) system at 303.15 K in this work

i	*j*	a_{ij} (K)	a_{ji} (K)	*OF*	%Δ *w*
1	2	192.60	81.68	0.0024	0.4022
1	3	397.18	615.44		
2	3	402.66	6244.73		

Remark: a_{12} and a_{21} from UNIQUAC model of the system water(1)+1-butanol(2) (Winkelman et al., 2009)

Table 3.4 All adjusted of the binary interaction parameters and the objective function for water(1) + 1-butanol(2) + lactic acid(3) system at 303.15 K in this work

i	*j*	a_{ij} (K)	a_{ji} (K)	*OF*	%Δ *w*
1	2	135.47	173.10	0.0014	0.3417
1	3	335.95	5251.91		
2	3	383.43	14771.60		

In addition, the present work has a reported the correlated model of this system at 298.20 K with NRTL model (Domingues et al., 2013). The binary interaction parameters of NRTL model are shown in Table 3.5. It was observed that the values of binary interaction parameters are quite different from the parameters with an estimated by UNIQUAC model in this work, which make sense of the result of used different model estimation. The *OF* value has been obtained from NRTL model is 0.0068, which is quite low value. It means that NRTL model gives a good agreement for LLE behavior. Although, this *OF* value based on NRTL model was found to be good, but it is still higher than that the value from the UNIQUAC model in reported here. The NRTL model is must be set the value of α_{ij} for each pair compounds. It is one of important factor that affects on ability of the NRTL model as an effect on the *OF* value. However, with this value of α_{ij}, there are some cases in which no suitable value of the binary parameters can be found (Simoni et. al., 2008). Therefore, if no suitable parameter solutions are determined with this value of α_{ij}, It should be emphasized that by varying α_{ij}, while this reference is not vary this value. It was fixed at 0.2 between each pair of compounds.

Table 3.5 The binary interaction parameters and the objective function for water(1) + 1-butanol(2) + lactic acid(3) system at 303.15 K from NRTL model (Domingues et al., 2013)

i	***j***	***a_{ij}* (K)**	***a_{ji}* (K)**	***OF***	**%Δ *w***
1	2	1442.40	-270.66	0.0068	-
1	3	-128.98	-148.07		
2	3	1537.60	-654.60		

In each Table, the results of a more suitable model with less *OF* and %w value. It is easy to see that there is a good agreement between the experimental and calculated liquid phase compositions especially for those results are obtained by the UNIQUAC model. From the *OF* values and visual analysis of the figures, it can be concluded that all the models are able to correlate liquid–liquid equilibrium of the ternary system in this work with good precision but the results of the UNIQUAC model is more satisfactory. In addition, these results indicate that using the UNIQUAC model with all adjustable the binary interaction parameters in development of local composition is suitable assumption in applying for this ternary system.

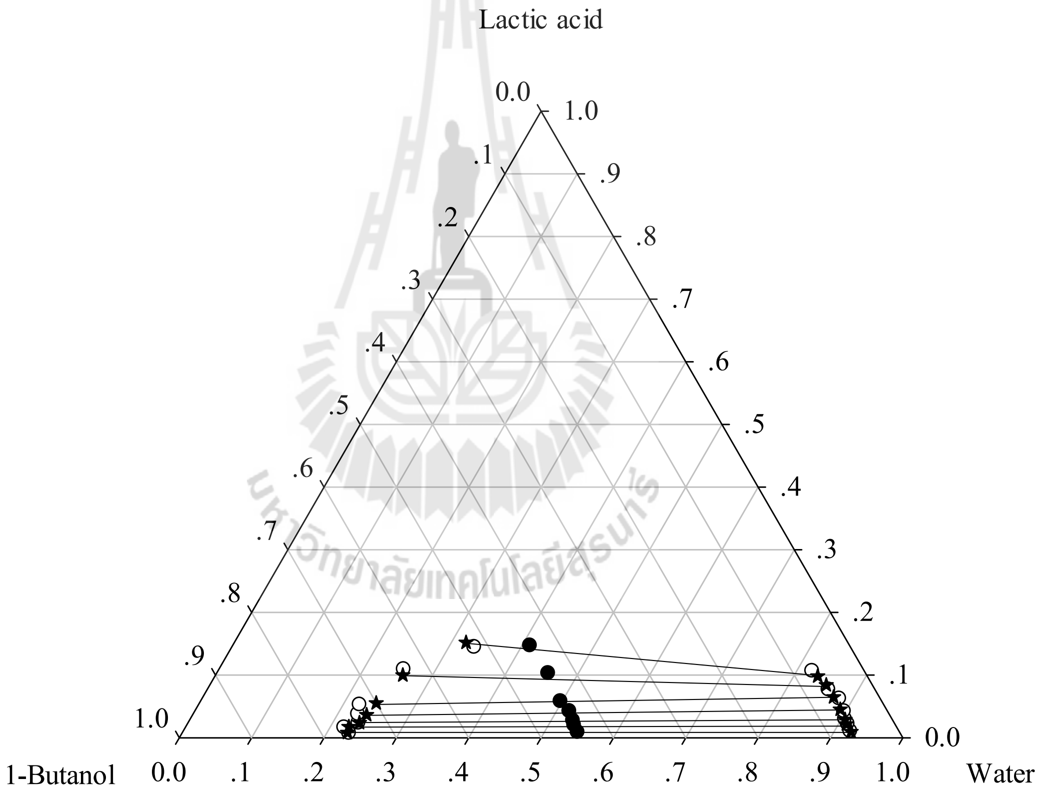


Figure 3.2 Experimental(○), calculated(-★-) and feed points(●) of liquid-liquid equilibrium tie-lines for water(1)+1-butanol(2)+lactic acid(3) at 303.15 K, when the interaction parameters between water-1-butanol were fixed

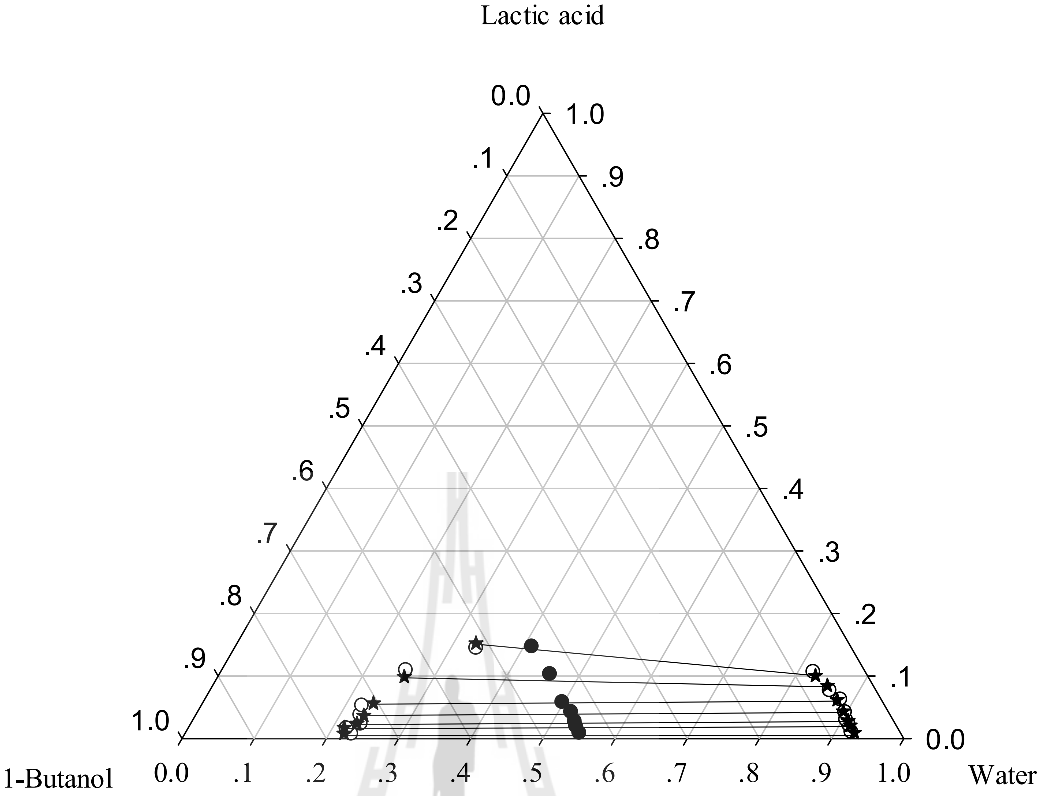


Figure 3.3 Experimental(○), calculated(-★-) and feed points(●) of liquid-liquid equilibrium tie-lines for water(1)+1-butanol(2)+lactic acid(3) at 303.15 K, when all interaction parameters were adjusted

มหาวิทยาลัยเทคโนโลยีสุรนารี

3.6 Conclusion

The LLE data of the ternary mixtures, water + 1-butanol + lactic acid was presented at 303.15 K. The separation factor and distribution coefficient in this work were calculated. The results show that 1-butanol is less soluble in organic phase as compared to the aqueous phase, but miscible with lactic acid. In separation of lactic acid, the experimental results indicate the 1-butanol is suitable separating agents for lactic acid removal from water. The distribution coefficient and degree of extraction was also enhanced by increasing lactic acid concentration in the aqueous phase. However, since 1-butanol is partially miscible in water, proper organic-to-aqueous volume ratio must be used in order to avoid the incorporation between both phases, which might lead to an efficiency of solvent in the extraction.

In correlation model, the UNIQUAC model was used to calculate the phase compositions of the mixtures. The corresponding optimized binary interaction parameters were also calculated. It was observed that the UNIQUAC give a satisfactory description of LLE data obtained in this work.

มหาวิทยาลัยเทคโนโลยีสุรนารี

3.7 References

Yankov, D., Molinier, J., Albet, J., Malmary, G., and Kyuchoukov, G. (2004). Lactic acid extraction from aqueous solution with tri-n-octylamine dissolved in decanol and dodecane. **Biochemical Engineering Journal.** 21: 63-71.

Duke, M. C., Limb, A., da Luz, S. C., and Nielsen, L. (2008). Lactic acid enrichment with inorganic nanofiltration and molecular sieving membranes by pervaporation. **Food Bioprod. Process.** 86: 290–295.

Geanta, R. M., Ruiz, M. O., and Escudero, I. (2013). Micellar-enhanced ultrafilteration for the recovery of lactic acid and citric acid from beet molasses with sodium dodecyl sulphate. **J. Membrane Sci.** 430: 11-13.

Juang, R. S., and H, R. H. (1997). Equilibrium studies on reactive extraction of lactic acid with amine extractant. **The Chemical Engineering Journal.** 65: 47-53

Kahya, E., Bayraktar, E., and Mehmetoglu, Ü. (2001). Optimization of Process Parameters for Reactive Lactic Acid Extraction. **Turkish Journal of Chemistry.** 25: 223-230.

Kertes, A. S. and King, C. J. (1986). Extraction chemistry of fermentation product carboxylic acids. **Biotechnology and Bioengineering.** 28: 269-282.

Tamada, J. A., Kertes, A. S., and King, C. J.(1990). Extraction of carboxylic acids with amine extractants, 3.Effect of Temperature, Water Coextraction, and Process Considerations. **Industrial Engineering and Chemistry Resources.** 29: 333-1338.

Yang, S. T., White, S. A. and Hsu, S. T. (1991). Extraction of carboxylic acid with tertiary and quaternary amines: Effect of pH. **Ind. Eng. Chem. Res.** 30: 1335-1342.

Weiser, R. B., and Geankoplis, C. J. (1955). Lactic Acid Purification by Extraction. **Ind. Eng. Chem.** 47: 858-863.

Petritis, V. E., and Geankoplis, C. J. (1959). Phase Equilibria in 1-Butanol-Water-Lactic Acid System. **J. Chem. Eng. Data.** 4(3): 197-198.

Chawong, K., and Rattanaphanee, P. (2011). n-Butanol as an extractant for lactic acid recovery. **World Acad. Sci. Eng. Tech.** 56: 1437-1440.

Domingues, L., Cussolin, P. A., da Silva Jr, J. L., de Oliveira, L. H., and Aznar, M. (2013). Liquid-liquid equilibrium data for ternary systems of water + lactic acid + C_4-C_7 alcohols at 298.20 K and atmospheric pressure. **Fluid Phase Equilibria.** 354: 12-18.

Gilani, H. G., and Asan, Sh. (2013). Liquid–liquid equilibrium data for systems containing of formic acid, water, and primary normal alcohols at T = 298.2 K. **Fluid Phase Equlibria.** 354: 24-28.

Kailas, L., Wasewar, Amit, K., and Seema. (2010). Physical extraction of propionic acid. **IJRRAS**. 3(3): 290-302.

Abrams, D. S., and Prausnitz, J. M. (1975). Statistical thermodynamics of liquid mixtures. New expression for the excess Gibbs energy of partly or completely miscible systems. **AIChE Journal.** 21(1): 116-28.

Renon, H., and Prausnitz, J. M. (1968). Local compositions in thermodynamic excess functions for liquid Mixtures. **American Institute of Chemical Engineers Journal.** 14: 135-144.

Walas, S. M. (1985). Phase equilibriumin chemical engineering. Butterworth. Boston

Patricia, D., María, T. S., and Sagrario, B. (2007). Isobaric vapor–liquid equilibria for the quaternary reactive system: Ethanol + water + ethyl lactate + lactic acid at 101.33 kPa. **Fluid Phase Equilibria.** 255(1): 17-23.

Winkelmam, J. G. M., Kraai, G. N., and Heeres, H. J. (2009). Binary, ternary and quaternary liquid–liquid equilibria in 1-butanol, oleic acid, water and n-heptane mixtures. **Fluid Phase Equilibria.** 284:71-79.

Simoni, L. D., Lin, Y., Brennecke, J. F., and Stadtherr, M. A. (2008). Modeling liquid-liquid equilibrium of ionic liquid system with NRTL, Electrolyte-NRTL and UNIQUAC. **Ind. Eng. Chem. Res.** 47: 256-272.

มหาวิทยาลัยเทคโนโลยีสุรนารี

CHAPTER IV

EFFECT OF INORGANIC SALTS ON EXTRACTION OF LACTIC ACID WITH 1-BUTANOL

4.1 Abstract

Extraction of lactic acid from its aqueous solution using 1-butanol containing inorganic salt at constant temperature of 303.15 K was studied. The effect of changing process variables of salt type and concentration on extraction efficiency was investigated. Four inorganic salts, i.e. NaCl, Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$ were used. Efficiency of extraction was represented by value of the distribution coefficient of lactic acid in each system. The result was compared with salt-free system of the same extracting conditions. Salting-in and salting-out effects were clearly observed for all the salts within the studied concentration. When the salt concentration was sufficiently high, the distribution coefficient and degree of extraction increased with increasing salt concentration. Among these four salts, Na_2SO_4 demonstrated the highest distribution coefficient of lactic acid extraction using 1-butanol. It is concluded that the salt enhanced the heterogeneity of the system in a way that favoured the extraction of lactic acid from its aqueous solution using 1-butanol.

มหาวิทยาลัยเทคโนโลยีสุรนารี

4.2 Introduction

Liquid-liquid extraction by a suitable organic solvent that gives high distribution coefficient has been found to be a promising method for lactic acid recovery. This process has the advantage that lactic acid can be removed easily from aqueous solution. This technique depends greatly upon how solute distributes between the aqueous and organic phase, which in Chapter III found that 1-butanol is partially miscible in water, consequently, lead to incomplete solvent recovery after the operation. Various means for altering the distribution is desirable way exists, but one of the most commonly used nowadays is salting effect. The presence of salt may influence the phase equilibrium behavior of a mixture significantly. This phenomena is often referred to as salting in and salting out effect. This phenomena is often referred to as salting in and salting out effect. The application of the salt effect in extraction is important to alter miscibility gabs to change the distribution coefficient.. Addition of inorganic salts in an aqueous solution of an organic acid can result in either decrease or increase in the solubility of the solute in the solution (Ghalami-Choobar et al, 2011). In addition, inorganic salts were found to influence distribution characteristic of other solutes between the partial miscible phases in the system.

Several researchers in the past have worked on this liquid-liquid extraction system. But few of them have worked on the salt effect on liquid-liquid extraction system. It is observed that the use of salt has proven to be advantageous, although a relative few significant advances and developments in this field are reported at experimental level. Tan and Aravinth (1999) studied effects of sodium chloride (NaCl) and potassium chloride (KCl) on liquid-liquid equilibrium of water+acetic acid+1-butanol system at different temperatures. NaCl and KCl were experimentally shown to be effective in modifying the liquid–liquid equilibrium LLE in favour of the solvent extraction of acetic acid from an aqueous solution with 1-butanol, particularly at high salt concentrations. Both the salts enlarged the area of the two-phase region decreased the mutual solubilitys of water and marginally decreased the concentrations of 1-butanol and acetic acid in the aqueous phase while significantly increased the concentrations of the same components in the organic phase.

Vakili-Nezhaad et al. (2004) and Roy et al. (2007) investigated effect of electrolytes on the LLE for the ternary systems. The report showed that the electrolytes studies in this work, i.e., NaCl and KCl significantly affected the solubility of propionic acid (PA) in the organic solvents (isopropyl methyl ketone and isobutyl methyl ketone) used in systems. Distribution coefficient of PA and the selectivity of the solvents in extracting PA, increased in presence of electrolytes in the systems. For extraction of lactic acid, Chawong and Rattanaphanee (2012) studied effect of chloride salts: NaCl, $MgCl_2$ and $CaCl_2$ on extraction of lactic acid from its aqueous solution. It was observed that, when the salt concentration was sufficiently high, the distribution coefficient increased with increasing salt concentration.

This Chapter therefore, aims to investigate the extraction of lactic acid from its aqueous solution using 1-butanol when different inorganic salts were added. Effects of salt type and concentration on the distribution coefficient of the acid in these systems were studied.

4.3 Theory

Separation processes in which two immiscible or partially soluble liquid phases are brought into contact for the transfer of one or more components are referred to as liquid-liquid extraction or solvent extraction. The processes taking place are primarily physical, since the solutes being transferred are ordinarily recovered without chemical change. On the other hand the physical equilibrium relationships on which such operations are based depends mainly on the chemical characteristics of the solutes and solvents. Thus, use of a solvent that chemically resembles one component of a mixture more than the other components will lead to concentration of that component in the solvent phase, with the exclusion from that phase of dissimilar components.

Extraction is distribution of a solute between two liquids that must not be completely mutually miscible. This method makes use of an organic compound capable of extracting the solute of interest, or a complex of it, from the aqueous phase into an immiscible organic solution. It consists in separation of one or several substances (solute) present in liquid phase by contact with another liquid phase (solvent). The extraction is governed by distribution law with states that at equilibrium, a given solute will always be distributed between two essentially immiscible liquids in the same proportion. Equilibrium is established when the chemical potential (free energy) of the solute in the two phases is equal. The distribution coefficient is a reflection of the relative solubilities of the solute in the two phases.

มหาวิทยาลัยเทคโนโลยีสุรนารี

For extraction of lactic acid in aqueous solution with 1-butanol, most of lactic acid will be transfer to 1-butanol. Lactic acid must exist in the same form in both phases and if there is no complex form between lactic acid and organic solvent, a solute's partitioning between two phases is described by the distribution coefficient (*D*) and Efficiency of lactic acid extraction is represented by the degree of extraction (*%E*). These values were calculated as follows Eq. (3.18) and (3.7), respectively.

มหาวิทยาลัยเทคโนโลยีสุรนารี

4.4 Experimental procedure

4.4.1 Chemicals

Lactic acid with concentration of 88 %wt and 1-butanol with 99.9% purity were purchased from Acros. Ammonium sulfate ($(NH_4)_2SO_4$), sodium sulfate (Na_2SO_4), ammonium Chloride (NH_4Cl) and sodium chloride (NaCl) were obtain from CARLO ERBA and deionized water was used in the experiments.

4.4.2 Preparation of Lactic Acid Aqueous Solution

Aqueous lactic acid solution was prepared by dissolving lactic acid solution in deionized water until the desired concentration (1 M of lactic acid). Inorganic salts (NaCl, Na_2SO_4, NH_4Cl and $(NH_4)_2SO_4$) with quantities in range of 1 to 3 g were added into 10 ml lactic acid solution.

4.4.3 Extraction of Lactic Acid

1-Butanol was used as a single solvent for extraction of lactic acid in this study. Equal volumes (10 ml each) of aqueous and organic phase were then mixed in 125 ml of Erlenmeyer flask and shaken with 90 rpm at a constant temperature of 30°C in temperature-controlled shaking bath for 12 h and settling for 12 h for a complete phase separation. After the phase separation, pH and volume of the aqueous phase were measured. Samples of the top and bottom phase were taken for analysis.

4.4.4 Method for Analysis of Salt

In the system contain of lactic acid, salt content in the aqueous and organic phase were determined by using rotary evaporator R-210/R-215. About 10 ml of sample was charged into the flask, which was then attached to the rotary evaporator. Evaporation temperature was controlled at 130°C. Pressure for evaporation was initially at atmostpheric value before it was graduately decreased at a rate of 5 mmHg per min until all the liquid was removed.

Water and 1-butanol concentration was analyzed by GC method (details described in Chapter II). Lactic acid concentration was determined by HPLC (details described in Chapter III) and salt content was determined by rotary evaporator.

มหาวิทยาลัยเทคโนโลยีสุรนารี

4.5 Results and Discussion

The results of the experiments performed to describe the equilibria for lactic acid extraction from aqueous solutions are presented and discussed in this section. Salts type and effect of salt content in lactic acid aqueous solution on extraction of the acid using 1-butanol was investigated.

Table 4.1 Liquid-liquid equilibrium data of water(1) + 1-buttanol(2) + lactic acid(3) + inorganic salt(4) system at 303.15 K

Aqueous phase				**Organic phase**			
%w_1	**%w_2**	**%w_3**	**%w_4**	**%w_1**	**%w_2**	**%w_3**	**%w_4**
Na_2SO_4							
88.11	5.65	6.24	0	22.31	72.41	5.27	0
82.19	2.55	4.67	10.59	9.56	84.98	5.38	0.08
77.75	0.74	3.48	18.03	7.67	86.39	5.85	0.10
72.06	0.00	2.45	25.49	5.95	86.67	6.23	1.16
$(NH_4)_2SO_4$							
88.11	5.65	6.24	0	22.31	72.41	5.27	0
83.60	2.48	4.28	9.64	10.32	84.91	4.73	0.04
76.51	1.38	3.77	18.34	8.79	85.06	4.86	1.29
69.59	0.79	3.46	26.17	7.53	85.78	4.90	1.79
61.14	0.00	2.82	36.04	5.53	86.72	4.63	3.12
NaCl							
88.11	5.65	6.24	0	22.31	72.41	5.27	0
81.84	2.85	5.49	9.82	12.87	80.30	5.64	1.20
77.85	1.25	4.68	16.21	7.39	85.48	5.61	1.52
72.96	0.65	4.05	22.34	7.21	85.68	5.49	1.61
NH_4Cl							
88.11	5.65	6.24	0	22.31	72.41	5.27	0
79.79	4.05	5.52	10.64	18.89	75.38	5.37	0.36
74.10	2.77	5.44	17.69	13.58	80.43	5.53	0.46
69.42	1.69	5.26	23.64	12.47	81.07	5.15	1.31

The measured compositions of the LLE for water(1) + 1-butanol(2) + lactic acid(3) + inorganic salt(4) system at 303.15 K under atmospheric pressure are shown in Table 4.1. Phase diagram with free lactic acid basis are plotted and shown in Figure 4.1-4.4 for the systems containing Na_2SO_4, $(NH_4)_2SO_4$, NaCl and NH_4Cl, respectively. The compositions of LLE data in Table 4.1 and Figure 4.1-4.4 are expressed in mass percent and mass fraction.

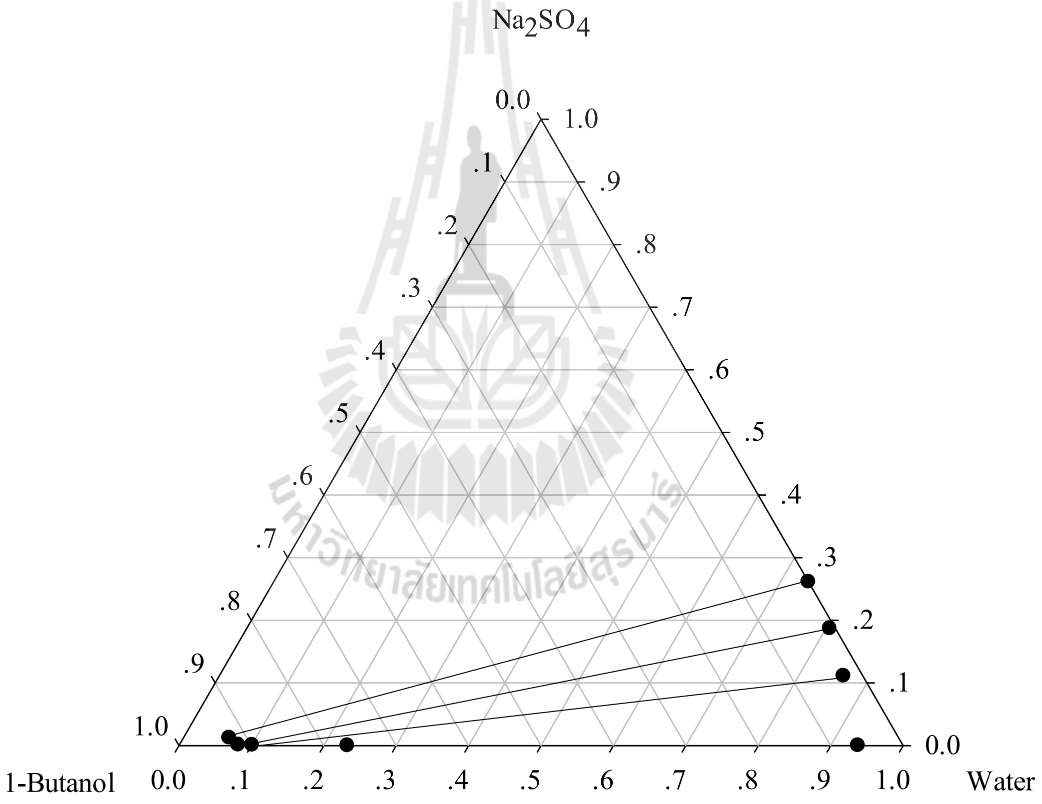


Figure 4.1 Experimental (●) of liquid-liquid equilibrium diagram for water(1) + 1-butanol(2) + lactic acid(3) + Na_2SO_4 system of 1 M of initial lactic acid aqueous solution at 303.15 K

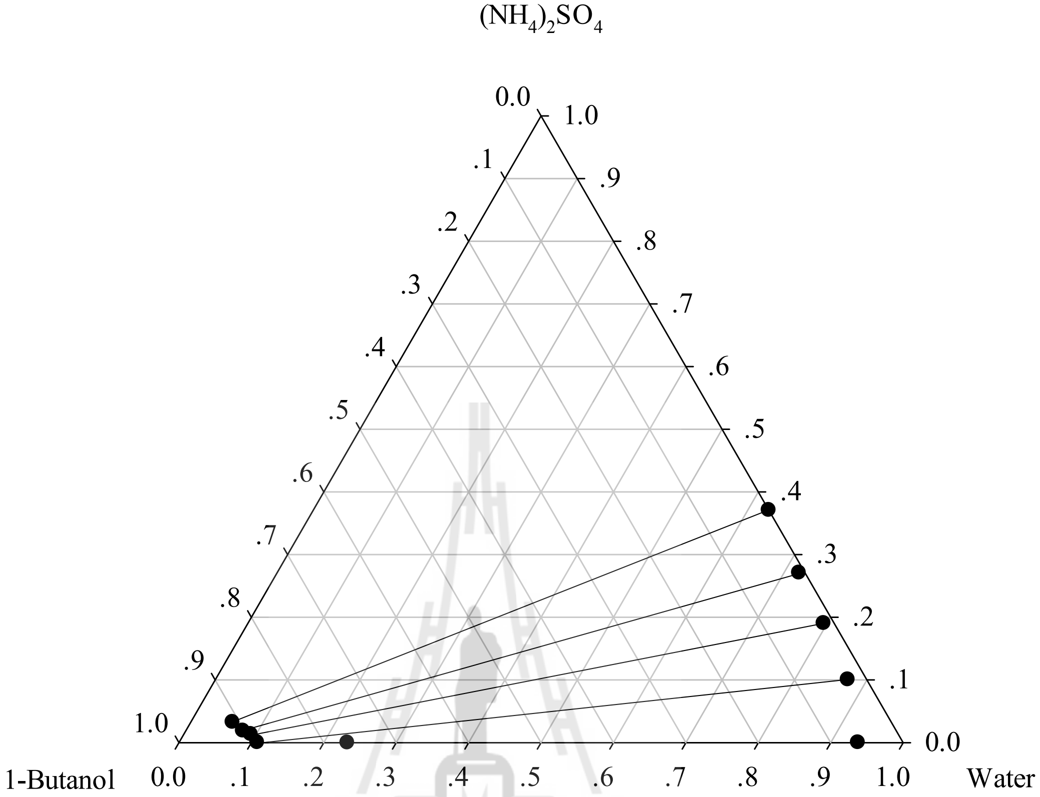


Figure 4.2 Experimental (●) of liquid-liquid equilibrium diagram for water(1) + 1-butanol(2) + lactic acid(3) + $(NH_4)_2SO_4$ system of 1 M of initial lactic acid aqueous solution at 303.15 K

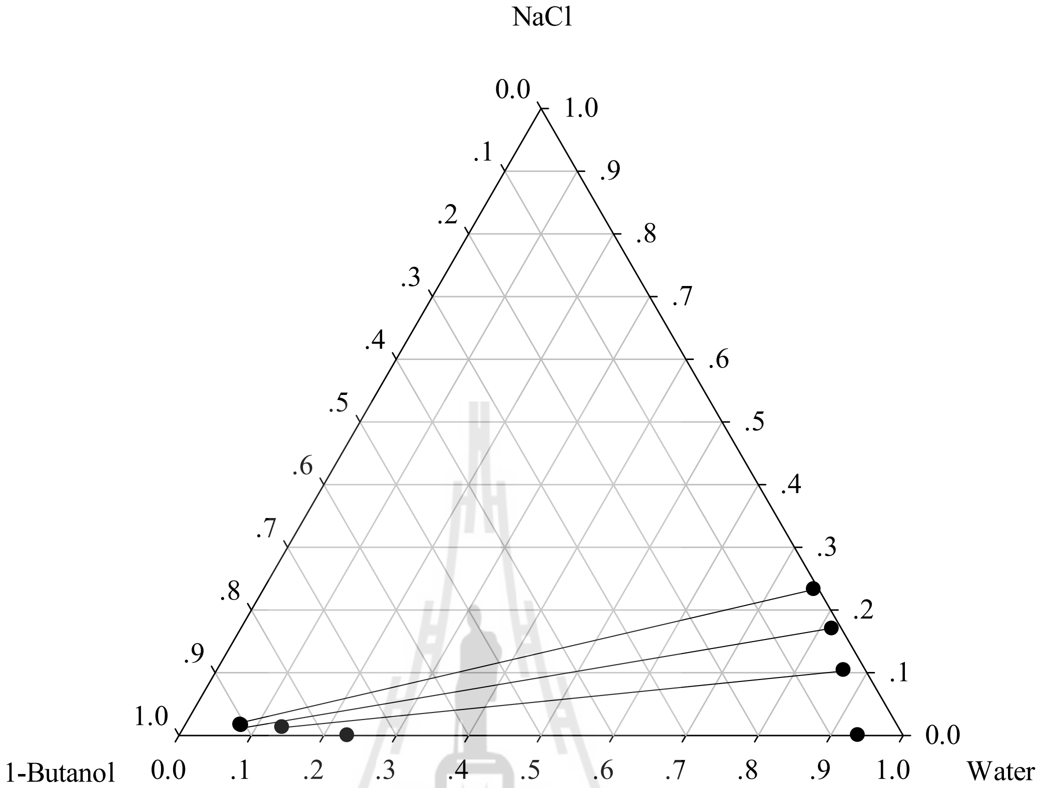


Figure 4.3 Experimental (●) of liquid-liquid equilibrium diadram for water(1) + 1-butanol(2) + lactic acid(3) + NaCl system of 1 M of initial lactic acid aqueous solution at 303.15 K

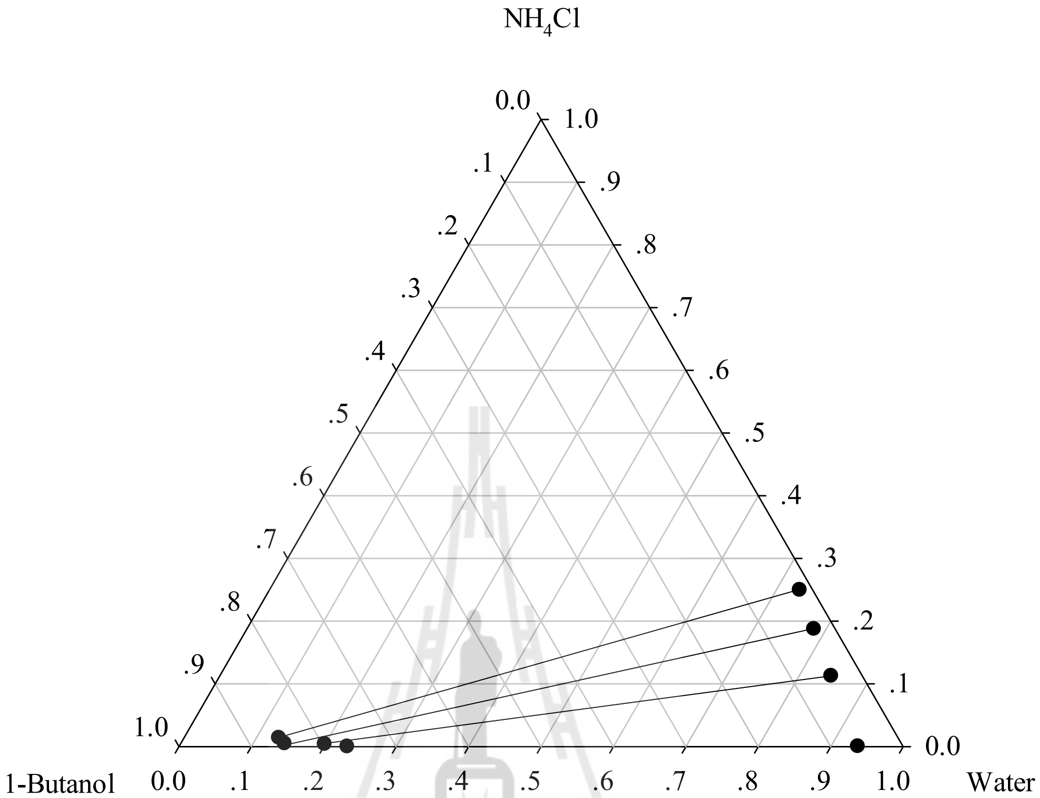


Figure 4.4 Experimental (●) of liquid-liquid equilibrium diagram for water(1) + 1-butanol(2) + lactic acid(3) + NH_4Cl system of 1 M of initial lactic acid aqueous solution at 303.15 K

It is evident from the Table 4.1 that the mass percent of water in the organic phase for all systems with salt decreased with increasing salt concentration. The effect of salt for decreasing of water solubility in organic phase in these systems is in order Na_2SO_4 > $(NH_4)_2SO_4$ > NaCl > NH_4Cl, respectively. In addition, when addition of salt into the aqueous phase, mass percent of lactic acid in aqueous phase decreased, it means that lactic acid are likely transferred to the organic phase. It can be observed that the mass percent of lactic acid in the aqueous phase in the system containing

Na_2SO_4 decreased more than the system with $(NH_4)_2SO_4$, NaCl and NH_4Cl, respectively. Amount of salt in the organic phase for its application on extraction of lactic acid could be considered because it is important for separation of lactic acid from the organic phase in the future. Figure 4.1-4.4, it should be noted that mass fractions of all salts in organic phase are likely small values. Thus, it is quite sensible to use the application of salt on extraction of lactic acid.

It is known that addition of a salt in a solvent mixture can significantly change two-phase equilibrium. Specifically, addition of salt to an aqueous solution can result in either decrease (salting-out) or increase (salting-in) in the solubility of the solute in the solution. In addition to the behavior of a particular solute in aqueous solution, ability to induce salting-in and salting-out of a solute in aqueous solution depends on type and concentration of the salts as well as the ions presenting in the solution after ionization of the salts.

The effectiveness of extraction of lactic acid by 1-butanol in the system containing inorganic salt is given by its separation factor, which is a measure of the ability of 1-butanol to separate the lactic acid from the aqueous acid solution containing salt. The separation factors (*S*) were calculated as follows:

$$S = \frac{D}{D_w + D_s} \tag{4.1}$$

where D_s is the distribution coefficient of salt, which is defined as follows:

$$D_s = \frac{[Salt]_{org} V_{org}}{[Salt]_{aq} V_{aq}} \tag{4.2}$$

where $[Salt]_{org}$ and $[Salt]_{aq}$ are the equilibrium concentration of salt in the organic and aqueous phase, respectively. The results show that the separation factor obtained in this is than 1 for the system reported here, which means that extraction of lactic acid by 1-butanol in these system is possible. However, it was found that the separation factor values at the same initial salt concentration of Na_2SO_4 system are likely higher than $(NH_4)_2SO_4$, NaCl and NH_4Cl, respectively were the distribution coefficient values of water and salt are slightly different. Therefore, the separation factor depends on the distribution coefficient of lactic acid. If high separation factor means mainly of lactic acid is transferred from the aqueous phase to organic phase.

Efficiency of lactic acid extraction was represented by the distribution coefficient and degree of extraction as shown in Table 4.2. The extraction without salt was used as a controlled experiment in order to reveal the effect of salt on the process performance. A higher degree of extraction means that more lactic acid is transferred from the aqueous phase to the organic phase, which implies a successful forward extraction.

Table 4.2 Distribution coefficient and degree of lactic acid extraction with 1-butanol containing inorganic salt in 1M of lactic acid aqueous solution at 303.15 K

Ionic strength (M)	pH	Equilibrium phase volume (ml)		Concentration of lactic acid (M)		D_w	D_s	D	S	$\%E$
		water	1-butanol	Aqueous phase	organic phase					
				Na_2SO_4						
0	2.15	7.90	12.00	0.64	0.46	0.33	0	1.11	3.37	56.68
2.12	2.36	8.50	12.00	0.57	0.47	0.21	0.01	1.15	5.32	56.75
4.06	2.46	8.50	11.50	0.48	0.50	0.15	0.00	1.41	9.18	62.56
6.15	2.53	8.50	11.50	0.37	0.60	0.14	0.04	2.32	13.12	71.69
				$(NH_4)_2SO_4$						
0	2.15	7.90	12.00	0.64	0.46	0.33	0	1.11	3.37	56.68
2.16	2.60	8.40	11.70	0.56	0.41	0.21	0.02	1.03	4.54	56.56
4.28	2.74	8.40	11.60	0.48	0.41	0.19	0.06	1.17	4.64	60.31
5.92	2.80	8.50	11.50	0.42	0.41	0.18	0.06	1.30	5.39	62.94
9.16	2.90	9.00	11.00	0.36	0.42	0.14	0.07	1.41	6.58	63.18
				NaCl						
0	2.15	7.90	12.00	0.64	0.46	0.33	0	1.11	3.37	56.68
1.70	1.60	8.50	11.50	0.65	0.49	0.21	0.12	1.02	3.07	49.77
3.17	1.38	8.90	11.20	0.62	0.50	0.19	0.08	1.01	3.75	47.34
4.84	1.20	9.30	10.70	0.58	0.49	0.16	0.05	0.96	4.64	46.62
				NH_4Cl						
0	2.15	7.90	12.00	0.64	0.46	0.33	0	1.11	3.37	56.68
1.78	1.76	8.50	11.70	0.62	0.48	0.35	0.04	1.05	2.70	49.60
3.25	1.64	8.90	11.10	0.65	0.49	0.21	0.02	0.94	3.99	41.17
4.64	1.54	9.10	10.90	0.64	0.46	0.19	0.05	0.85	3.62	36.66

มหาวิทยาลัยเทคโนโลยีสุรนารี

For extraction of lactic acid using 1-butanol in presence of Na_2SO_4, it was found that the distribution coefficient and degree of lactic acid extraction were increased with concentration of Na_2SO_4 increasing and the effect of salt was more significant at high the concentration of the salt. It can be explained that salt ions solvated water in aqueous solution. Water was a preferred component for solvation. In hydration theory, it was assumed that each salt ion binding with water molecules as a shell of oriented water dipoles surrounding the ion. This “bound” water was then unavailable as solvent for the lactic acid. Therefore, the lactic acid tends to be less soluble in water and finally transfer to the organic phase. As the added mass of Na_2SO_4 increased, more water molecules are bound to its ions, which led to the increased of the distribution coefficient and degree of lactic acid extraction. It means that Na_2SO_4 showed the salting-out effect of lactic acid extraction.

For case of extraction in a presence of $(NH_4)_2SO_4$, the system with $(NH_4)_2SO_4$ induces a salting-in effect with a magnitude dependent on the salt concentration. For small amounts of $(NH_4)_2SO_4$ was added, the distribution coefficient and degree of lactic acid extraction were decreased, which signified that lactic acid preferred to be in aqueous phase rather than the organic phase. The reason why salting-in effect found in the system with a small amount of $(NH_4)_2SO_4$ may be because of this salt contain large monovalent ions (NH_4^+), which is small hydration number. So, when small amounts dissolved in aqueous solution may less the ionic charges attracted to the water molecules. Then, the higher the distribution coefficient and degree of lactic acid extraction is, the higher concentration of $(NH_4)_2SO_4$. This result verifies the “salting-out” effect in the present system by adding suitable amount of $(NH_4)_2SO_4$.

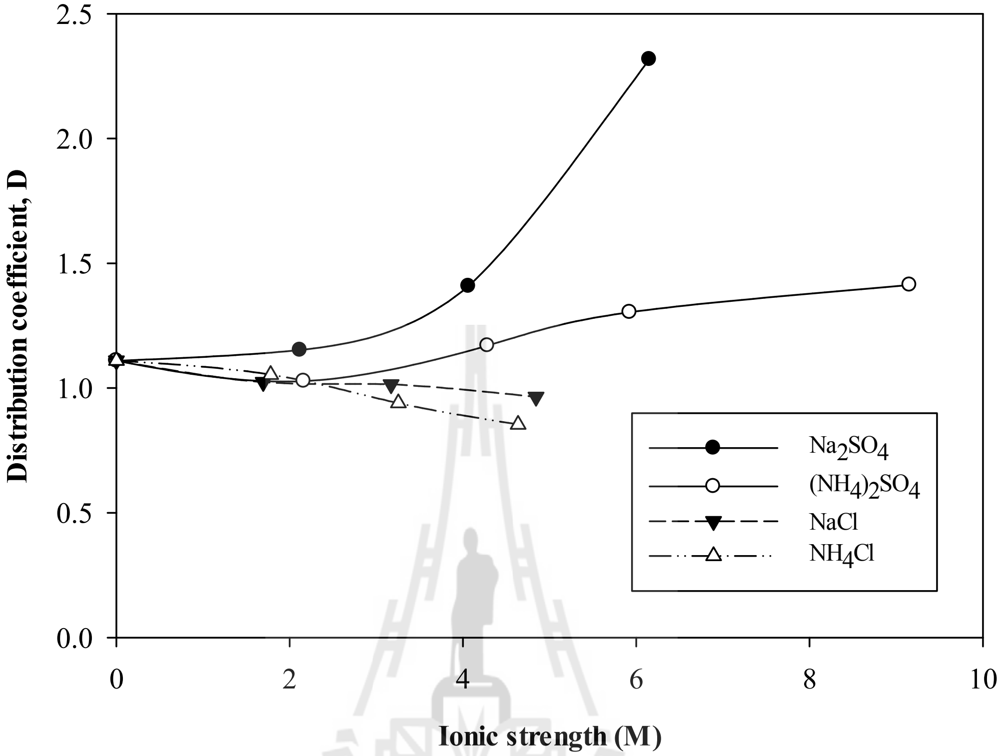


Figure 4.5 Effect of ionic strength on distribution of lactic acid for extraction with initial acid concentration 1 M

มหาวิทยาลัยเทคโนโลยีสุรนารี

Extraction of lactic acid in a presence of chloride salts was observed to be interestingly different from that with the sulfate salts, distribution coefficient and degree of extraction decreases with increasing salt concentration. It can be explained that Cl^- is large ion and it has a small hydration number when compared with other ion studied here. Thus, the salt of this ion is exhibit weaker interactions with water than water with itself and thus interfering little in the hydrogen bonding of the surrounding water. While sulfate salt with SO_4^{2-} is exhibit stronger interactions with water molecules than water with itself and therefore capable of breaking water-water hydrogen bonds (Santos et. al., 2010). As a result, when the addition of chloride salt, lactic acid is likely surrounded by the salt counter ions (ions of opposite net charge) and this screening results in decreasing electrostatic free energy of the lactic acid and increasing activity of the water, which in turn, leads to increasing solubility of lactic acid in aqueous solution (Debye and Hückel, 1923).

Salting-in and salting-out effect of each salt are more apparent when the distribution coefficient was plotted against the ionic strength of aqueous solution in each system. Figure 4.5 shows that Na_2SO_4 and $(NH_4)_2SO_4$ pose similar effect on lactic acid extraction using 1-butanol, i.e. values of the distribution coefficient and degree of lactic acid extraction obtained from the system when equal amounts of these salts were added are quite similar. However, the result indicates that Na_2SO_4 might be more powerful to induce salting out of lactic acid since higher distribution coefficient was achieved in the system with Na_2SO_4 than the system with $(NH_4)_2SO_4$ of equal ionic strength. Furthermore, the value of the distribution coefficient is in the order of $Na_2SO_4 > (NH_4)_2SO_4 > NaCl > NH_4Cl$, which is the same arrangement of salts in Hofmeister series as previously shown in Chapter II.

4.6 Conclusions

Extraction of lactic acid using 1-butanol with addition of inorganic salts was studied. The results show that Na_2SO_4 was the most powerful in enhancing the extraction of this acid under the experimental conditions used in this study. Ability of the salts in increasing the distribution coefficient and degree of lactic acid extraction is in the order of Na_2SO_4 > $(NH_4)_2SO_4$ > NaCl > NH_4Cl, which is the same arrangement of these salts in Hofmeister series.

มหาวิทยาลัยเทคโนโลยีสุรนารี

4.7 References

Ghalami-Choobar, B., Ghanadzadeh, A, and Kousarimehr, S. (2011). Salt effect on the liquid-liquid equilibrium of (water + propionic acid + cyclohexanol) system at T = (298.2, 303.2, and 305.2) K. **Chin. J. Chem. Eng.** 19(4): 565-569.

Tan, T. C. and Aravinth, S. (1999). Liquid-liquid equilibria of water/acetic acid/1-butanol system-effect of sodium (potassium) chloride and correlations. **J. Fluid Phase Equilibria.** 163: 243-257.

Vakili-Nezhaad, G. R., Mohsen-Nia, M., Taghikhani, V., Behpoor, M., and Aghahosseini, M. (2004). Salting-Out effect of NaCl and KCl on the ternay LLE data for the systems of (water+propionic acid+isopropyl methyl ketone) and of (water+propionic acid+isobuthyl methyl ketone). **J. Chem. Thermodynamics.** 36: 341-348.

Chawong, K., and Rattanaphanee, P. (2012). Effect of chloride salt on extraction of lactic acid with n-butanol. **Engineering Transections.** 15: 66-71.

Santos, A. P., Diehl, A., and Levin, Y. (2010). Surface tensions, surface potentials, and the Hofmeister series of electrolyte solutions. **Langmuir.** 26: 10778-10783.

Debye, P., and Hückel, E. (1923). The theory of electrolytes. I. Lowering of freezing point and related phenomena. **Physikalische Zeitschrift.** 24: 185–206.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 CONCLUSIONS

5.1.1 The presence of inorganic salt changed mutual solubility upon solvent in aqueous and organic phase, thus increase the heterogeneous zone of the system.

5.1.2 Temperatures seem to pose a small effect on liquid-liquid equilibrium behavior.

5.1.3 Distribution coefficient of lactic acid and selectivity of 1-butanol in extraction of lactic acid increase with increasing of acid concentration.

5.1.4 Salting-in effect was observed in the system with NaCl and NH_4Cl where the distribution coefficient of lactic acid decreased with increasing salt concentration.

5.1.5 Salting-out effect was observed in the system with Na_2SO_4 and $(NH_4)_2SO_4$ where the distribution coefficient of lactic acid increased with increasing salt concentration.

5.1.6 Effect of salt increasing the distribution coefficient is in order:

Na_2SO_4 > $(NH_4)_2SO_4$ > NaCl > NH_4Cl, which is the same arrangement of these salts in Hofmeister series.

มหาวิทยาลัยเทคโนโลยีสุรนารี

5.1.7 The tie line data of water + 1-butanol + salt system and water +1-butanol + lactic acid system were correlated using the modified extended UNIQUAC and UNIQUAC model, respectively. Both models appeared to accurately correlate the experimental data of each concerning system.

5.2 Recommendation

Some recommendations for the future work are summarized as follows:

- All the works in this thesis focus only on extraction of lactic acid from its prepared aqueous solution. However, the actual future application of the technique is aimed toward extraction of the acid from a fermentation broth after it is biologically produced. It is concerned that other organics and inorganic impurities in the fermentation broth might interfere with the acid extraction and hinder the yield and purity of the acid product. As a result, it should be worthwhile to extensively investigate the inorganic salt effect on extraction of lactic acid from real fermentation broth using 1-butanol.
- Stage extraction is more widely used in industry than a single batch extraction due to its higher efficiency as well as smaller unit equipment and labor operation required. Continuous or semi-continuous recovery of lactic acid from aqueous solution using 1-butanol should, therefore, be investigated. Kinetic parameters for the extraction should also be obtained, before designing a pilot scale stage extractor for this purpose.

APPENDIX A

PROPERTIES OF LACTIC ACID, 1-BUTANOL AND INORGANIC SALT

มหาวิทยาลัยเทคโนโลยีสุรนารี

A.1 Lactic acid

Lactic acid, also known as 2-hydroxypropionic acid, is present in almost all forms of organized life. Lactic acid is first produced by the fermentation of carbohydrates such as sucrose, lactose, mannitol, starch and dextrin by Fremy in 1839. Industrial manufacture of lactic acid was established in 1881 (Elvers et al, 1990). Lactic acid which has both a hydroxyl group and a carboxyl group is the simplest hydroxycarboxylic acid and one of the smallest molecules that is optically active (Lipinsky and Sinclair, 1986). Structural formula of lactic acid is represented in Figure A.1

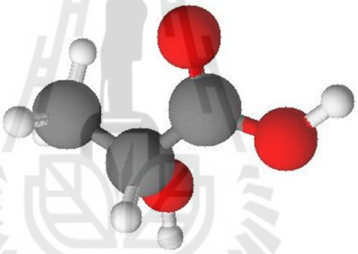


Figure A.1 Molecular structure of lactic acid

มหาวิทยาลัยเทคโนโลยีสุรนารี

This acid is an odorless and colorless substance and is normally obtained as a concentrated solution up to 90 wt%. It is completely soluble in water, ethanol, diethyl ether and other organic solvents that are miscible with water (Elvers et. al., 1990).

Physical and chemical properties of lactic acid are as follows (http://en.wikipedia.org);

Table A.1 Chemical and physical properties of lactic acid

Chemical and Physical properties	
Molecular formula:	$C_3H_6O_3$
Purity:	88%wt from ACROS organics
Molar mass:	90.08 g mol-1
Physical appearance:	aqueous solution
Melting temperature:	53°C
Boiling temperature:	122°C at 12 mmHg
Density:	1.22 g cm-3
Acidity (pKa):	3.86
Dissociation Constant	1.38×10^{-4}

A.2 1-Butanol

1-butanol, C_4H_9OH (also referred to as n-butanol, butan-1-ol or butyl alcohol) is a primary alcohol with a 4 carbon atoms, meaning that the carbon atom carrying the hydroxyl group is connected to one other carbon atom. 1-butanol is of one of the group of fusel alcohols, which have more than two carbon atoms and have significant solubility in water. It can generally be produced along two different ways. First is a petrochemical way which is well established for decades now, and second is a biotechnological way, that also was in use in former days but has been outstripped by the production on a fossil basis.

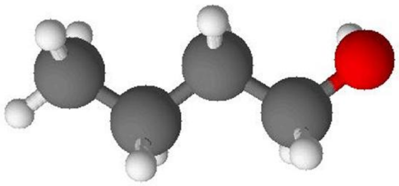


Figure A.2 Molecular structure of 1-butanol

1-butanol is an intermediate in the production of butyl acrylate, butyl acetate, dibutyl phthalate, dibutyl sebacate, and other butyl esters. Other industrial uses include the manufacture of pharmaceuticals, polymers, pyroxylin plastics, herbicide esters. It is also used as a diluent/reactant in the manufacture of urea–formaldehyde and melamine–formaldehyde resins. In addition, It is used as a solvent for the extraction process. Structural formula of lactic acid is represented in Figure A.2

The physical as well as chemical properties of the alcohols are determined significantly by the presence and position of the functional groups (alkyl- and hydroxyl groups). The physical and chemical properties of 1-butanol are shown in Table A.2

Table A.2 Chemical and physical properties of 1-butanol

Chemical and Physical properties	
Molecular formula:	$C_4H_{10}O$
Purity:	99.9%wt from ACROS organics
Molar mass:	74.12 g mol-1
Physical appearance:	Colourless, refractive liquid
Melting temperature:	-89.8 °C
Boiling temperature:	117 °C
Density:	0.81 g cm-3
Acidity (pKa):	16.1

มหาวิทยาลัยเทคโนโลยีสุรนารี

A.3 Probberties of Inorgamic Salt

Table A.3 Properties of some ions in aqueous solutions and thermodynamic quantities of ion hydration at 298.15 K. (Marcus, 1997)

Ions	**M_I (g mol^{-1})**	**r_I (nm)**	**Δr_I (nm)**	**h_I**	**$\Delta_{hydr}H_I^{\infty}$ kJ mol^{-1}**
Li^+	6.94	0.069	0.171	5.2	-531
Na^+	22.94	0.102	0.116	3.5	-416
K^+	39.1	0.138	0.075	2.6	-334
Cs^+	132.91	0.170	0.050	2.1	-283
NH_4	18.04	0.148	-	2.4	-329
F^-	18.99	0.133	0.081	2.7	-510
Cl^-	35.45	0.181	0.044	2.0	-367
I^-	126.91	0.220	0.028	1.6	-291
ClO_4^-	99.45	0.240	0.023	1.5	-246
Mg^{2+}	24.31	0.072	0.225	10	-1,949
Ca^{2+}	40.08	0.100	0.169	7.2	-1,602
Ba^{2+}	137.33	0.136	0.118	5.3	-1,332
CO_3^{2-}	60.01	0.178	0.076	4.0	-1,397
SO_4^{2-}	96.07	0.230	0.045	3.1	-1,138
La^{3+}	138.91	0.105	0.197	10.3	-3,312
PO_4^{3-}	94.97	0.238	0.057	4.5	-2,879

มหาวิทยาลัยเทคโนโลยีสุรนารี

APPENDIX B

EXAMPLE OF COMPONENT ANALYSIS OF WATER, 1-BUTABOL, LACTIC ACID AND INORGANIC SALT

B.1 Calibration Standard Curve of Water

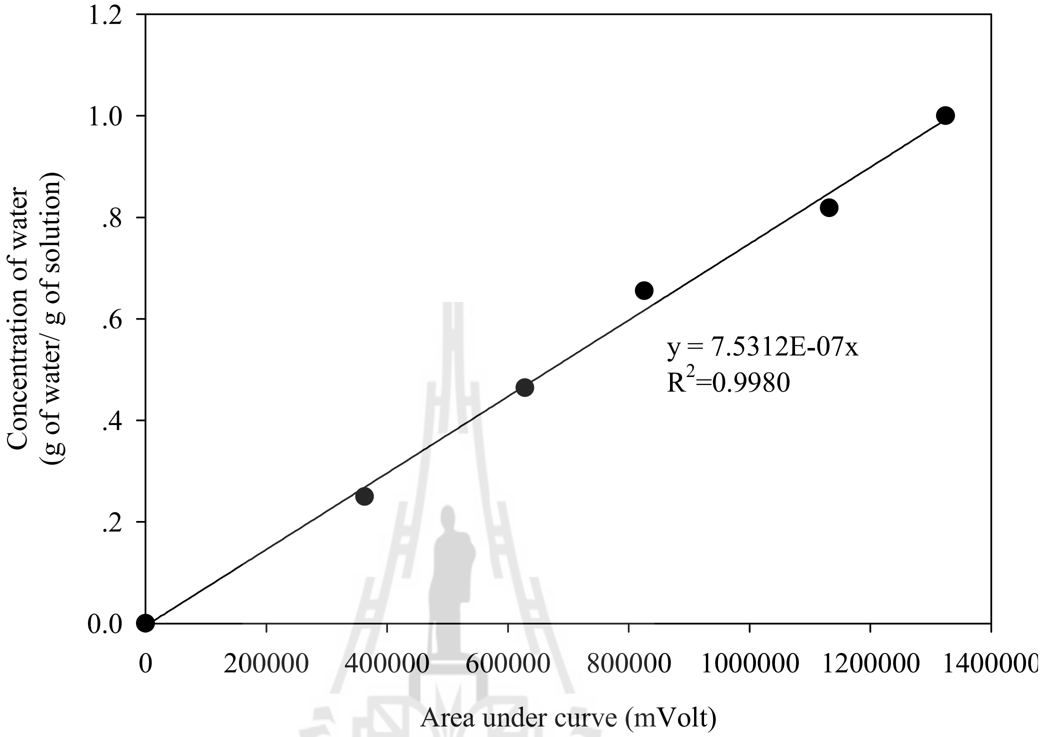


Figure B.1 Calibration standard curve of water

มหาวิทยาลัยเทคโนโลยีสุรนารี

B.2 Calibration Standard Curve of Lactic Acid

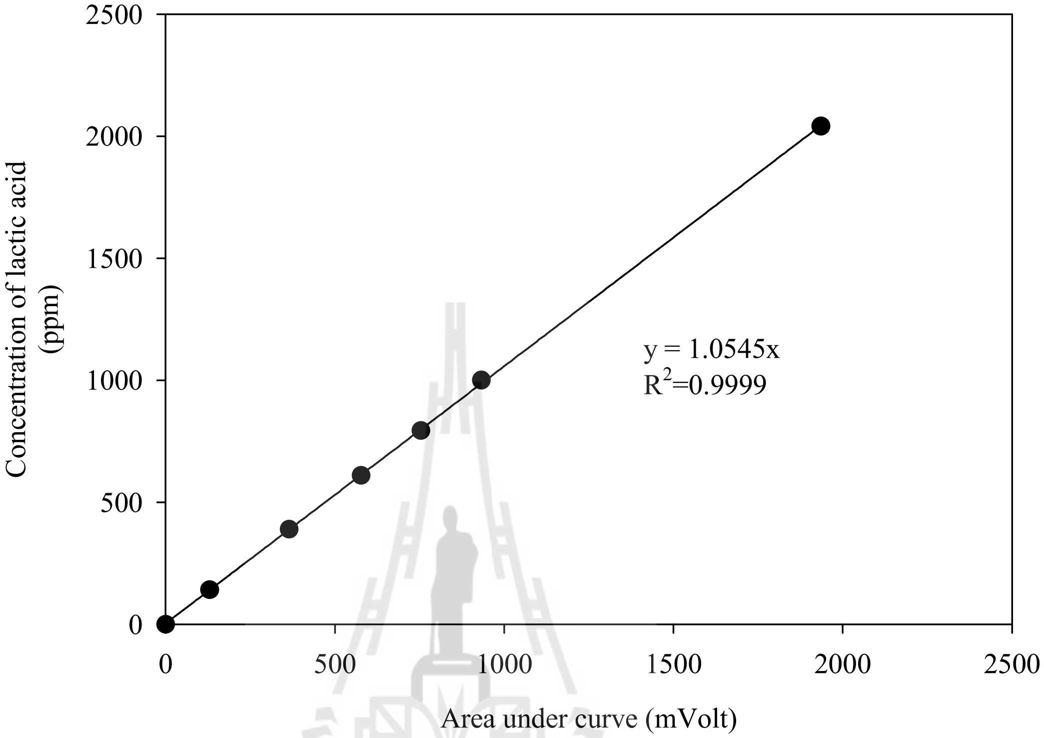


Figure B.2 Calibration standard curve of lactic acid

B.3 Calibration Standard Curve of 1-Butanol

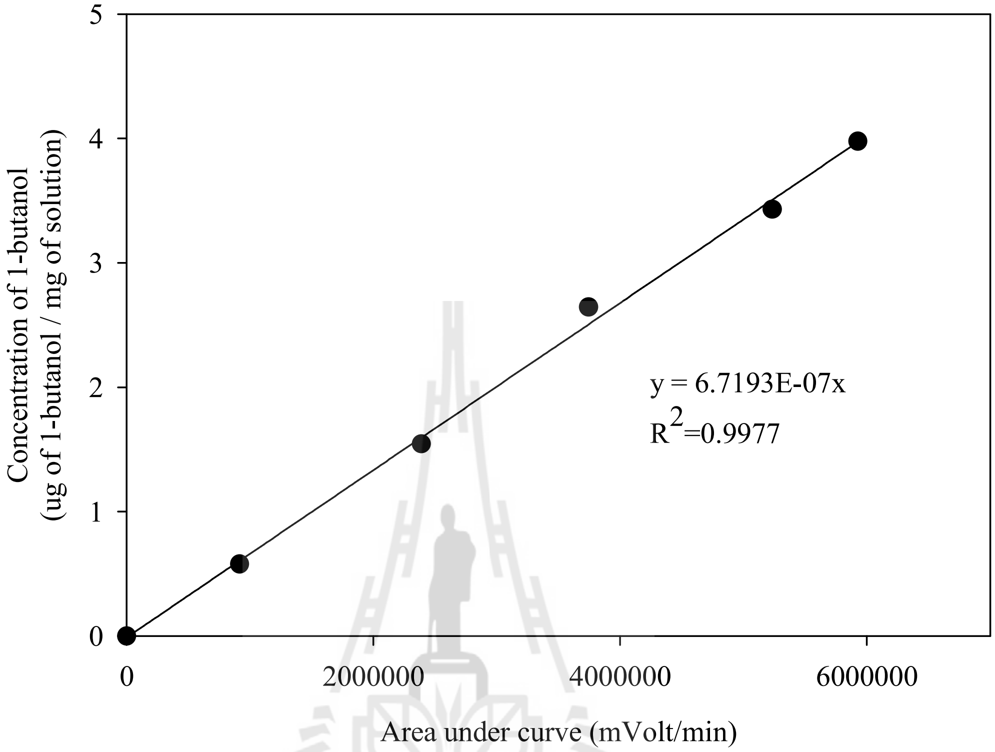


Figure B.3 Calibration standard curve of 1-butanol

มหาวิทยาลัยเทคโนโลยีสุรนารี

B.4 Component Analysis of Water, 1-Butanol, Lactic acid and in Aqueous Phase

Example analysis of water+1-butanol+lactic acid+Na_2SO_4 system

After liquid-liquid equilibrium:

Total volume of aqueous phase = 8.50 ml

Density of aqueous phase = 1.20 g/ml

Total weight of aqueous solution $= 8.50\ \text{ml} \times 1.2000 \frac{\text{g}}{\text{ml}} = 10.2000\ \text{g}$

Water analysis with TCD-GC in 1 μL of pure sample is shown in Fig. B.4. The area of water will be taken to calculate the quantity from the water calibration curve. It is calculated that the concentration of water = 0.7984 g/g

$$\therefore \text{water} = 0.7984 \frac{\text{g}}{\text{g}} \times 1.2000 \frac{\text{g}}{\text{ml}} \times 8.50\text{ml} = 8.1439\ \text{g}$$

มหาวิทยาลัยเทคโนโลยีสุรนารี

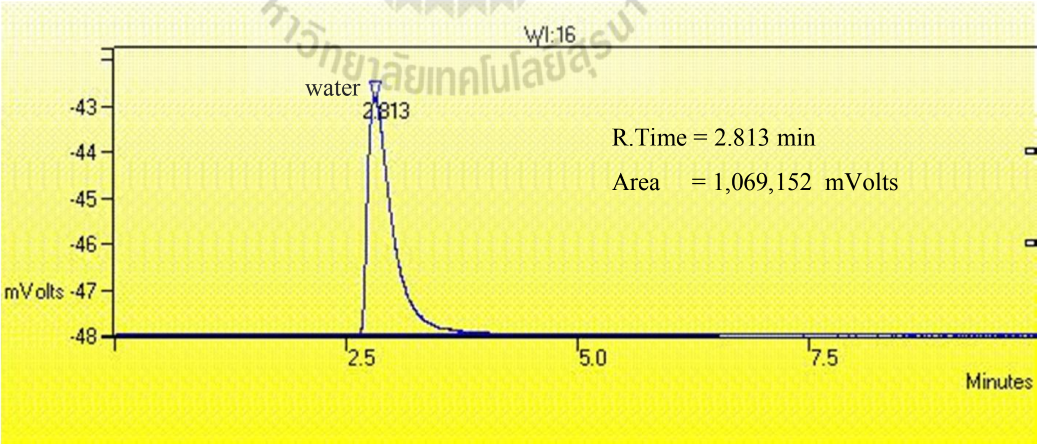


Figure B.4 Water analysis in aqueous phase

Dilution of sample with DI water for analysis 1-butanol and lactic acid:

Weight of sample = 0.0205 g

Weight of DI water = 2.3096 g

Total weight = 0.0205 + 2.3096 = 2.3301 g

The area under curve of 1-butanol analysis is 305,696 mAU/s. The area will be taken to determine the quantity of 1-butanol from calibration curve. The concentration of 1-butanol = 0.2054 μg/mg

$$\therefore \text{ 1-butanol } = \frac{0.2054\times10^{-6}\,\text{g}}{10^{-3}\,\text{g solution}}\times\frac{2.3301\text{g solution}}{0.0205\text{g sample}}\times10.20\text{g sample} = 0.2381\,\text{g}$$

Lactic acid analysis with HPLC is shown in Fig. B.6. The calculation of acid concentration from calibration curve is 401.9633 ppm

มหาวิทยาลัยเทคโนโลยีสุรนารี

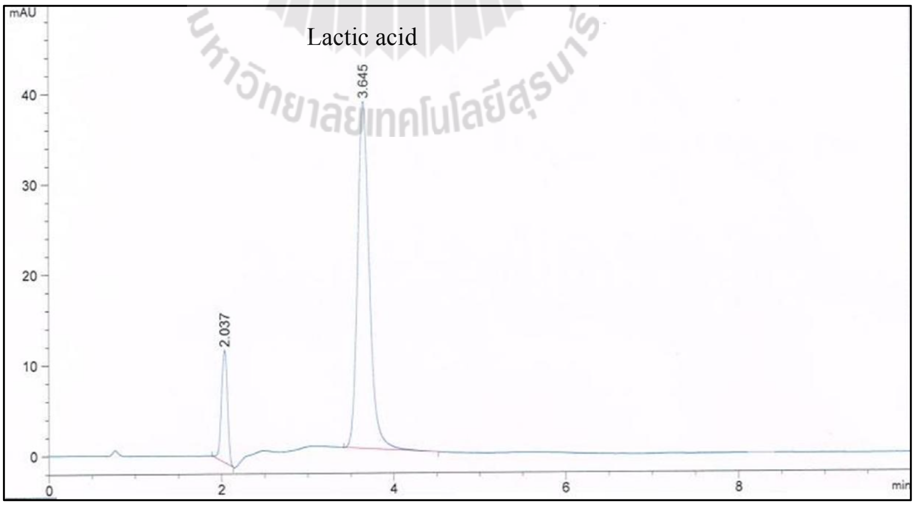


Figure B.5 Lactic acid analysis in aqueous phase

∴ Lactic acid:

$$= \frac{401.9633\text{mg}}{\text{ml}} \times \left(\frac{\left(\dfrac{0.0205\text{g sample}}{1.2000\,\dfrac{\text{g}}{\text{ml}}} \right) + \left(\dfrac{2.3096\text{g water}}{0.9957\,\dfrac{\text{g}}{\text{ml}}} \right)}{0.0205\text{g sample}} \right) \times 10.20\text{g sample} = 0.4673 \text{ g}$$

Preparation of Na_2SO_4 analysis by Drying:

Weight of tube = 285.6800 g

Weight of sample = 5.1100 g

Total weight of tube + sample = 285.6800 + 5.1100 = 290.7900 g

After Drying:

Total weight of tube + sample = 286.2100 g

∴ Na_2SO_4 = $(286.1800 - 285.6800)\text{g} \times \dfrac{10.20\text{g}}{5.11\text{g}} = 0.9980$ g

Therefore, in total weight of aqueous phase (10.2000 g):

Water = 8.1439 g

1-butanol = 0.2318 g

Lactic acid = 0.4673 g

Na_2SO_4 = 0.9980 g

Total weight = 9.8272 g

Percent error $= \dfrac{10.2000 - 9.8272}{10.2000} \times 100 = +3.6549\%$

B.5 Component Analysis of Water, 1-Butanol, Lactic acid and Na_2SO_4 in Organic Phase

Example analysis of water+1-butanol+lactic acid+Na_2SO_4 system

After liquid-liquid equilibrium:

Total volume of aqueous phase = 12.00 ml

Density of aqueous phase = 0.8000 g/ml

Total weight of aqueous solution $= 12.00\ \text{ml} \times 0.8000 \frac{\text{g}}{\text{ml}} = 9.6000\ \text{g}$

Water analysis with TCD-GC in 1 μL of pure sample is shown in Fig. B.7. The area of water will be taken to calculate the quantity from the water calibration curve. It is calculated that the concentration of water = 0.1992 g/g

$$\therefore \text{ water} = 0.1992 \frac{\text{g}}{\text{g}} \times 0.8000 \frac{\text{g}}{\text{ml}} \times 12.00\text{ml} = 1.9123\ \text{g}$$

มหาวิทยาลัยเทคโนโลยีสุรนารี

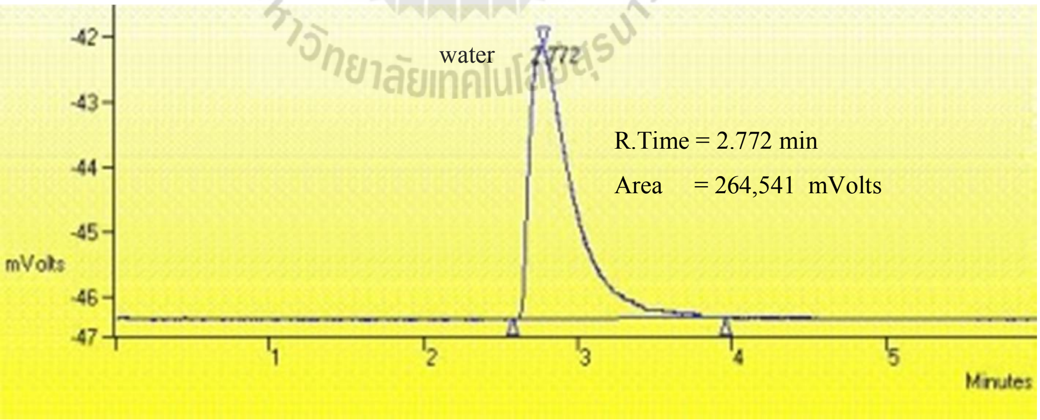


Figure B.6 Water analysis in organic phase

Dilution of sample with DI water for analysis 1-butanol and lactic acid:

Weight of sample = 0.0085 g

Weight of DI water = 2.1622 g

Total weight = 0.0085 + 2.1622 = 2.1707 g

The area under curve of 1-butanol analysis is 4,856,607 mAU/s. The area will be taken to determine the quantity of 1-butanol from calibration curve. The concentration of 1-butanol = 3.2633 μg/mg

$$\therefore \text{ 1-butanol } = \frac{3.2633\times10^{-6}\,\text{g}}{10^{-3}\,\text{g solution}}\times\frac{2.1707\text{g solution}}{0.0085\text{g sample}}\times 9.6000\text{g sample} = 8.0004\,\text{g}$$

Lactic acid analysis with HPLC is shown in Fig. B.9. The calculation of acid concentration from calibration curve is 206.2453 ppm

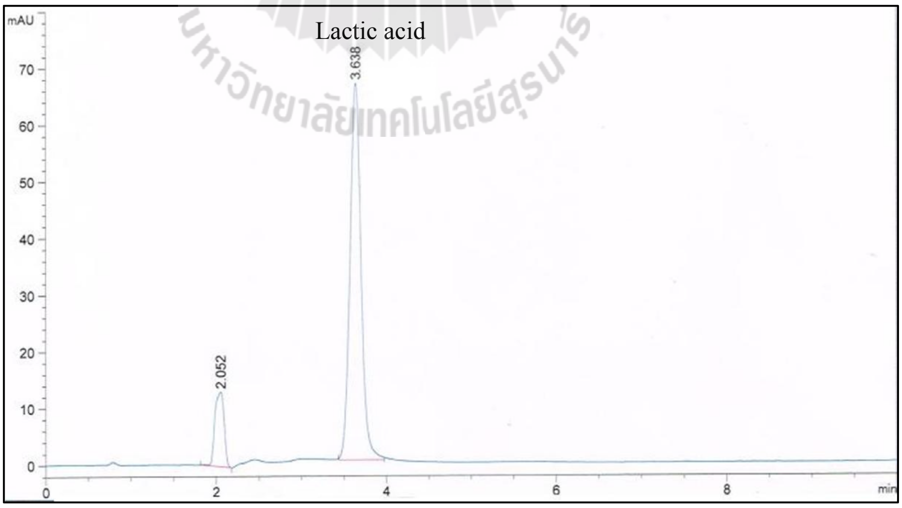


Figure B.7 Lactic acid analysis in organic phase

$\therefore$ Lactic acid:

$$= \frac{206.2453\text{mg}}{\text{ml}} \times \left(\frac{\left(\dfrac{0.0085\text{g sample}}{0.8000\dfrac{\text{g}}{\text{ml}}} \right) + \left(\dfrac{2.1622\text{g water}}{0.9957\dfrac{\text{g}}{\text{ml}}} \right)}{0.0085\text{g sample}} \right) \times 9.60\text{g sample} = 0.5083\text{ g}$$

Na_2SO_4 in organic phase determined by mass balance:

Initial weight of Na_2SO_4 in aqueous solution = 1.0036 g

Weight of Na_2SO_4 in aqueous phase = 0.9980 g

$\therefore$ Weight of Na_2SO_4 in organic phase = 1.0036 + 0.9980 = 0.0056 g

Therefore, in total weight of aqueous phase (10.20 g):

Water = 0.1992 g

1-butanol = 8.0004 g

Lactic acid = 0.5083 g

Na_2SO_4 = 0.0056 g

Total weight = 8.7135 g

$$\text{Percent error} = \frac{9.6000 - 8.7135}{9.6000} \times 100 = +9.2343\%$$

มหาวิทยาลัยเทคโนโลยีสุรนารี

B.6 Mass Balance

Total mass balance of water, 1-butanol, and lactic acid in aqueous and organic phase shows that the percent error of each component is less than ±10%

Initial weight of water = 9.1640 g

Initial weight of 1-butanol = 7.9141

Initial weight of lactic acid = 1.0163 g

Initial weight of Na_2SO_4 = 1.0036 g

Water = 8.1493+1.9123 = 10.0616 g

Percent error of water = $\frac{9.1640-10.0616}{9.1640}\times 100=-9.7948\%$

1-butanol = 2.2381+8.0004 = 8.2385 g

Percent error of 1-butanol = $\frac{7.9140-8.2385}{7.9140}\times 100=-4.1003\%$

Lactic acid = 0.4683+0.5083 = 0.9756 g

Percent error of lactic acid = $\frac{1.0163-0.9756}{10.0183}\times 100=+4.0047\%$

Na_2SO_4 = 0.9980+0.0056 = 1.0036 g

Percent error of Na_2SO_4 = $\frac{1.0036-1.0036}{1.0036}\times 100=0\%$

มหาวิทยาลัยเทคโนโลยีสุรนารี

APPENDIX C

LIQUID-LIQUID EQUILIBRIUM BY UNIQUAC AND MODIFIED EXTENDED UNIQUAC MODELS

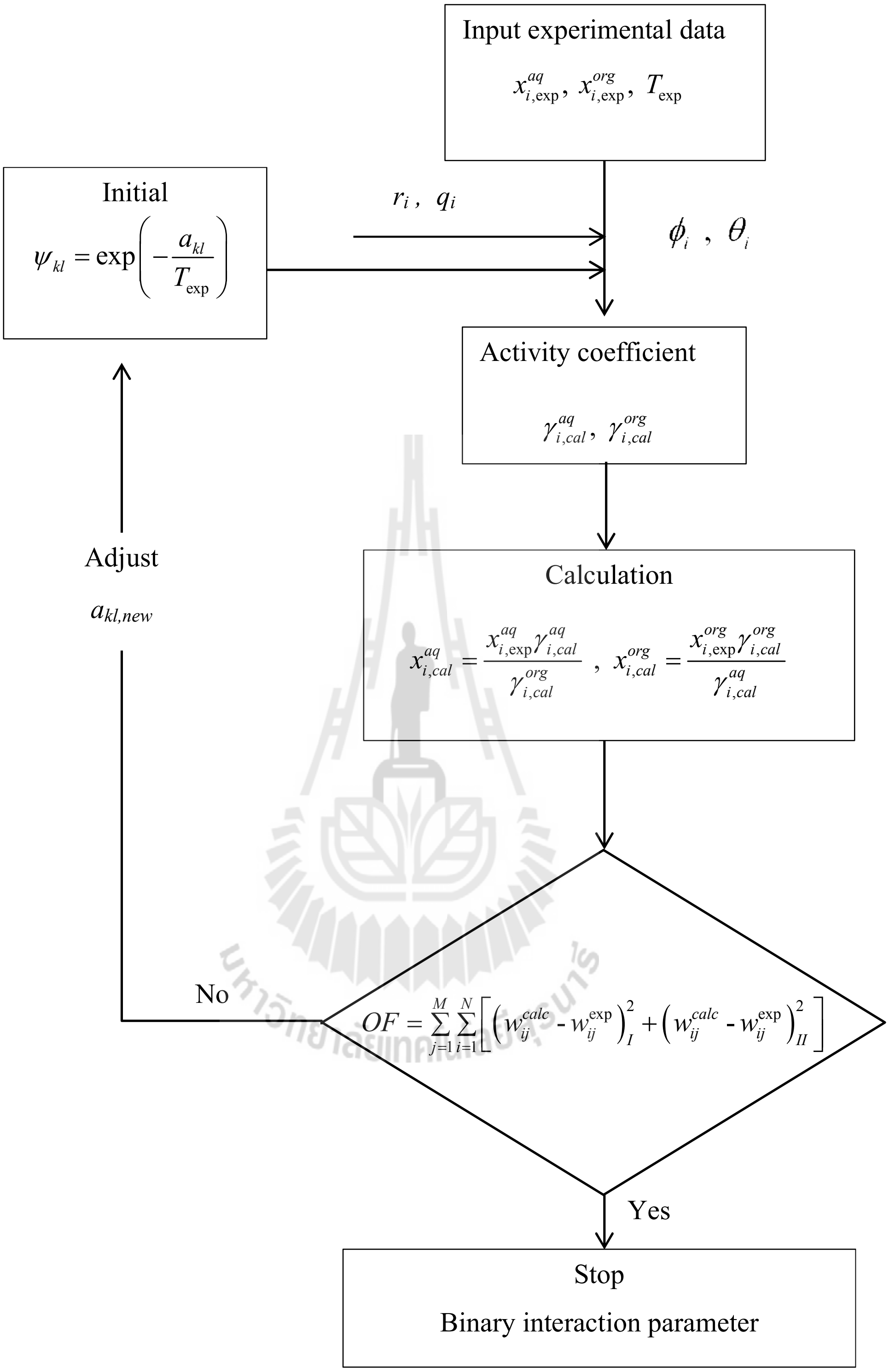
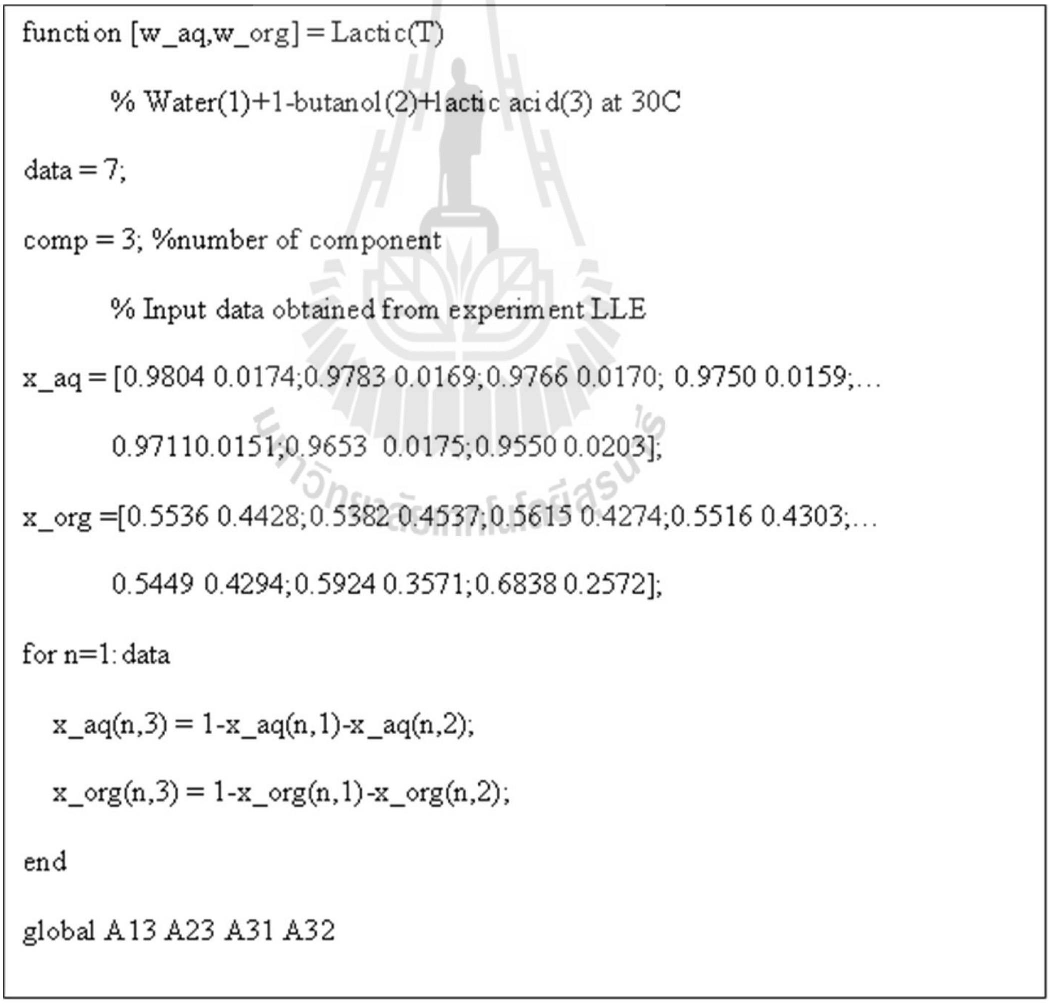


Figure C.1 Calulation of binary interaction parameter diagram

Modified extended UNIQUAC model is used to correlation of the data of liquid-liquid quilibrium of water + 1-butanol + inorganic salt system and UNIQUAC model is used to correlation of the ternary water + 1-butanol + lactic acid system. The tie lines of both model were optimized with the objective function. The regression was ccomplished using MATLAB®(VersionR2012). The built-in optimization function, fminunc was used which finds the minimum of an unconstrained multi variable function.

C.1 UNIQUAC Model



```
function [w_aq,w_org] = Lactic(T)
        % Water(1)+1-butanol(2)+lactic acid(3) at 30C
data = 7;
comp = 3; %number of component
        % Input data obtained from experiment LLE
x_aq = [0.9804 0.0174;0.9783 0.0169;0.9766 0.0170; 0.9750 0.0159;...
        0.97110.0151;0.9653  0.0175;0.9550 0.0203];
x_org =[0.5536 0.4428;0.5382 0.4537;0.5615 0.4274;0.5516 0.4303;...
        0.5449 0.4294;0.5924 0.3571;0.6838 0.2572];
for n=1: data
   x_aq(n,3) = 1-x_aq(n,1)-x_aq(n,2);
   x_org(n,3) = 1-x_org(n,1)-x_org(n,2);
end
global A13 A23 A31 A32
```

```
    % data Aij at 30C
A11=0;
A22=0;
A33=0;
% calculated activity coeefficient by UNIQUAC term
        % Volume parameters of pure components
%Water (1)
R1 = 0.9200; Q1 = 1.4000;
%1-Butanol(2)
R2 = 3.9243; Q2 = 3.6680;
%Lactic acid(3)
R3 = 3.1648; Q3 = 2.8800;
for i=1:data
   %Aqueous phase
       sigma_AQ_r(i,1) = x_aq(i,1).*R1+x_aq(i,2).*R2+x_aq(i,3).*R3;
       phi_AQ(i,1) = x_aq(i,1)*R1./sigma_AQ_r(i,1);
       phi_AQ(i,2) = x_aq(i,2)*R2./sigma_AQ_r(i,1);
       phi_AQ(i,3) = x_aq(i,3)*R3./sigma_AQ_r(i,1);

       sigma_AQ_q(i,1) = x_aq(i,1).*Q1+x_aq(i,2).*Q2+x_aq(i,3).*Q3;
       theta_AQ(i,1) = x_aq(i,1)*Q1./sigma_AQ_q(i,1);
       theta_AQ(i,2) = x_aq(i,2)*Q2./sigma_AQ_q(i,1);
       theta_AQ(i,3) = x_aq(i,3)*Q3./sigma_AQ_q(i,1);
       %Organic phase
```

```
    sigma_ORG_r(i,1) = x_org(i,1).*R1+x_org(i,2).*R2+x_org(i,3).*R3;
    phi_ORG(i,1) = x_org(i,1)*R1./sigma_ORG_r(i,1);
    phi_ORG(i,2) = x_org(i,2)*R2./sigma_ORG_r(i,1);
    phi_ORG(i,3) = x_org(i,3)*R3./sigma_ORG_r(i,1);

    sigma_ORG_q(i,1) = x_org(i,1).*Q1+x_org(i,2).*Q2+x_org(i,3).*Q3;
    theta_ORG(i,1) = x_org(i,1)*Q1./sigma_ORG_q(i,1);
    theta_ORG(i,2) = x_org(i,2)*Q2./sigma_ORG_q(i,1);
    theta_ORG(i,3) = x_org(i,3)*Q3./sigma_ORG_q(i,1);
end
      tao11 = exp(-(A11./T));
      tao12 = exp(-(A12./T));
      tao13 = exp(-(A13./T));
      tao21 = exp(-(A21./T));
      tao22 = exp(-(A22./T));
      tao23 = exp(-(A23./T));
      tao31 = exp(-(A31./T));
      tao32 = exp(-(A32./T));
      tao33 = exp(-(A33./T));
for i=1:data
  %Calculated Activity Poefficient in Aqueous Phase
%Combinatorial Term
lnG_AQcomb(i,1) = 1-phi_AQ(i,1)./x_aq(i,1)+log(phi_AQ(i,1)./x_aq(i,1))-5*Q1...
              *(log(phi_AQ(i,1)./theta_AQ(i,1))+1-phi_AQ(i,1)./theta_AQ(i,1));
```

```
lnG_AQcomb(i,2) = 1-phi_AQ(i,2)./x_aq(i,2)+log(phi_AQ(i,2)./x_aq(i,2))-5*Q2...
                  *(log(phi_AQ(i,2)./theta_AQ(i,2))+1-phi_AQ(i,2)./theta_AQ(i,2));
lnG_AQcomb(i,3) = 1-phi_AQ(i,3)./x_aq(i,3)+log(phi_AQ(i,3)./x_aq(i,3))-5*Q3...
                  *(log(phi_AQ(i,3)./theta_AQ(i,3))+1-phi_AQ(i,3)./theta_AQ(i,3));
%Residual Term
lnG_AQres(i,1) = Q1.*(1-log(theta_AQ(i,1).*tao11+theta_AQ(i,2).*tao21…
                  +theta_AQ(i,3).*tao31)-theta_AQ(i,1).*tao11./(theta_AQ(i,1)…
                  .*tao11+theta_AQ(i,2).*tao21+theta_AQ(i,3).*tao31)...
                  -theta_AQ(i,2).*tao12./(theta_AQ(i,1).*tao12…
                  +theta_AQ(i,2).*tao22+theta_AQ(i,3).*tao32)...
                  -theta_AQ(i,3).*tao13./(theta_AQ(i,1).*tao13…
                  +theta_AQ(i,2).*tao23+theta_AQ(i,3).*tao33));
lnG_AQres(i,2) = Q2.*(1-log(theta_AQ(i,1).*tao12+theta_AQ(i,2).*tao22…
                  +theta_AQ(i,3).*tao32) -theta_AQ(i,1).*tao21./(theta_AQ(i,1)…
                  .*tao11+theta_AQ(i,2).*tao21+theta_AQ(i,3).*tao31)...
                  -theta_AQ(i,2).*tao22./(theta_AQ(i,1).*tao12…
                  +theta_AQ(i,2).*tao22+theta_AQ(i,3).*tao32)...
                  -theta_AQ(i,3).*tao23./(theta_AQ(i,1).*tao13…
                  +theta_AQ(i,2).*tao23+theta_AQ(i,3).*tao33));
lnG_AQres(i,3) = Q3.*(1-log(theta_AQ(i,1).*tao13+theta_AQ(i,2).*tao23…
                  +theta_AQ(i,3).*tao33)-theta_AQ(i,1).*tao31./(theta_AQ(i,1)…
                  .*tao11+theta_AQ(i,2).*tao21+theta_AQ(i,3).*tao31)...
                  -theta_AQ(i,2).*tao32./(theta_AQ(i,1).*tao12…
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

```
                    +theta_AQ(i,2).*tao22+theta_AQ(i,3).*tao32)...
                    -theta_AQ(i,3).*tao33./(theta_AQ(i,1).*tao13…
                    +theta_AQ(i,2).*tao23+theta_AQ(i,3).*tao33));
  lnG_U_AQ(i,1) = lnG_AQcomb(i,1)+lnG_AQres(i,1); %for water
  lnG_U_AQ(i,2) = lnG_AQcomb(i,2)+lnG_AQres(i,2); %for 1-butanol
  lnG_U_AQ(i,3) = lnG_AQcomb(i,3)+lnG_AQres(i,3); %for lactic acid
    %Calculated activity coeeficient in Organic phase
%Combinatorial Term
lnG_ORGcomb(i,1) = 1-phi_ORG(i,1)./x_org(i,1)+log(phi_ORG(i,1)./x_org(i,1))…
-5*Q1*(log(phi_ORG(i,1)./theta_ORG(i,1))+1-phi_ORG(i,1)./theta_ORG(i,1));

lnG_ORGcomb(i,2) = 1-phi_ORG(i,2)./x_org(i,2)+log(phi_ORG(i,2)./x_org(i,2))…
-5*Q2*(log(phi_ORG(i,2)./theta_ORG(i,2))+1-phi_ORG(i,2)./theta_ORG(i,2));

lnG_ORGcomb(i,3) = 1-phi_ORG(i,3)./x_org(i,3)+log(phi_ORG(i,3)./x_org(i,3))…
5*Q3*(log(phi_ORG(i,3)./theta_ORG(i,3))+1-phi_ORG(i,3)./theta_ORG(i,3));

%Residual Term
lnG_ORGres(i,1) = Q1.*(1-log(theta_ORG(i,1).*tao11+theta_ORG(i,2).*tao21…
        +theta_ORG(i,3).*tao31)-theta_ORG(i,1).*tao11./(theta_ORG(i,1).*tao11…
        +theta_ORG(i,2).*tao21+theta_ORG(i,3).*tao31)-theta_ORG(i,2).*tao12…
        ./(theta_ORG(i,1).*tao12+theta_ORG(i,2).*tao22+theta_ORG(i,3).*tao32)...
        -theta_ORG(i,3).*tao13./(theta_ORG(i,1).*tao13…
        +theta_ORG(i,2).*tao23+theta_ORG(i,3).*tao33));
```

```
lnG_ORGres(i,2) = Q2.*(1-log(theta_ORG(i,1).*tao12+theta_ORG(i,2).*tao22…
        +theta_ORG(i,3).*tao32)-theta_ORG(i,1).*tao21./(theta_ORG(i,1).*tao11…
        +theta_ORG(i,2).*tao21+theta_ORG(i,3).*tao31)-theta_ORG(i,2).*tao22…
        ./(theta_ORG(i,1).*tao12+theta_ORG(i,2).*tao22+theta_ORG(i,3).*tao32)...
         -theta_ORG(i,3).*tao23./(theta_ORG(i,1).*tao13…
        +theta_ORG(i,2).*tao23+theta_ORG(i,3).*tao33));
lnG_ORGres(i,3) = Q3.*(1-log(theta_ORG(i,1).*tao13+theta_ORG(i,2).*tao23…
        +theta_ORG(i,3).*tao33)-theta_ORG(i,1).*tao31./(theta_ORG(i,1).*tao11…
        +theta_ORG(i,2).*tao21+theta_ORG(i,3).*tao31)-theta_ORG(i,2).*tao32…
        ./(theta_ORG(i,1).*tao12+theta_ORG(i,2).*tao22+theta_ORG(i,3).*tao32)...
        -theta_ORG(i,3).*tao33./(theta_ORG(i,1).*tao13…
        +theta_ORG(i,2).*tao23+theta_ORG(i,3).*tao33));
  lnG_U_ORG(i,1) = lnG_ORGcomb(i,1)+lnG_ORGres(i,1);
  lnG_U_ORG(i,2) = lnG_ORGcomb(i,2)+lnG_ORGres(i,2);
  lnG_U_ORG(i,3) = lnG_ORGcomb(i,3)+lnG_ORGres(i,3);
end
for i=1:data
   for j=1:3
      %Activity Coefficient
      Gamma_AQCal(i,j)=exp(lnG_U_AQ(i,j));
      Gamma_ORGCal(i,j)=exp(lnG_U_ORG(i,j));
      %Calculated mole fraction
      x_aqCal(i,j)=x_org(i,j).*Gamma_ORGCal(i,j)./Gamma_AQCal(i,j);
      x_orgCal(i,j)=x_aq(i,j).*Gamma_AQCal(i,j)./Gamma_ORGCal(i,j);
```

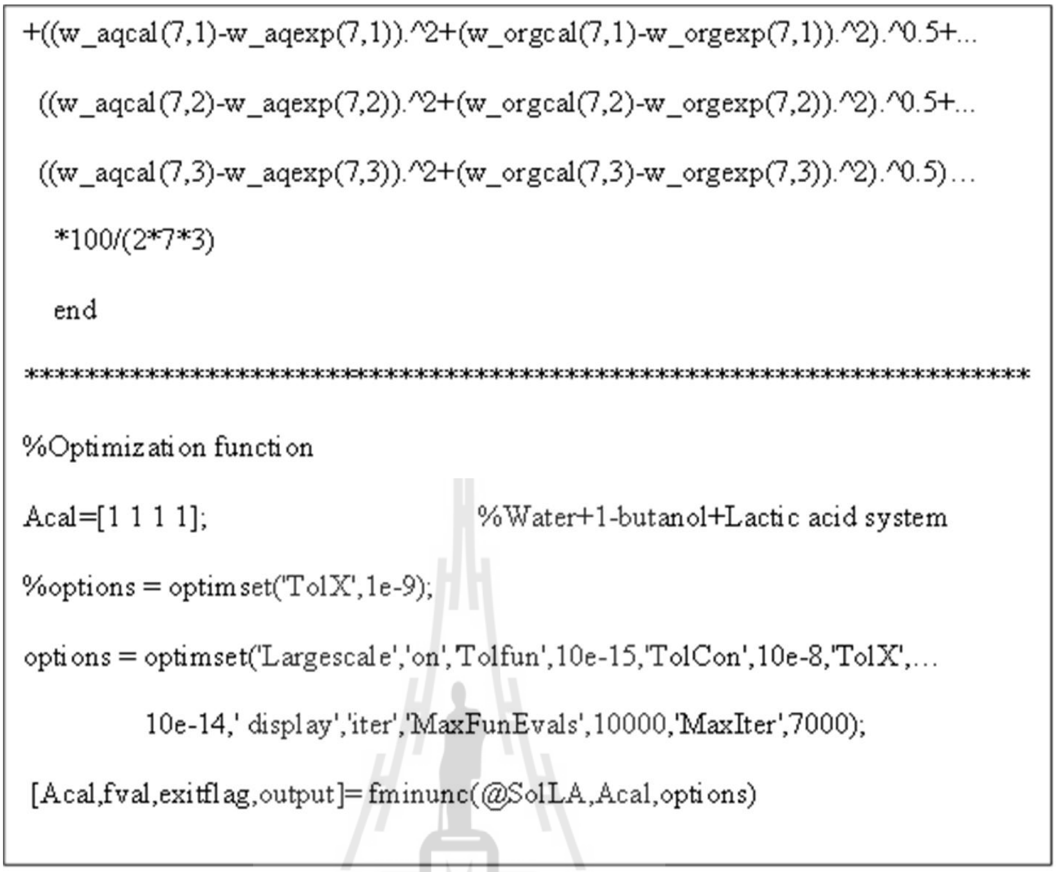
มหาวิทยาลัยเทคโนโลยีสุรนารี

```
   end
    %calculated molecular weight of mixture (Mx)
Mx_aq(i,1) = (x_aqCal(i,1).*18+x_aqCal(i,2).*74.12+x_aqCal(i,3).*90.08)./1;
Mx_org(i,1) = (x_orgCal(i,1).*18+x_orgCal(i,2).*74.12+x_orgCal(i,3).*90.08)./1;
%Calculated weight fraction for aqueous phase
  w_aq(i,1)= x_aqCal(i,1).*18./Mx_aq(i,1);
  w_aq(i,2)= x_aqCal(i,2).*74.12./Mx_aq(i,1);
  w_aq(i,3)= x_aqCal(i,3).*90.08./Mx_aq(i,1);
 %Calculated weight fraction for organic phase
  w_org(i,1)=x_orgCal(i,1).*18./Mx_org(i,1);
  w_org(i,2)=x_orgCal(i,2).*74.12./Mx_org(i,1);
  w_org(i,3)=x_orgCal(i,3).*90.08./Mx_org(i,1);
end
********************************************************************
function f=SolLA(Acal)        %Objective function
global A13 A23 A31 A32
%A12=Acal(1);
A13=Acal(1);
A23=Acal(2);
A31=Acal(3);
A32=Acal(4);
%Input the experimental data (mass fraction)
w_aqexp =[0.9224 0.0673 0.0103;0.9129 0.0651 0.0221;0.9053 0.0648 0.0299;...
            0.8978 0.0602 0.0420;0.8811 0.0565 0.0624;0.8591 0.0641 0.0768;...
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

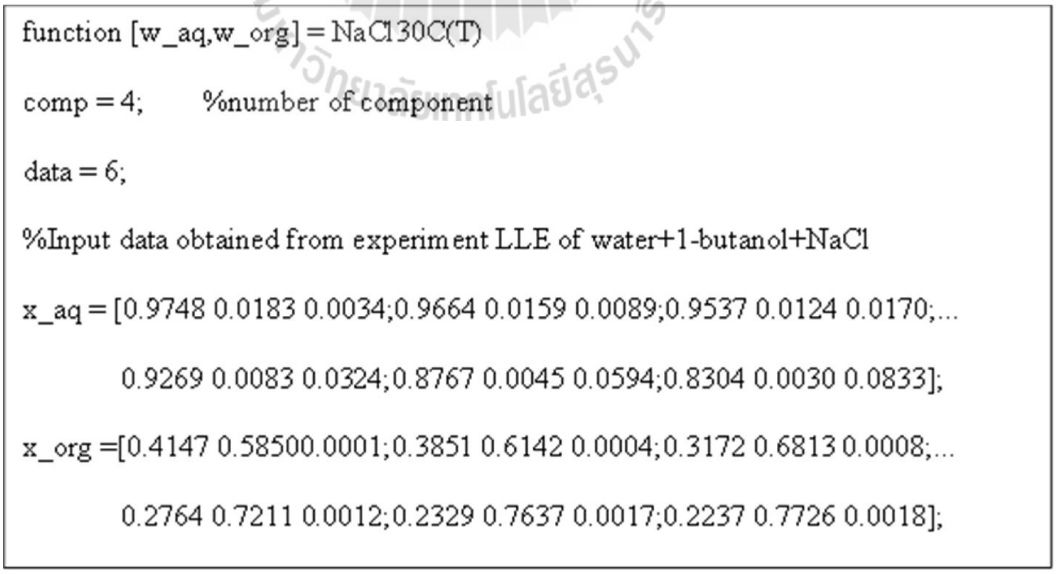
```
                0.8217 0.0719 0.1065];
w_orgexp =[0.23120.7614 0.0074;0.2200 0.7636 0.0164;0.2362 0.7404 0.0234;...
                0.2285 0.7339 0.0376;0.2231 0.7241 0.0527;0.2558 0.6350 0.1092;...
                0.3355 0.5197 0.1448];
[w_aq,w_org] = Lactic(303.15);
 w_aqcal = w_aq
 w_orgcal = w_org
%The objective funcetin
    f =  ((w_aqcal(1,1)-w_aqexp(1,1)).^2+(w_orgcal(1,1)-w_orgexp(1,1)).^2+...
          (w_aqcal(1,2)-w_aqexp(1,2)).^2+(w_orgcal(1,2)-w_orgexp(1,2)).^2+...
          (w_aqcal(1,3)-w_aqexp(1,3)).^2+(w_orgcal(1,3)-w_orgexp(1,3)).^2)...
      +((w_aqcal(2,1)-w_aqexp(2,1)).^2+(w_orgcal(2,1)-w_orgexp(2,1)).^2+...
         (w_aqcal(2,2)-w_aqexp(2,2)).^2+(w_orgcal(2,2)-w_orgexp(2,2)).^2+...
         (w_aqcal(2,3)-w_aqexp(2,3)).^2+(w_orgcal(2,3)-w_orgexp(2,3)).^2)...
      +((w_aqcal(3,1)-w_aqexp(3,1)).^2+(w_orgcal(3,1)-w_orgexp(3,1)).^2+...
        (w_aqcal(3,2)-w_aqexp(3,2)).^2+(w_orgcal(3,2)-w_orgexp(3,2)).^2+...
        (w_aqcal(3,3)-w_aqexp(3,3)).^2+(w_orgcal(3,3)-w_orgexp(3,3)).^2)...
      +((w_aqcal(4,1)-w_aqexp(4,1)).^2+(w_orgcal(4,1)-w_orgexp(4,1)).^2+...
        (w_aqcal(4,2)-w_aqexp(4,2)).^2+(w_orgcal(4,2)-w_orgexp(4,2)).^2+...
        (w_aqcal(4,3)-w_aqexp(4,3)).^2+(w_orgcal(4,3)-w_orgexp(4,3)).^2)...
      +((w_aqcal(5,1)-w_aqexp(5,1)).^2+(w_orgcal(5,1)-w_orgexp(5,1)).^2+...
        (w_aqcal(5,2)-w_aqexp(5,2)).^2+(w_orgcal(5,2)-w_orgexp(5,2)).^2+...
        (w_aqcal(5,3)-w_aqexp(5,3)).^2+(w_orgcal(5,3)-w_orgexp(5,3)).^2)...
      +((w_aqcal(6,1)-w_aqexp(6,1)).^2+(w_orgcal(6,1)-w_orgexp(6,1)).^2+...
```

```
        (w_aqcal(6,2)-w_aqexp(6,2)).^2+(w_orgcal(6,2)-w_orgexp(6,2)).^2+...
        (w_aqcal(6,3)-w_aqexp(6,3)).^2+(w_orgcal(6,3)-w_orgexp(6,3)).^2)...
      +((w_aqcal(7,1)-w_aqexp(7,1)).^2+(w_orgcal(7,1)-w_orgexp(7,1)).^2+...
        (w_aqcal(7,2)-w_aqexp(7,2)).^2+(w_orgcal(7,2)-w_orgexp(7,2)).^2+...
        (w_aqcal(7,3)-w_aqexp(7,3)).^2+(w_orgcal(7,3)-w_orgexp(7,3)).^2);
%The root mean square absolute deviation
dW = (((w_aqcal(1,1)-w_aqexp(1,1)).^2+(w_orgcal(1,1)-w_orgexp(1,1)).^2).^0.5+...
        ((w_aqcal(1,2)-w_aqexp(1,2)).^2+(w_orgcal(1,2)-w_orgexp(1,2)).^2).^0.5+...
        ((w_aqcal(1,3)-w_aqexp(1,3)).^2+(w_orgcal(1,3)-w_orgexp(1,3)).^2).^0.5...
      +((w_aqcal(2,1)-w_aqexp(2,1)).^2+(w_orgcal(2,1)-w_orgexp(2,1)).^2).^0.5+...
        ((w_aqcal(2,2)-w_aqexp(2,2)).^2+(w_orgcal(2,2)-w_orgexp(2,2)).^2).^0.5+...
        ((w_aqcal(2,3)-w_aqexp(2,3)).^2+(w_orgcal(2,3)-w_orgexp(2,3)).^2).^0.5...
      +((w_aqcal(3,1)-w_aqexp(3,1)).^2+(w_orgcal(3,1)-w_orgexp(3,1)).^2).^0.5+...
        ((w_aqcal(3,2)-w_aqexp(3,2)).^2+(w_orgcal(3,2)-w_orgexp(3,2)).^2).^0.5+...
        ((w_aqcal(3,3)-w_aqexp(3,3)).^2+(w_orgcal(3,3)-w_orgexp(3,3)).^2).^0.5...
      +((w_aqcal(4,1)-w_aqexp(4,1)).^2+(w_orgcal(4,1)-w_orgexp(4,1)).^2).^0.5+...
        ((w_aqcal(4,2)-w_aqexp(4,2)).^2+(w_orgcal(4,2)-w_orgexp(4,2)).^2).^0.5+...
        ((w_aqcal(4,3)-w_aqexp(4,3)).^2+(w_orgcal(4,3)-w_orgexp(4,3)).^2).^0.5...
      +((w_aqcal(5,1)-w_aqexp(5,1)).^2+(w_orgcal(5,1)-w_orgexp(5,1)).^2).^0.5+...
        ((w_aqcal(5,2)-w_aqexp(5,2)).^2+(w_orgcal(5,2)-w_orgexp(5,2)).^2).^0.5+...
        ((w_aqcal(5,3)-w_aqexp(5,3)).^2+(w_orgcal(5,3)-w_orgexp(5,3)).^2).^0.5...
      +((w_aqcal(6,1)-w_aqexp(6,1)).^2+(w_orgcal(6,1)-w_orgexp(6,1)).^2).^0.5+...
       ((w_aqcal(6,2)-w_aqexp(6,2)).^2+(w_orgcal(6,2)-w_orgexp(6,2)).^2).^0.5+...
       ((w_aqcal(6,3)-w_aqexp(6,3)).^2+(w_orgcal(6,3)-w_orgexp(6,3)).^2).^0.5...
```



```
+((w_aqcal(7,1)-w_aqexp(7,1)).^2+(w_orgcal(7,1)-w_orgexp(7,1)).^2).^0.5+...
  ((w_aqcal(7,2)-w_aqexp(7,2)).^2+(w_orgcal(7,2)-w_orgexp(7,2)).^2).^0.5+...
  ((w_aqcal(7,3)-w_aqexp(7,3)).^2+(w_orgcal(7,3)-w_orgexp(7,3)).^2).^0.5)...
   *100/(2*7*3)
   end
************************************************************************
%Optimization function
Acal=[1 1 1 1];                         %Water+1-butanol+Lactic acid system
%options = optimset('TolX',1e-9);
options = optimset('Largescale','on','Tolfun',10e-15,'TolCon',10e-8,'TolX',...
            10e-14,' display','iter','MaxFunEvals',10000,'MaxIter',7000);
 [Acal,fval,exitflag,output]= fminunc(@SolLA,Acal,options)
```

C.2 Modified extended UNIQUAC Model



```
function [w_aq,w_org] = NaCl30C(T)
comp = 4;      %number of component
data = 6;
%Input data obtained from experiment LLE of water+1-butanol+NaCl
x_aq = [0.9748 0.0183 0.0034;0.9664 0.0159 0.0089;0.9537 0.0124 0.0170;...
          0.9269 0.0083 0.0324;0.8767 0.0045 0.0594;0.8304 0.0030 0.0833];
x_org =[0.4147 0.58500.0001;0.3851 0.6142 0.0004;0.3172 0.6813 0.0008;...
          0.2764 0.7211 0.0012;0.2329 0.7637 0.0017;0.2237 0.7726 0.0018];
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

```
for n=1:data
   x_aq(n,4) = 1-x_aq(n,1)-x_aq(n,2)-x_aq(n,3);
   x_org(n,4) = 1-x_org(n,1)-x_org(n,2)-x_org(n,3);
end
global A12 A13 A14 A21 A23 A24 A31 A32 A34 A41 A42 A43


%Binary interaction parameter (Aii=0)
A11=0;A22=0;A33=0;A44=0;
% Calculated activity coeeficient by UNIQUAC term for Solvent
         % Volume parameters of pure components
         %Water (1)
R1 = 0.9200 ;
Q1 = 1.4000;
         %Butanol (2)
R2 = 3.9243;
Q2 = 3.6680;
         %Cation of salt (3)
R3 = 0.5570;
Q3 = 0.6860;
         %Aion of salt (4)
R4 = 1.0200;
Q4 = 1.0250;
for i=1:data
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

```
   %Aqueous phase
sigma_AQ_r(i,1) = x_aq(i,1).*R1+x_aq(i,2).*R2+x_aq(i,3).*R3+x_aq(i,4).*R4;
       phi_AQ(i,1) = x_aq(i,1)*R1./sigma_AQ_r(i,1);
       phi_AQ(i,2) = x_aq(i,2)*R2./sigma_AQ_r(i,1);
       phi_AQ(i,3) = x_aq(i,3)*R3./sigma_AQ_r(i,1);
       phi_AQ(i,4) = x_aq(i,4)*R4./sigma_AQ_r(i,1);
sigma_AQ_q(i,1) = x_aq(i,1).*Q1+x_aq(i,2).*Q2+x_aq(i,3).*Q3+x_aq(i,4).*Q4;
       theta_AQ(i,1) = x_aq(i,1)*Q1./sigma_AQ_q(i,1);
       theta_AQ(i,2) = x_aq(i,2)*Q2./sigma_AQ_q(i,1);
       theta_AQ(i,3) = x_aq(i,3)*Q3./sigma_AQ_q(i,1);
       theta_AQ(i,4) = x_aq(i,4)*Q4./sigma_AQ_q(i,1);
   %Organic phase
sigma_ORG_r(i,1) = x_org(i,1).*R1+x_org(i,2).*R2+x_org(i,3).*R3+x_org(i,4).*R4;
phi_ORG(i,1) = x_org(i,1)*R1./sigma_ORG_r(i,1);
phi_ORG(i,2) = x_org(i,2)*R2./sigma_ORG_r(i,1);
phi_ORG(i,3) = x_org(i,3)*R3./sigma_ORG_r(i,1);
phi_ORG(i,4) = x_org(i,4)*R4./sigma_ORG_r(i,1);
sigma_ORG_q(i,1) =x_org(i,1).*Q1+x_org(i,2).*Q2+x_org(i,3).*Q3+x_org(i,4).*Q4;
theta_ORG(i,1) = x_org(i,1)*Q1./sigma_ORG_q(i,1);
theta_ORG(i,2) = x_org(i,2)*Q2./sigma_ORG_q(i,1);
theta_ORG(i,3) = x_org(i,3)*Q3./sigma_ORG_q(i,1);
theta_ORG(i,4) = x_org(i,4)*Q4./sigma_ORG_q(i,1);
end
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

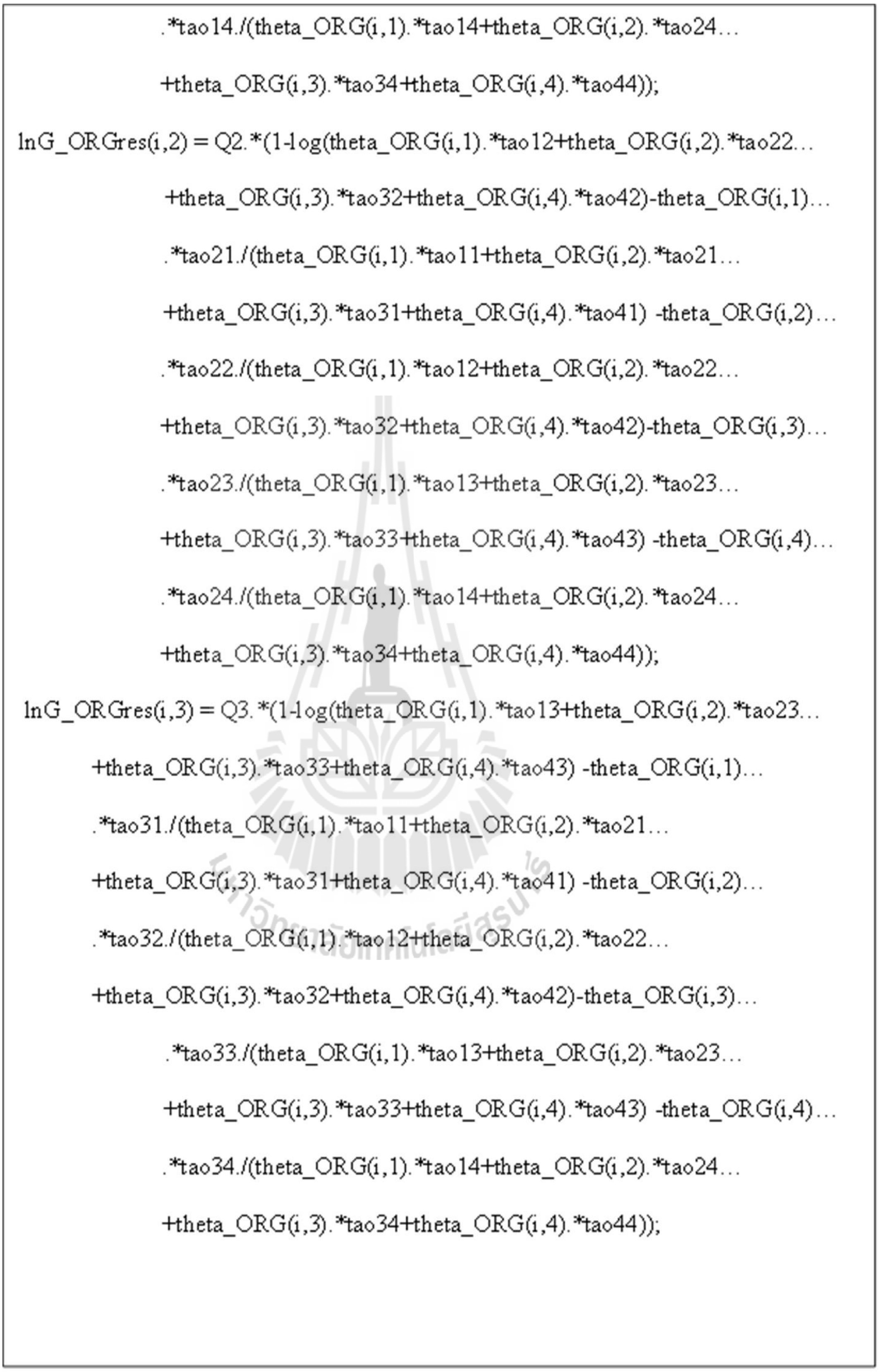
```
        % tao = exp(-(A./T));
tao11 = exp(-(A11./T));tao12 = exp(-(A12./T));
tao13 = exp(-(A13./T));tao14 = exp(-(A14./T));
tao21 = exp(-(A21./T));tao22 = exp(-(A22./T));
tao23 = exp(-(A23./T));tao24 = exp(-(A24./T));
tao31 = exp(-(A31./T));tao32 = exp(-(A32./T));
tao33 = exp(-(A33./T));tao34 = exp(-(A34./T));
tao41 = exp(-(A41./T));tao42 = exp(-(A42./T));
tao43 = exp(-(A43./T));tao44 = exp(-(A44./T));
for i=1:data
%Calculated activity coeficient for solvents
   %Calculated activity coeficient in Aqueous phase
lnG_AQcomb(i,1) = 1-phi_AQ(i,1)./x_aq(i,1)+log(phi_AQ(i,1)./x_aq(i,1))-5*Q1...
                *(log(phi_AQ(i,1)./theta_AQ(i,1))+1-phi_AQ(i,1)./theta_AQ(i,1));
lnG_AQcomb(i,2) = 1-phi_AQ(i,2)./x_aq(i,2)+log(phi_AQ(i,2)./x_aq(i,2))-5*Q2...
                *(log(phi_AQ(i,2)./theta_AQ(i,2))+1-phi_AQ(i,2)./theta_AQ(i,2));
lnG_AQcomb(i,3) = 1-phi_AQ(i,3)./x_aq(i,3)+log(phi_AQ(i,3)./x_aq(i,3))-5*Q3...
                *(log(phi_AQ(i,3)./theta_AQ(i,3))+1-phi_AQ(i,3)./theta_AQ(i,3));
lnG_AQres(i,1) = Q1.*(1-log(theta_AQ(i,1).*tao11+theta_AQ(i,2).*tao21...
        +theta_AQ(i,3).*tao31+theta_AQ(i,4).*tao41)-theta_AQ(i,1).*tao11…
        ./(theta_AQ(i,1).*tao11+theta_AQ(i,2).*tao21+theta_AQ(i,3).*tao31…
+theta_AQ(i,4).*tao41)-theta_AQ(i,2).*tao12./(theta_AQ(i,1).*tao12…
        +theta_AQ(i,2).*tao22+theta_AQ(i,3).*tao32+theta_AQ(i,4).*tao42)...
        -theta_AQ(i,3).*tao13./(theta_AQ(i,1).*tao13+theta_AQ(i,2).*tao23…
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

```
        +theta_AQ(i,3).*tao33+theta_AQ(i,4).*tao43)-theta_AQ(i,4).*tao14...
        ./(theta_AQ(i,1).*tao14+theta_AQ(i,2).*tao24+theta_AQ(i,3).*tao34...
        +theta_AQ(i,4).*tao44));

  lnG_AQres(i,2) = Q2.*(1-log(theta_AQ(i,1).*tao12+theta_AQ(i,2).*tao22...
+theta_AQ(i,3).*tao32+theta_AQ(i,4).*tao42)-Theta_AQ(i,1).*tao21...
        ./(theta_AQ(i,1).*tao11+theta_AQ(i,2).*tao21+theta_AQ(i,3).*tao31...
        +theta_AQ(i,4).*tao41)-theta_AQ(i,2).*tao22./(theta_AQ(i,1).*tao12...
        +theta_AQ(i,2).*tao22+theta_AQ(i,3).*tao32+theta_AQ(i,4).*tao42)...
        -theta_AQ(i,3).*tao23./(theta_AQ(i,1).*tao13+theta_AQ(i,2).*tao23...
        +theta_AQ(i,3).*tao33+theta_AQ(i,4).*tao43)-theta_AQ(i,4).*tao24...
        ./(theta_AQ(i,1).*tao14+theta_AQ(i,2).*tao24+theta_AQ(i,3).*tao34...
        +theta_AQ(i,4).*tao44));

  lnG_AQres(i,3) = Q3.*(1-log(theta_AQ(i,1).*tao13+theta_AQ(i,2).*tao23...
        +theta_AQ(i,3).*tao33+theta_AQ(i,4).*tao43)-theta_AQ(i,1).*tao31...
        ./(theta_AQ(i,1).*tao11+theta_AQ(i,2).*tao21+theta_AQ(i,3).*tao31...
        +theta_AQ(i,4).*tao41)-theta_AQ(i,2).*tao32./(theta_AQ(i,1).*tao12...
        +theta_AQ(i,2).*tao22+theta_AQ(i,3).*tao32+theta_AQ(i,4).*tao42)...
        -theta_AQ(i,3).*tao33./(theta_AQ(i,1).*tao13+theta_AQ(i,2).*tao23...
        +theta_AQ(i,3).*tao33+theta_AQ(i,4).*tao43)-theta_AQ(i,4).*tao34...
        ./(theta_AQ(i,1).*tao14+theta_AQ(i,2).*tao24+theta_AQ(i,3).*tao34...
        +theta_AQ(i,4).*tao44));
```

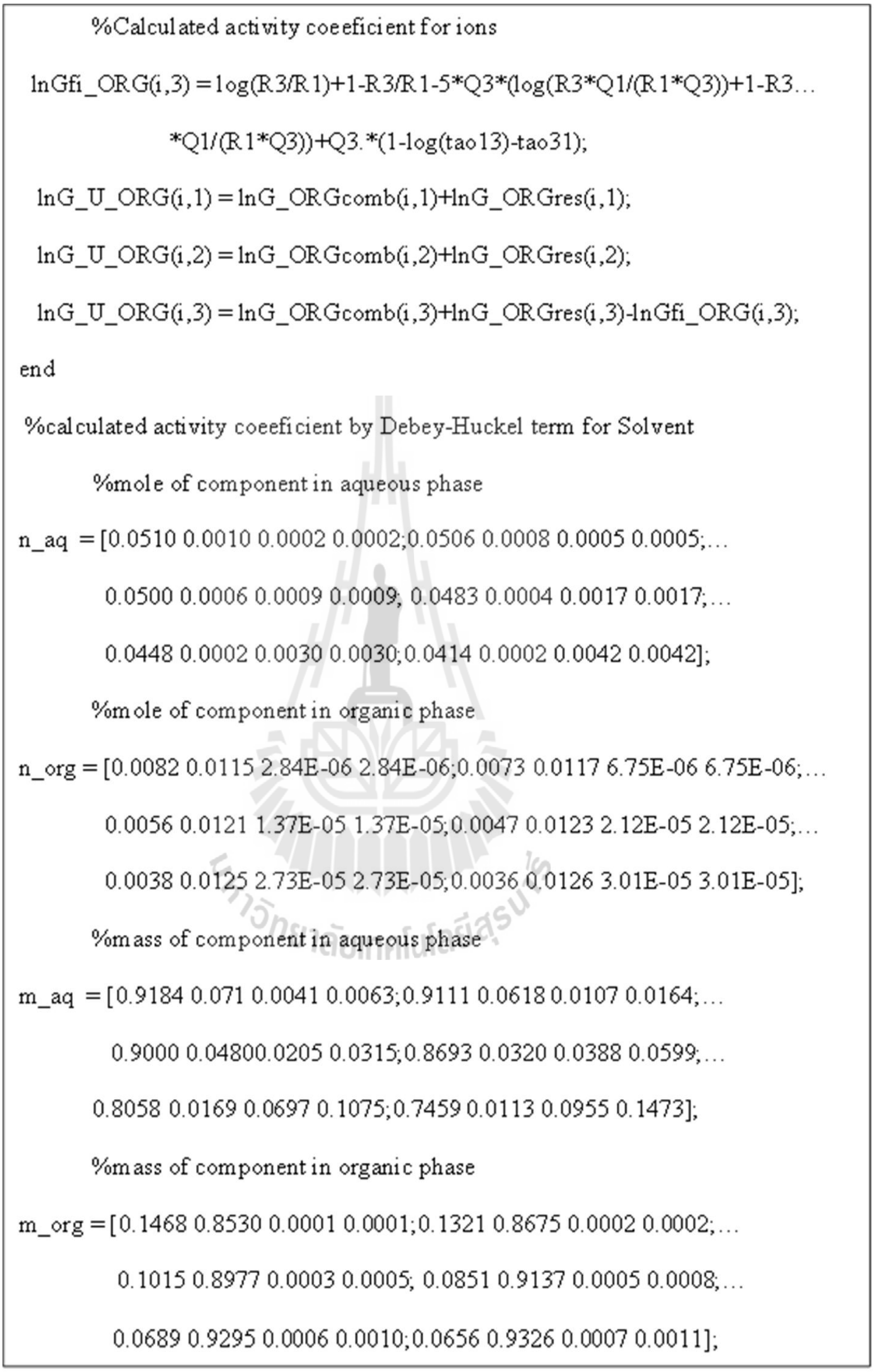
```
%Calculated activity coefficient for ions
lnGfi_AQ(i,3) = log(R3/R1)+1-R3/R1-5*Q3*(log(R3*Q1/(R1*Q3))+1-R3…
          *Q1/(R1*Q3))+Q3.*(1-log(tao13)-tao31);
lnG_U_AQ(i,1) = lnG_AQcomb(i,1)+lnG_AQres(i,1);       %for solvents
lnG_U_AQ(i,2) = lnG_AQcomb(i,2)+lnG_AQres(i,2);       %for solvents
lnG_U_AQ(i,3) = lnG_AQcomb(i,3)+lnG_AQres(i,3)-lnGfi_AQ(i,3);      %for ions
%Calculated activity coeeficient in Organic phase
lnG_ORGcomb(i,1) = 1-phi_ORG(i,1)./x_org(i,1)+log(phi_ORG(i,1)./x_org(i,1))…
          -5*Q1*(log(phi_ORG(i,1)./theta_ORG(i,1))+1-phi_ORG(i,1)…
          ./theta_ORG(i,1));
lnG_ORGcomb(i,2) = 1-phi_ORG(i,2)./x_org(i,2)+log(phi_ORG(i,2)./x_org(i,2))…
          -5*Q2*(log(phi_ORG(i,2)./theta_ORG(i,2))+1-phi_ORG(i,2)…
          ./theta_ORG(i,2));
lnG_ORGcomb(i,3) = 1-phi_ORG(i,3)./x_org(i,3)+log(phi_ORG(i,3)./x_org(i,3))…
                    -5*Q3*(log(phi_ORG(i,3)./theta_ORG(i,3))+1-phi_ORG(i,3)…
                    ./theta_ORG(i,3));
lnG_ORGres(i,1) = Q1.*(1-log(theta_ORG(i,1).*tao11+theta_ORG(i,2).*tao21…
                    +theta_ORG(i,3).*tao31+theta_ORG(i,4).*tao41)-theta_ORG(i,1)…
                    .*tao11./(theta_ORG(i,1).*tao11+theta_ORG(i,2).*tao21…
                    +theta_ORG(i,3).*tao31+theta_ORG(i,4).*tao41) -theta_ORG(i,2)…
                    .*tao12./(theta_ORG(i,1).*tao12+theta_ORG(i,2).*tao22…
                    +theta_ORG(i,3).*tao32+theta_ORG(i,4).*tao42) -theta_ORG(i,3)…
                    .*tao13./(theta_ORG(i,1).*tao13+theta_ORG(i,2).*tao23…
                    +theta_ORG(i,3).*tao33+theta_ORG(i,4).*tao43)-theta_ORG(i,4)…
```

มหาวิทยาลัยเทคโนโลยีสุรนารี



```
                  .*tao14./(theta_ORG(i,1).*tao14+theta_ORG(i,2).*tao24…
                  +theta_ORG(i,3).*tao34+theta_ORG(i,4).*tao44));
lnG_ORGres(i,2) = Q2.*(1-log(theta_ORG(i,1).*tao12+theta_ORG(i,2).*tao22…
                  +theta_ORG(i,3).*tao32+theta_ORG(i,4).*tao42)-theta_ORG(i,1)…
                  .*tao21./(theta_ORG(i,1).*tao11+theta_ORG(i,2).*tao21…
                  +theta_ORG(i,3).*tao31+theta_ORG(i,4).*tao41) -theta_ORG(i,2)…
                  .*tao22./(theta_ORG(i,1).*tao12+theta_ORG(i,2).*tao22…
                  +theta_ORG(i,3).*tao32+theta_ORG(i,4).*tao42)-theta_ORG(i,3)…
                  .*tao23./(theta_ORG(i,1).*tao13+theta_ORG(i,2).*tao23…
                  +theta_ORG(i,3).*tao33+theta_ORG(i,4).*tao43) -theta_ORG(i,4)…
                  .*tao24./(theta_ORG(i,1).*tao14+theta_ORG(i,2).*tao24…
                  +theta_ORG(i,3).*tao34+theta_ORG(i,4).*tao44));
lnG_ORGres(i,3) = Q3.*(1-log(theta_ORG(i,1).*tao13+theta_ORG(i,2).*tao23…
          +theta_ORG(i,3).*tao33+theta_ORG(i,4).*tao43) -theta_ORG(i,1)…
          .*tao31./(theta_ORG(i,1).*tao11+theta_ORG(i,2).*tao21…
          +theta_ORG(i,3).*tao31+theta_ORG(i,4).*tao41) -theta_ORG(i,2)…
          .*tao32./(theta_ORG(i,1).*tao12+theta_ORG(i,2).*tao22…
          +theta_ORG(i,3).*tao32+theta_ORG(i,4).*tao42)-theta_ORG(i,3)…
                  .*tao33./(theta_ORG(i,1).*tao13+theta_ORG(i,2).*tao23…
                  +theta_ORG(i,3).*tao33+theta_ORG(i,4).*tao43) -theta_ORG(i,4)…
                  .*tao34./(theta_ORG(i,1).*tao14+theta_ORG(i,2).*tao24…
                  +theta_ORG(i,3).*tao34+theta_ORG(i,4).*tao44));
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

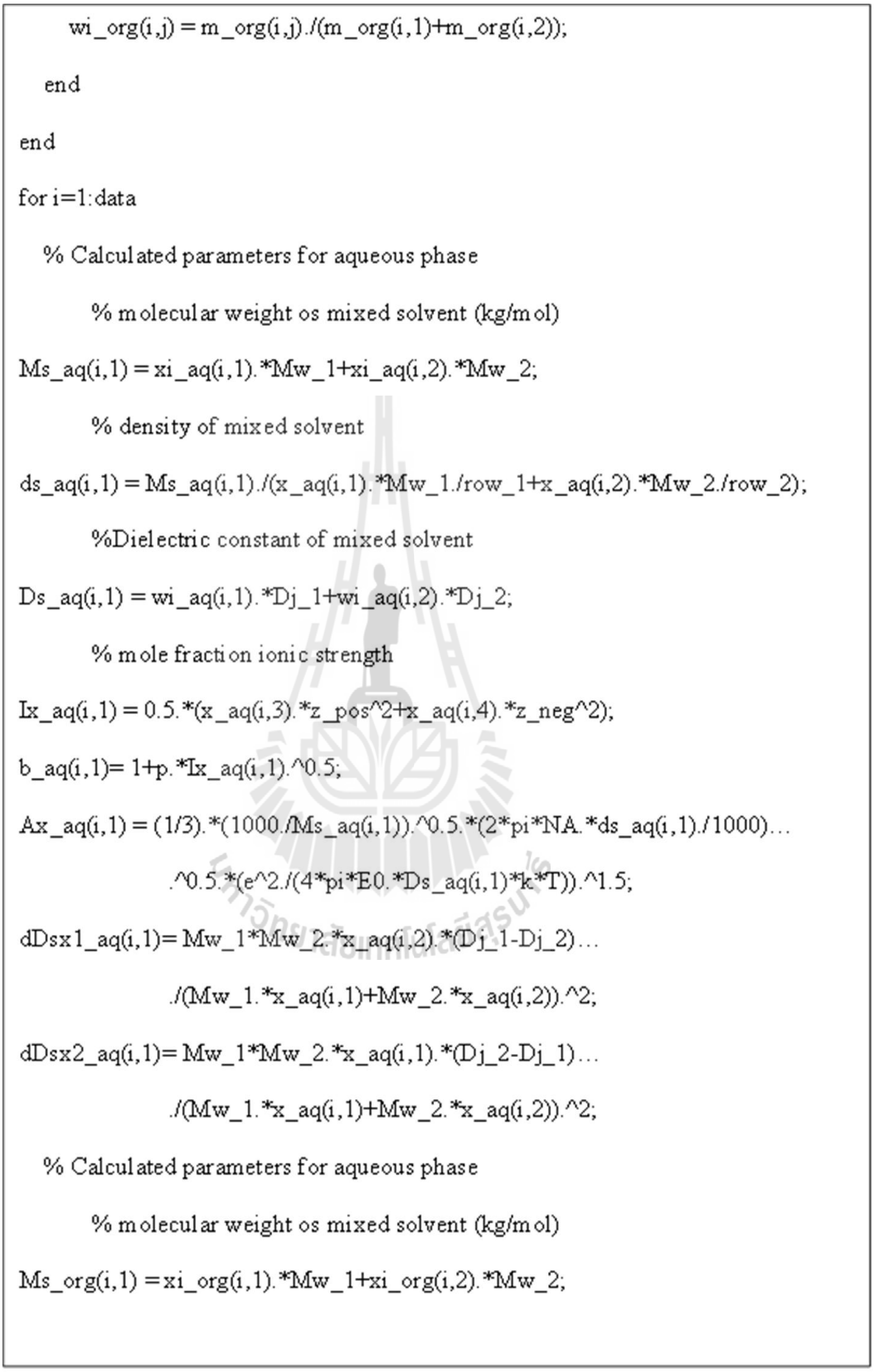


```
        %Calculated activity coeeficient for ions
  lnGfi_ORG(i,3) = log(R3/R1)+1-R3/R1-5*Q3*(log(R3*Q1/(R1*Q3))+1-R3…
              *Q1/(R1*Q3))+Q3.*(1-log(tao13)-tao31);
   lnG_U_ORG(i,1) = lnG_ORGcomb(i,1)+lnG_ORGres(i,1);
   lnG_U_ORG(i,2) = lnG_ORGcomb(i,2)+lnG_ORGres(i,2);
   lnG_U_ORG(i,3) = lnG_ORGcomb(i,3)+lnG_ORGres(i,3)-lnGfi_ORG(i,3);
end
 %calculated activity coeeficient by Debey-Huckel term for Solvent
        %mole of component in aqueous phase
n_aq  = [0.0510 0.0010 0.0002 0.0002;0.0506 0.0008 0.0005 0.0005;…
         0.0500 0.0006 0.0009 0.0009; 0.0483 0.0004 0.0017 0.0017;…
         0.0448 0.0002 0.0030 0.0030;0.0414 0.0002 0.0042 0.0042];
        %mole of component in organic phase
n_org = [0.0082 0.0115 2.84E-06 2.84E-06;0.0073 0.0117 6.75E-06 6.75E-06;…
         0.0056 0.0121 1.37E-05 1.37E-05;0.0047 0.0123 2.12E-05 2.12E-05;…
         0.0038 0.0125 2.73E-05 2.73E-05;0.0036 0.0126 3.01E-05 3.01E-05];
        %mass of component in aqueous phase
m_aq  = [0.9184 0.071 0.0041 0.0063;0.9111 0.0618 0.0107 0.0164;…
          0.9000 0.04800.0205 0.0315;0.8693 0.0320 0.0388 0.0599;…
        0.8058 0.0169 0.0697 0.1075;0.7459 0.0113 0.0955 0.1473];
        %mass of component in organic phase
m_org = [0.1468 0.8530 0.0001 0.0001;0.1321 0.8675 0.0002 0.0002;…
          0.1015 0.8977 0.0003 0.0005; 0.0851 0.9137 0.0005 0.0008;…
         0.0689 0.9295 0.0006 0.0010;0.0656 0.9326 0.0007 0.0011];
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

```
row_1 = 995.772;        %density of water (kg/m3)

row_2 = 801.845;        %density of n-buanol (kg/m3)

Mw_1 = 18/1000;         % molecular weight of water (kg/mol)

Mw_2 = 74.12/1000;  %molecular weight of n-butanol (kg/mol)

Mw_3 = 22.993;          %molecular weight of NH4 (g/mol)

Mw_4 = 35.45;           %molecular weight of Cl (g/mol)

Dj_1 = 76.75;           %Dielectric constant of water at 30C

Dj_2 = 16.50;           %Dielectric constant of n-butanol at 30C

  %Constant

  e  = 1.602*10^-19;          % electronic charge (Coulombs)

  NA = 6.0221*10^-23;         % Avogadro's number (mol-1)

  E0 = 8.8542*10^-12;         %Vacuum permittivity (F.m-1)

  k  = 1.3806*10^-23;         %Boltmann's constant (J.K-1)

  p  = 1.50;                  %closest approach paramerter (kg/mol)^1/2

% 1 NaCl <--> 1 Na+ + 1 Cl-%charge of ions

z_pos= 1; %Na+

z_neg= -1; %Cl

r_pos = 1.375e-10;      %Born radius of Na+

r_neg = 1.86e-10;       %Born radius of Cl-

for i=1:data

  for j=1:2

      xi_aq(i,j) = n_aq(i,j)./(n_aq(i,1)+n_aq(i,2));         % xi : free salt mole fraction

      xi_org(i,j) = n_org(i,j)./(n_org(i,1)+n_org(i,2));

      wi_aq(i,j) = m_aq(i,j)./(m_aq(i,1)+m_aq(i,2));      % xi : free salt mass fraction
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

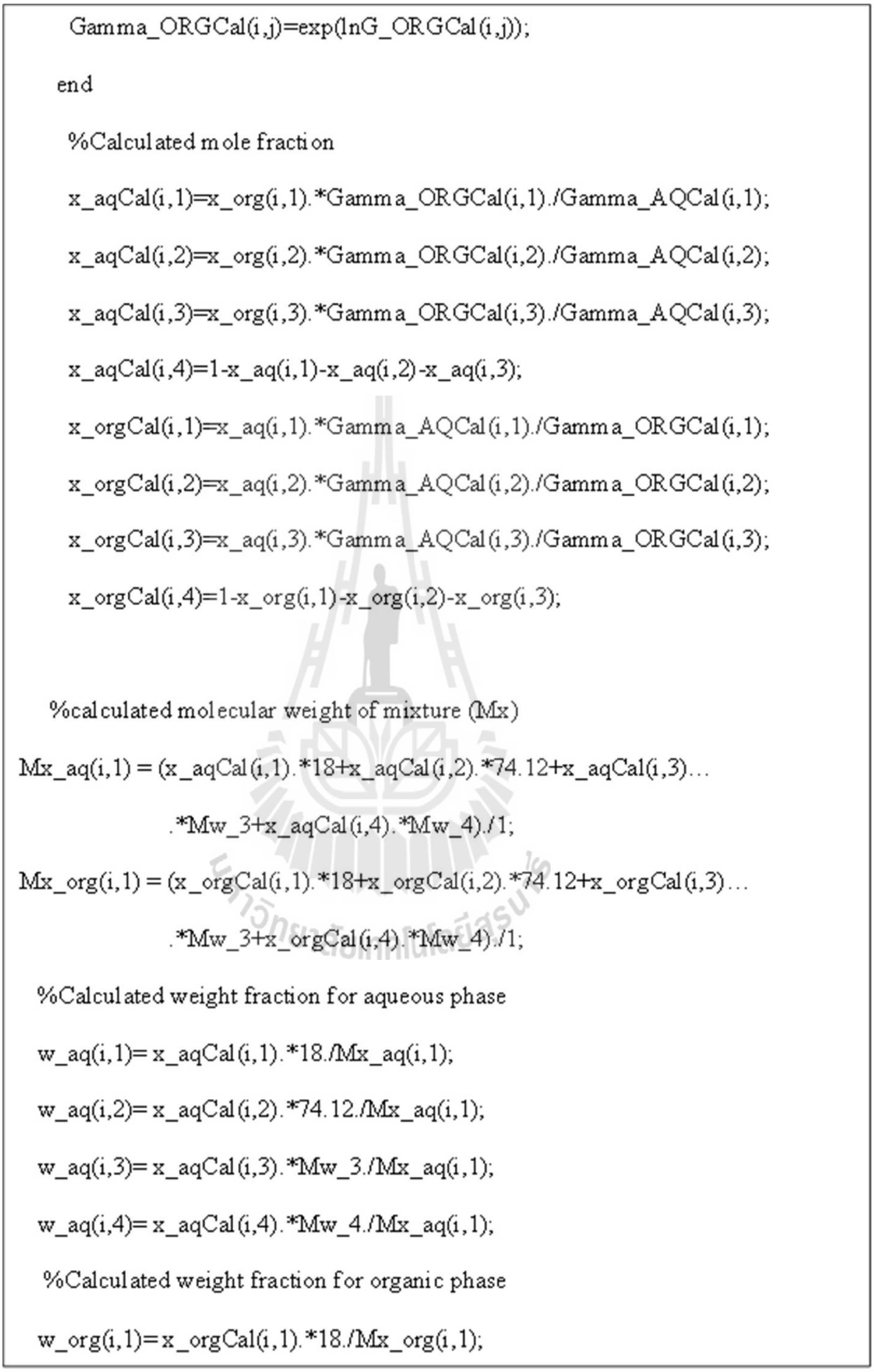


```
        wi_org(i,j) = m_org(i,j)./(m_org(i,1)+m_org(i,2));
    end
end
for i=1:data
    % Calculated parameters for aqueous phase
            % molecular weight os mixed solvent (kg/mol)
Ms_aq(i,1) = xi_aq(i,1).*Mw_1+xi_aq(i,2).*Mw_2;
            % density of mixed solvent
ds_aq(i,1) = Ms_aq(i,1)./(x_aq(i,1).*Mw_1./row_1+x_aq(i,2).*Mw_2./row_2);
            %Dielectric constant of mixed solvent
Ds_aq(i,1) = wi_aq(i,1).*Dj_1+wi_aq(i,2).*Dj_2;
            % mole fraction ionic strength
Ix_aq(i,1) = 0.5.*(x_aq(i,3).*z_pos^2+x_aq(i,4).*z_neg^2);
b_aq(i,1)= 1+p.*Ix_aq(i,1).^0.5;
Ax_aq(i,1) = (1/3).*(1000./Ms_aq(i,1)).^0.5.*(2*pi*NA.*ds_aq(i,1)./1000)...
                        .^0.5.*(e^2./(4*pi*E0.*Ds_aq(i,1)*k*T)).^1.5;
dDsx1_aq(i,1)= Mw_1*Mw_2.*x_aq(i,2).*(Dj_1-Dj_2)...
                        ./(Mw_1.*x_aq(i,1)+Mw_2.*x_aq(i,2)).^2;
dDsx2_aq(i,1)= Mw_1*Mw_2.*x_aq(i,1).*(Dj_2-Dj_1)...
                        ./(Mw_1.*x_aq(i,1)+Mw_2.*x_aq(i,2)).^2;
    % Calculated parameters for aqueous phase
            % molecular weight os mixed solvent (kg/mol)
Ms_org(i,1) =xi_org(i,1).*Mw_1+xi_org(i,2).*Mw_2;
```

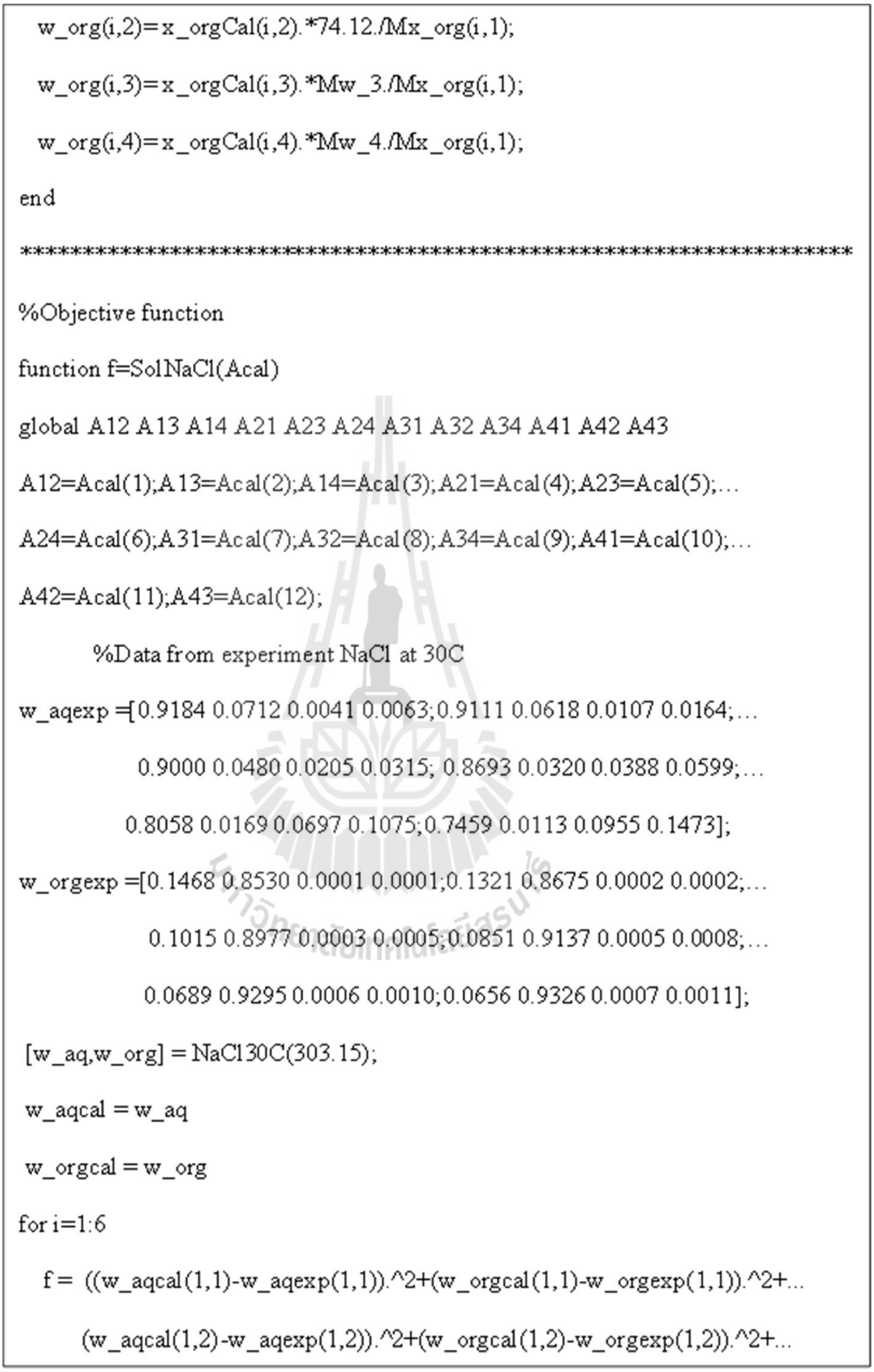
มหาวิทยาลัยเทคโนโลยีสุรนารี

```
        % density of mixed sollvent
ds_org(i,1) = Ms_org(i,1)./(x_org(i,1).*Mw_1./row_1+x_org(i,2).*Mw_2./row_2);
        %Dielectric constant of mixed solvent
Ds_org(i,1) = wi_org(i,1).*Dj_1+wi_org(i,2).*Dj_2;
        % mole fraction ionic strength
Ix_org(i,1) = 0.5.*(x_org(i,3)*z_pos^2+x_org(i,4)*z_neg^2);
b_org(i,1)= 1+p.*Ix_org(i,1).^0.5;
Ax_org(i,1) = (1/3).*(1000./Ms_org(i,1)).^0.5.*(2*pi*NA.*ds_org(i,1)...
                ./1000).^0.5.*(e^2./(4*pi*E0.*Ds_org(i,1)*k*T)).^1.5;
dDsx1_org(i,1)= Mw_1*Mw_2.*x_org(i,2).*(Dj_1-Dj_2)...
                ./(Mw_1.*x_org(i,1)+Mw_2.*x_org(i,2)).^2;
dDsx2_org(i,1)= Mw_1*Mw_2.*x_org(i,1).*(Dj_2-Dj_1)...
                ./(Mw_1.*x_org(i,1)+Mw_2.*x_org(i,2)).^2;
 %Calculated the activity coefficient by Debye Huckel term
   %Calculated DPH term of solvents and ions in aqueous phase
 lnG_PDH_AQ(i,1) = 2*Mw_1.*Ax_aq(i,1).*ds_aq(i,1).*(b_aq(i,1)...
                        -(1./b_aq(i,1))-2*log(b_aq(i,1)))./(p^3*row_1);
 lnG_PDH_AQ(i,2) = 2*Mw_2.*Ax_aq(i,1).*ds_aq(i,1).*(b_aq(i,1)...
                        -(1./b_aq(i,1))-2*log(b_aq(i,1)))./(p^3*row_2);
 lnG_PDH_AQ(i,3) = -(2.*Ax_aq(i,1).*z_pos^2.*log(b_aq(i,1))./p)...
                        -(Ax_aq(i,1).*Ix_aq(i,1).^0.5.*z_pos^2./b_aq(i,1));
 %Calculated DPH term of solvents and ions in oraganic phase
lnG_PDH_ORG(i,1) = 2*Mw_1.*Ax_org(i,1).*ds_org(i,1).*(b_org(i,1)...
                        -(1./b_org(i,1))-2*log(b_org(i,1)))./(p^3*row_1);
```

```
lnG_PDH_ORG(i,2) = 2*Mw_2.*Ax_org(i,1).*ds_org(i,1).*(b_org(i,1)...
                          -(1./b_org(i,1))-2*log(b_org(i,1)))./(p^3*row_2);
lnG_PDH_ORG(i,3) = -(2.*Ax_org(i,1).*z_pos^2.*log(b_org(i,1))./p)...
                          -(Ax_org(i,1).*Ix_org(i,1).^0.5.*z_pos^2./b_org(i,1));
          %calculated activity coeeficient by Born term for Solvent
 %Calculated Born term of solvents and ions in aqueous phase
lnG_B_AQ(i,1) = -(e^2.*dDsx1_aq(i,1)./(2*k*T*4*pi*E0.*Ds_aq(i,1).^2))...
                  .*(x_aq(i,3).*z_pos^2./r_pos+x_aq(i,4).*z_neg^2./r_neg);
lnG_B_AQ(i,2) = -(e^2.*dDsx2_aq(i,1)./(2*k*T*4*pi*E0.*Ds_aq(i,1).^2))...
                  .*(x_aq(i,3).*z_pos^2./r_pos+x_aq(i,4).*z_neg^2./r_neg);
lnG_B_AQ(i,3) = (e^2*z_pos^2/(2*k*T*4*pi*E0*r_pos)).*(1./Ds_aq(i,1)-1/Dj_1);
         %Calculated Born term of solvents and ions in oraganic phase
lnG_B_ORG(i,1) = -(e^2.*dDsx1_org(i,1)./(2*k*T*4*pi*E0.*Ds_org(i,1).^2))...
                  .*(x_org(i,3).*z_pos^2./r_pos+x_org(i,4).*z_neg^2./r_neg);
lnG_B_ORG(i,2) = -(e^2.*dDsx1_org(i,1)./(2*k*T*4*pi*E0.*Ds_org(i,1).^2))...
                  .*(x_org(i,3).*z_pos^2./r_pos+x_org(i,4).*z_neg^2./r_neg);
lnG_B_ORG(i,3) = (e^2*z_pos^2/(2*k*T*4*pi*E0*r_pos)).*(1./Ds_org(i,1)-1/Dj_2);
end
for i=1:data
  for j=1:3
    %Total activity coefficient
    lnG_AQCal(i,j)=lnG_U_AQ(i,j)+lnG_PDH_AQ(i,j)+lnG_B_AQ(i,j);
    lnG_ORGCal(i,j)=lnG_U_ORG(i,j)+lnG_PDH_ORG(i,j)+lnG_B_ORG(i,j);
    Gamma_AQCal(i,j)=exp(lnG_AQCal(i,j));
```



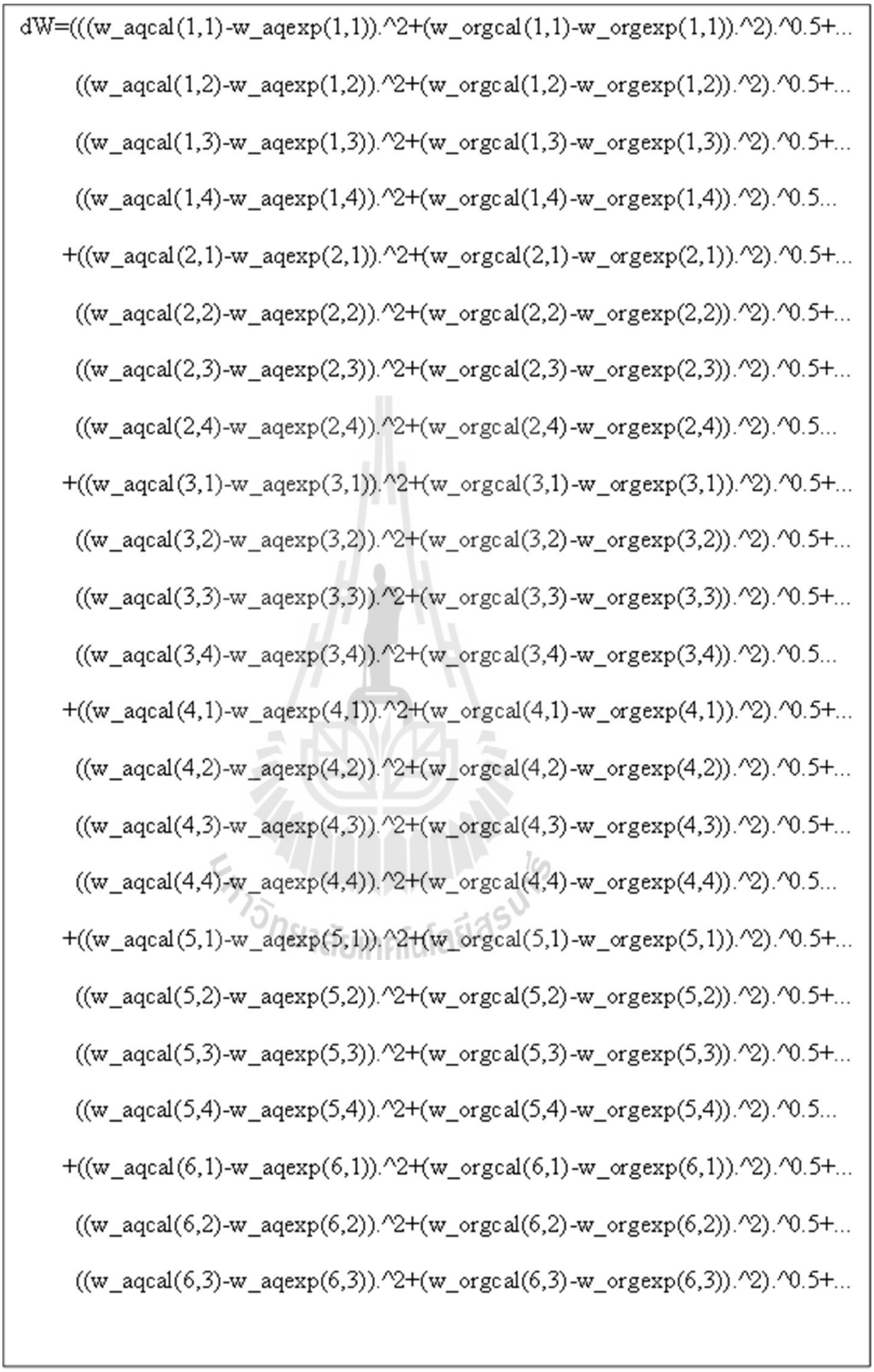
```
      Gamma_ORGCal(i,j)=exp(lnG_ORGCal(i,j));
     end
      %Calculated mole fraction
      x_aqCal(i,1)=x_org(i,1).*Gamma_ORGCal(i,1)./Gamma_AQCal(i,1);
      x_aqCal(i,2)=x_org(i,2).*Gamma_ORGCal(i,2)./Gamma_AQCal(i,2);
      x_aqCal(i,3)=x_org(i,3).*Gamma_ORGCal(i,3)./Gamma_AQCal(i,3);
      x_aqCal(i,4)=1-x_aq(i,1)-x_aq(i,2)-x_aq(i,3);
      x_orgCal(i,1)=x_aq(i,1).*Gamma_AQCal(i,1)./Gamma_ORGCal(i,1);
      x_orgCal(i,2)=x_aq(i,2).*Gamma_AQCal(i,2)./Gamma_ORGCal(i,2);
      x_orgCal(i,3)=x_aq(i,3).*Gamma_AQCal(i,3)./Gamma_ORGCal(i,3);
      x_orgCal(i,4)=1-x_org(i,1)-x_org(i,2)-x_org(i,3);

    %calculated molecular weight of mixture (Mx)
Mx_aq(i,1) = (x_aqCal(i,1).*18+x_aqCal(i,2).*74.12+x_aqCal(i,3)...
                  .*Mw_3+x_aqCal(i,4).*Mw_4)./1;
Mx_org(i,1) = (x_orgCal(i,1).*18+x_orgCal(i,2).*74.12+x_orgCal(i,3)...
                  .*Mw_3+x_orgCal(i,4).*Mw_4)./1;
  %Calculated weight fraction for aqueous phase
  w_aq(i,1)= x_aqCal(i,1).*18./Mx_aq(i,1);
  w_aq(i,2)= x_aqCal(i,2).*74.12./Mx_aq(i,1);
  w_aq(i,3)= x_aqCal(i,3).*Mw_3./Mx_aq(i,1);
  w_aq(i,4)= x_aqCal(i,4).*Mw_4./Mx_aq(i,1);
   %Calculated weight fraction for organic phase
  w_org(i,1)=x_orgCal(i,1).*18./Mx_org(i,1);
```



```
  w_org(i,2)=x_orgCal(i,2).*74.12./Mx_org(i,1);
  w_org(i,3)=x_orgCal(i,3).*Mw_3./Mx_org(i,1);
  w_org(i,4)=x_orgCal(i,4).*Mw_4./Mx_org(i,1);
end
*******************************************************************
%Objective function
function f=SolNaCl(Acal)
global A12 A13 A14 A21 A23 A24 A31 A32 A34 A41 A42 A43
A12=Acal(1);A13=Acal(2);A14=Acal(3);A21=Acal(4);A23=Acal(5);...
A24=Acal(6);A31=Acal(7);A32=Acal(8);A34=Acal(9);A41=Acal(10);...
A42=Acal(11);A43=Acal(12);
        %Data from experiment NaCl at 30C
w_aqexp =[0.9184 0.0712 0.0041 0.0063;0.9111 0.0618 0.0107 0.0164;...
           0.9000 0.0480 0.0205 0.0315; 0.8693 0.0320 0.0388 0.0599;...
          0.8058 0.0169 0.0697 0.1075;0.7459 0.0113 0.0955 0.1473];
w_orgexp =[0.1468 0.8530 0.0001 0.0001;0.1321 0.8675 0.0002 0.0002;...
            0.1015 0.8977 0.0003 0.0005;0.0851 0.9137 0.0005 0.0008;...
            0.0689 0.9295 0.0006 0.0010;0.0656 0.9326 0.0007 0.0011];
 [w_aq,w_org] = NaCl30C(303.15);
 w_aqcal = w_aq
 w_orgcal = w_org
for i=1:6
   f = ((w_aqcal(1,1)-w_aqexp(1,1)).^2+(w_orgcal(1,1)-w_orgexp(1,1)).^2+...
       (w_aqcal(1,2)-w_aqexp(1,2)).^2+(w_orgcal(1,2)-w_orgexp(1,2)).^2+...
```

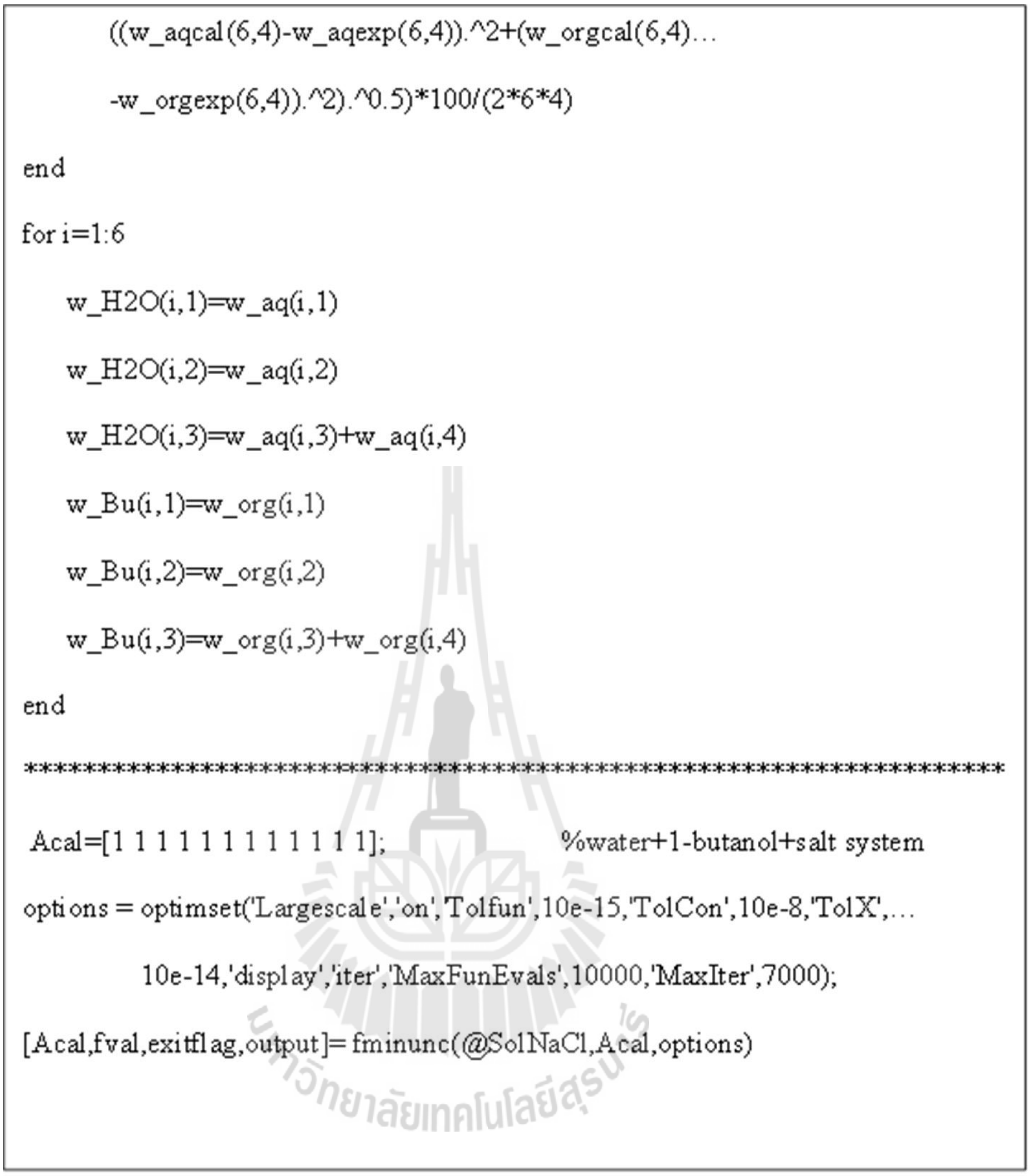
```
 (w_aqcal(1,3)-w_aqexp(1,3)).^2+(w_orgcal(1,3)-w_orgexp(1,3)).^2+...
 (w_aqcal(1,4)-w_aqexp(1,4)).^2+(w_orgcal(1,4)-w_orgexp(1,4)).^2)...
+((w_aqcal(2,1)-w_aqexp(2,1)).^2+(w_orgcal(2,1)-w_orgexp(2,1)).^2+...
 (w_aqcal(2,2)-w_aqexp(2,2)).^2+(w_orgcal(2,2)-w_orgexp(2,2)).^2+...
 (w_aqcal(2,3)-w_aqexp(2,3)).^2+(w_orgcal(2,3)-w_orgexp(2,3)).^2+...
 (w_aqcal(2,4)-w_aqexp(2,4)).^2+(w_orgcal(2,4)-w_orgexp(2,4)).^2)...
+((w_aqcal(3,1)-w_aqexp(3,1)).^2+(w_orgcal(3,1)-w_orgexp(3,1)).^2+...
 (w_aqcal(3,2)-w_aqexp(3,2)).^2+(w_orgcal(3,2)-w_orgexp(3,2)).^2+...
 (w_aqcal(3,3)-w_aqexp(3,3)).^2+(w_orgcal(3,3)-w_orgexp(3,3)).^2+...
 (w_aqcal(3,4)-w_aqexp(3,4)).^2+(w_orgcal(3,4)-w_orgexp(3,4)).^2)...
+((w_aqcal(4,1)-w_aqexp(4,1)).^2+(w_orgcal(4,1)-w_orgexp(4,1)).^2+...
 (w_aqcal(4,2)-w_aqexp(4,2)).^2+(w_orgcal(4,2)-w_orgexp(4,2)).^2+...
 (w_aqcal(4,3)-w_aqexp(4,3)).^2+(w_orgcal(4,3)-w_orgexp(4,3)).^2+...
 (w_aqcal(4,4)-w_aqexp(4,4)).^2+(w_orgcal(4,4)-w_orgexp(4,4)).^2)...
+((w_aqcal(5,1)-w_aqexp(5,1)).^2+(w_orgcal(5,1)-w_orgexp(5,1)).^2+...
 (w_aqcal(5,2)-w_aqexp(5,2)).^2+(w_orgcal(5,2)-w_orgexp(5,2)).^2+...
 (w_aqcal(5,3)-w_aqexp(5,3)).^2+(w_orgcal(5,3)-w_orgexp(5,3)).^2+...
 (w_aqcal(5,4)-w_aqexp(5,4)).^2+(w_orgcal(5,4)-w_orgexp(5,4)).^2)...
+((w_aqcal(6,1)-w_aqexp(6,1)).^2+(w_orgcal(6,1)-w_orgexp(6,1)).^2+...
 (w_aqcal(6,2)-w_aqexp(6,2)).^2+(w_orgcal(6,2)-w_orgexp(6,2)).^2+...
 (w_aqcal(6,3)-w_aqexp(6,3)).^2+(w_orgcal(6,3)-w_orgexp(6,3)).^2+...
 (w_aqcal(6,4)-w_aqexp(6,4)).^2+(w_orgcal(6,4)-w_orgexp(6,4)).^2);
```

มหาวิทยาลัยเทคโนโลยีสุรนารี



```
dW=(((w_aqcal(1,1)-w_aqexp(1,1)).^2+(w_orgcal(1,1)-w_orgexp(1,1)).^2).^0.5+...
     ((w_aqcal(1,2)-w_aqexp(1,2)).^2+(w_orgcal(1,2)-w_orgexp(1,2)).^2).^0.5+...
     ((w_aqcal(1,3)-w_aqexp(1,3)).^2+(w_orgcal(1,3)-w_orgexp(1,3)).^2).^0.5+...
     ((w_aqcal(1,4)-w_aqexp(1,4)).^2+(w_orgcal(1,4)-w_orgexp(1,4)).^2).^0.5...
    +((w_aqcal(2,1)-w_aqexp(2,1)).^2+(w_orgcal(2,1)-w_orgexp(2,1)).^2).^0.5+...
     ((w_aqcal(2,2)-w_aqexp(2,2)).^2+(w_orgcal(2,2)-w_orgexp(2,2)).^2).^0.5+...
     ((w_aqcal(2,3)-w_aqexp(2,3)).^2+(w_orgcal(2,3)-w_orgexp(2,3)).^2).^0.5+...
     ((w_aqcal(2,4)-w_aqexp(2,4)).^2+(w_orgcal(2,4)-w_orgexp(2,4)).^2).^0.5...
    +((w_aqcal(3,1)-w_aqexp(3,1)).^2+(w_orgcal(3,1)-w_orgexp(3,1)).^2).^0.5+...
     ((w_aqcal(3,2)-w_aqexp(3,2)).^2+(w_orgcal(3,2)-w_orgexp(3,2)).^2).^0.5+...
     ((w_aqcal(3,3)-w_aqexp(3,3)).^2+(w_orgcal(3,3)-w_orgexp(3,3)).^2).^0.5+...
     ((w_aqcal(3,4)-w_aqexp(3,4)).^2+(w_orgcal(3,4)-w_orgexp(3,4)).^2).^0.5...
    +((w_aqcal(4,1)-w_aqexp(4,1)).^2+(w_orgcal(4,1)-w_orgexp(4,1)).^2).^0.5+...
     ((w_aqcal(4,2)-w_aqexp(4,2)).^2+(w_orgcal(4,2)-w_orgexp(4,2)).^2).^0.5+...
     ((w_aqcal(4,3)-w_aqexp(4,3)).^2+(w_orgcal(4,3)-w_orgexp(4,3)).^2).^0.5+...
     ((w_aqcal(4,4)-w_aqexp(4,4)).^2+(w_orgcal(4,4)-w_orgexp(4,4)).^2).^0.5...
    +((w_aqcal(5,1)-w_aqexp(5,1)).^2+(w_orgcal(5,1)-w_orgexp(5,1)).^2).^0.5+...
     ((w_aqcal(5,2)-w_aqexp(5,2)).^2+(w_orgcal(5,2)-w_orgexp(5,2)).^2).^0.5+...
     ((w_aqcal(5,3)-w_aqexp(5,3)).^2+(w_orgcal(5,3)-w_orgexp(5,3)).^2).^0.5+...
     ((w_aqcal(5,4)-w_aqexp(5,4)).^2+(w_orgcal(5,4)-w_orgexp(5,4)).^2).^0.5...
    +((w_aqcal(6,1)-w_aqexp(6,1)).^2+(w_orgcal(6,1)-w_orgexp(6,1)).^2).^0.5+...
     ((w_aqcal(6,2)-w_aqexp(6,2)).^2+(w_orgcal(6,2)-w_orgexp(6,2)).^2).^0.5+...
     ((w_aqcal(6,3)-w_aqexp(6,3)).^2+(w_orgcal(6,3)-w_orgexp(6,3)).^2).^0.5+...
```

มหาวิทยาลัยเทคโนโลยีสุรนารี



```
        ((w_aqcal(6,4)-w_aqexp(6,4)).^2+(w_orgcal(6,4)…
        -w_orgexp(6,4)).^2).^0.5)*100/(2*6*4)
end
for i=1:6
    w_H2O(i,1)=w_aq(i,1)
    w_H2O(i,2)=w_aq(i,2)
    w_H2O(i,3)=w_aq(i,3)+w_aq(i,4)
    w_Bu(i,1)=w_org(i,1)
    w_Bu(i,2)=w_org(i,2)
    w_Bu(i,3)=w_org(i,3)+w_org(i,4)
end
***********************************************************************
 Acal=[1 1 1 1 1 1 1 1 1 1 1 1];                %water+1-butanol+salt system
options = optimset('Largescale','on','Tolfun',10e-15,'TolCon',10e-8,'TolX',…
            10e-14,'display','iter','MaxFunEvals',10000,'MaxIter',7000);
[Acal,fval,exitflag,output]= fminunc(@SolNaCl,Acal,options)
```

มหาวิทยาลัยเทคโนโลยีสุรนารี

APPENDIX D

LIST OF PUBLICATIONS

มหาวิทยาลัยเทคโนโลยีสุรนารี

List of Publications

Chawong, K., and Rattanaphanee, P. (2012). Effect of Chloride Salts on Extraction of Lactic Acid with n-Butanol. **Engineering Transactions.** 5(2): 66-71.

Chawong, K., and Rattanaphanee, P. (2014). Liquid-liquid equilibrium of water + 1-butanol + (NH4)2SO4 and its application on lactic acid extraction. **Pure and Applied Chemistry International Conference (PACCON2014).** Khon Kaen, Thailand Proceeding of Pure and Applied Chemistry International Conference 2014, p.196-199.

Chawong, K., Rayabsri, C., and Rattanaphanee, P. (2014). Extraction of Lactic Acid in Mixed Solvent Electrolyte System Containing Water, 1-Butanol and Ammonium Sulfate. **GPE-4th International Congress on Green Process Engineering.** Swvilla, Spain.

มหาวิทยาลัยเทคโนโลยีสุรนารี

Effect of Chloride Salt on Extraction of Lactic Acid with n-Butanol

Kanungnit Chawong and **Panarat Rattanaphanee**[*]

School of Chemical Engineering, Institute of Engineering,
Suranaree University of Technology, Nakornratchasima, 30000, Thailand
[*]E-mail: panarat@sut.ac.th

Manuscript received October 15, 2012
Revised November 9, 2012

ABSTRACT

Extraction of lactic acid from its aqueous solution using n-butanol containing inorganic salt was studied. Effect of changing process variables (salt type and concentration, initial lactic acid concentration and extraction temperature) on extraction efficiency was investigated. Three chloride salts, i.e. NaCl, $MgCl_2$ and $CaCl_2$ were used. Degree of extraction was represented by value of distribution coefficient of lactic acid in each system. The result was compared with salt-free system of the same extracting conditions. Salting-in and salting-out effects were clearly observed for all the salts within the studied concentration range. When the salt concentration was sufficiently high, the distribution coefficient increased with increasing salt concentration. Among these three salts, NaCl demonstrated the highest degree of lactic acid extraction using n-butanol. The distribution coefficient was found to decrease with increasing temperature in the range of 30-50 °C.

***Keyword**: Lactic acid, Liquid-Liquid extraction, n-Butanol, chloride salt*

1 INTRODUCTION

Lactic acid or 2-hydroxypropanoic acid is an acid that contains both hydroxyl and carboxylic group in its molecule. The acid is used as biologically produced acidulates and preservatives in food industry. It is also widely used as a starting material for chemical synthesis, because of its optical activity and its hydroxyl and carboxyl moieties. In addition, the acid has a potential of becoming a very large volume chemical intermediate, produced from renewable resources for use as a feedstock for biodegradable plastics and other environmental-friendly green compounds. But until now, the extensive use of lactic acid in chemical industry is hampered by the high production costs of optically pure lactic acid [1], which is strictly required in the production of the biodegradable poly (lactic acid) polymers, especially those to be used in biomedical applications and drug delivery [2].

Lactic acid can be produced by either chemical synthesis or by fermentation. The latter has proven to be the better alternative as it is more energy efficient and can produce stereospecific acid [3]. Unfortunately, fermentation comes with several disadvantages. For example, this process can produce rather dilute solution of lactic acid due to inhibitory nature of the acid to the microorganism. Furthermore, the fermentation broth always contains several impurities including cell biomass, other organic acids, and unconsumed nutrients. Recovery and purification of lactic acid from dilute media requires many steps and unit operations, which consequently contribute to high cost of production.

Reactive extraction has been one of the attractive methods for lactic acid recovery and has been studied by several researchers [4] – [7]. The method provides high selectivity and enhances the recovery by utilizing a combination of an extractant (also known as carrier) and diluents to intensify the separation through simultaneous reaction and extraction [3]. Depending on the extraction mechanism, two categories of the extractants have been studied. The first category is solvating extractants, which extraction mechanism is by competing with water in interaction with the solute of interest and convey it into the organic phase. Examples of solvating extractants include tertiary amine, such as tri-*n*-octylamin (TOA), which forms a water-insoluble complex with lactic acid and, therefore, selective extract the acid from the aqueous to the organic phase [7]. Other solvating extractants that have been reportedly used include alkyl phosphate esters, such as tributyl phosphate (TBP) and trioctyl phosphine oxide (TOPO) as well as neutral extractants with oxygen-containing polar groups such as ketones (e.g. methyl isobutyl ketone), alkyl sulfoxides, or esters (e.g., tri-*n*-butyl phosphate and trioctylphosphine oxide) [8]. The second category is the extractants that function as the ion exchangers. Examples are quaternary ammonium salts such as the commercial extractant Aliquat 336 or tri-(C_8C_{10}) methylammonium chloride, where chloride anion is replaced by the anion of the acid during the extraction [9].

Despite the high distribution coefficient obtained from the extraction with specified solvents, some of the extractants are expensive and might inherit some toxicity. As a result, recovery of lactic acid by extraction with more economical and environmental friendly solvents is still needed. Extraction of lactic acid from aqueous solution using n-butanol was explored [10]. It was reported that the process efficiency was significantly dependent on pH of the aqueous solution, especially in the pH range less than 1, where the degree of extraction decreased considerably with the increase of pH in that range. Degree of extraction was, therefore, higher in the extraction of more concentrated lactic acid solution. Disadvantage of lactic acid extraction with n-butanol, however, is the fact that this alcohol is partially miscible in water, which, consequently, leads to incomplete solvent recovery after the operation.

This work was aim to investigate extraction of lactic acid from its aqueous solution using n-butanol when different chloride salts were added. Effects of salt type and concentration, initial lactic acid concentration, as well as extraction temperature on distribution coefficient of the acid in these systems were studied. Loss of n-butanol after the extraction was also observed.

2 RESEARCH METHODOLOGY

2.1 Material and Equipments

Lactic acid with concentration of 88 %wt and n-butanol with 99.9% purity were purchased from Acros. Sodium hydroxide (NaOH), sodium chloride (NaCl) and Sulfuric acid (H_2SO_4) were of reagent grade and were both purchased from Sigma. Calcium chloride ($CaCl_2$) and Magnesium chloride hexahydrate ($MgCl_2 . 6H_2O$) were obtain from CARLO ERBA.

2.2 Procedure

Aqueous lactic acid solution was prepared from the commercial lactic acid to the desired concentration. Weighed quantity of chloride salt was added into the 20 ml of lactic acid solution. Equal volume of n-butanol was then mixed with the prepared solution, and the mixture was shaken in a temperature-controlled shaking bath for 3 hr. The two phases were separated after the mixture was left to settle for 1 h. Concentration of lactic acid in both phases were determined by HPLC using Hypersil BDS C_{18}-column 4.0×100 mm, 3-Micro (Agilent). Sulfuric acid solution with concentration of 0.005 M H_2SO_4 and flow rate of 0.7 mL/min was used as a mobile phase. The UV wavelength was set at 210 nm, and the injection volume was 10 µL. All samples were diluted.

3 RESULTS AND DISCUSSION

The concentration of lactic acid used in the present work ranged from 0.1 to 1 M. Chloride salts with quantities between 0.5 to 5 g were added into 20 ml lactic acid solution. Effect of salt concentration, initial lactic acid concentration and temperature were studied. Efficiency of lactic acid extraction in each system was represented by the distribution coefficient (D) and the degree of extraction (%E),

$$D = \frac{C_{org}}{C_{aq}} \tag{1}$$

$$\%E = \frac{V_0C_0 - V_{eq}C_{aq}}{V_0C_0} \tag{2}$$

where C_0 is the concentration of lactic acid in the starting solution, C_{org} and C_{aq} are equilibrium concentration of lactic acid in the organic and aqueous phase, respectively. V_0 is the volume of starting solution and V_{eq} is volume of the aqueous phase after extraction. Distribution coefficient is an indicator of degree of extraction, i.e. the higher the distribution coefficient, the more lactic acid is extracted into the organic phase.

3.1 Effect of salt concentration on lactic acid distribution coefficient and degree of extraction

It is known that addition of a salt or a non-volatile solute in a solvent mixture can significantly change tow-phase equilibrium. Specifically, adding salt to an aqueous solution of addition of salt to an aqueous solution of an organic acid can result in either decrease or increase in solubility of the acid in the solution [11]. If the acid solubility is increased upon addition of salt, the effect is called “salting in”. On the other hand, if its solubility is diminished when the salt is added, the effect is called “salting out”. In addition to the behavior of a particular solute in aqueous solution, ability to induce salting in and salting out of a solute in aqueous solution depends on type and concentration of the salts as well as the ions presenting in the solution after ionization of the salts.

Research by Franz Hofmeister in the early 20th century organized various anion and cation by their ability to salting out. The cations are arranged as follows.

$$NH_4^+ \rangle K^+ \rangle Na^+ \rangle Li^+ \rangle Mg^{2+} \rangle Ca^{2+}$$

The arrangement, which is called "Hofmeister series", indicates that, among the cations shown in the series, NH_4^+ has the highest ability of salting out, and Ca^{2+} has the lowest ability.

Distribution coefficient (D) and degree of lactic acid extraction (%E) with n-butanol containing different chloride salts are shown in Table 1. Extractions without addition of salt is used as controlled experiments.

It should be noted that, in extraction where no salt was added into the system, D and %E increased with increasing initial lactic acid concentration in its aqueous solution. This observation agrees with the result of previous study, where larger distribution coefficient was obtained at higher acid concentration in the starting aqueous solution [10].

It can be seen from Table 1 that, in all the extraction systems, both D and %E were decreased when 0.5 g of the salt was added. This observation signified that lactic acid preferred to be in the aqueous phase rather than the organic phase. In other word, the acid was more soluble in the aqueous phase when 0.5 g of salts was added, which could be considered as "salting-in" effect of the chloride salts in the process.

Table 1 *Distribution coefficient (D) and degree of lactic acid extraction (%E) with n-butanol containing different chloride salt*

gram of salt added	0.1 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	0.72	33.34	0.72	33.34	0.72	33.34
0.5	0.52	30.42	0.61	33.32	0.59	32.44
1.0	0.60	33.49	0.60	34.69	0.60	33.41
3.0	0.69	38.45	0.78	41.78	0.57	32.77
5.0	0.76	41.28	0.90	45.53	0.57	32.99
gram of salt added	0.3 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	0.72	35.60	0.72	35.60	0.72	35.60
0.5	0.65	34.05	0.67	35.55	0.61	33.45
1.0	0.72	36.14	0.72	37.41	0.63	34.02
3.0	0.85	42.22	0.80	40.87	0.58	33.53
5.0	1.11	49.04	0.92	46.58	0.61	35.79
gram of salt added	0.5 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	0.84	37.95	0.84	37.95	0.84	37.95
0.5	0.76	36.42	0.75	35.77	0.68	34.73
1.0	0.76	37.08	0.78	37.50	0.66	34.82
3.0	0.87	43.03	0.84	41.21	0.68	37.39
5.0	1.02	47.13	0.98	46.19	0.71	39.28
gram of salt added	0.7 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	1.01	40.26	1.01	40.26	1.01	40.26
0.5	0.68	31.35	0.68	33.41	0.65	30.52
1.0	0.71	33.13	0.74	35.44	0.65	32.03
3.0	0.88	41.27	0.85	40.90	0.63	34.02
5.0	1.06	47.86	1.10	47.40	0.62	34.77
gram of salt added	1.0 M Lactic acid					
	NaCl		$MgCl_2$		$CaCl_2$	
	D	%E	D	%E	D	%E
0	1.14	41.59	1.14	41.59	1.14	41.59
0.5	0.70	31.21	0.73	32.70	0.69	32.27
1.0	0.72	33.70	0.80	37.29	0.69	33.27
3.0	0.91	40.64	0.98	43.89	0.74	35.72
5.0	1.13	46.13	1.12	48.56	0.76	36.38

สำนักหอสมุด มหาวิทยาลัยเทคโนโลยีสุรนารี

When quantities of chloride salts were increased from 1 to 5 g, "salting-out" effect was observed in extraction with NaCl and $MgCl_2$, where both D and %E increased with the salt concentration. However, in extraction with addition of $CaCl_2$, these parameters appeared to be quite unvaried with increasing salt concentration.

Salting-in and salting-out effect of each salt are more apparent when D was plotted against the ionic strength of aqueous solution in each system. Ionic strength (I) is a measure of the concentration of ions in the solution and can be calculated from

$$I = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 \qquad (3)$$

where C_i is molar concentration of the i^{th} ion, Z_i is the charge of the ion and n is the number of ions presented in the solution. The plots are shown in Fig. 1, 2, 3, 4 and 5 for the system with initial lactic acid concentration of 0.1, 0.3, 0.5, 0.7 and 1 M.

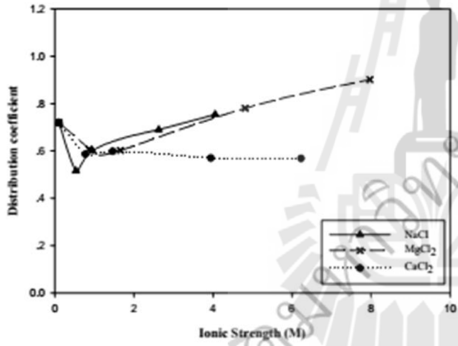


Fig. 1 *Effect of ionic strength on distribution coefficient of lactic acid for extraction with Initial acid concentration 0.1 M*

Result in Table 1 shows that NaCl and $MgCl_2$ pose similar effect on lactic acid extraction using n-butanol, i.e. values of D and %E obtained from the system when equal amount of these salts were added are quite similar. However, the plots in Fig. 1-5 indicate that NaCl might be more powerful to induce salting out of lactic acid since higher D was achieved in system with NaCl than the system with $MgCl_2$ of equal ionic strength. Furthermore, the value of D is in the order of NaCl>$MgCl_2$>$CaCl_2$, which is the same arrangement of these salts in Hofmeister series as previously shown.

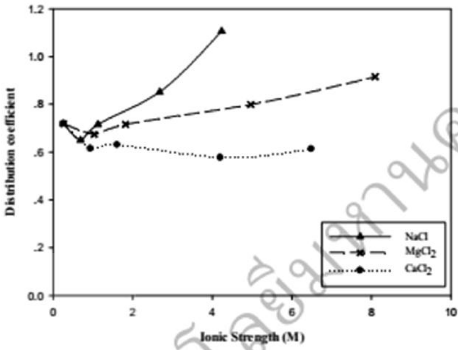


Fig. 2 *Effect of ionic strength on distribution coefficient of lactic acid for extraction with initial acid concentration 0.3 M*

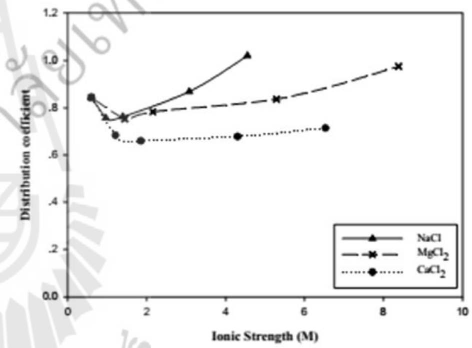


Fig. 3 *Effect of ionic strength on distribution coefficient of lactic acid for extraction with initial acid concentration 0.5 M*

3.2 Effect of temperature on lactic acid distribution coefficient and degree of extraction

Three temperatures (30, 40 and 50°C) and two chloride salts (NaCl, $MgCl_2$) were selected to study the effect of temperature for the extraction of lactic acid system. The mass of salt in aqueous solution was maintained at the same level (5 g chloride salt in 20 ml of 0.1, 0.5 and 1 M lactic acid).

ยาลัยเทคโนโลยีสุรนารี

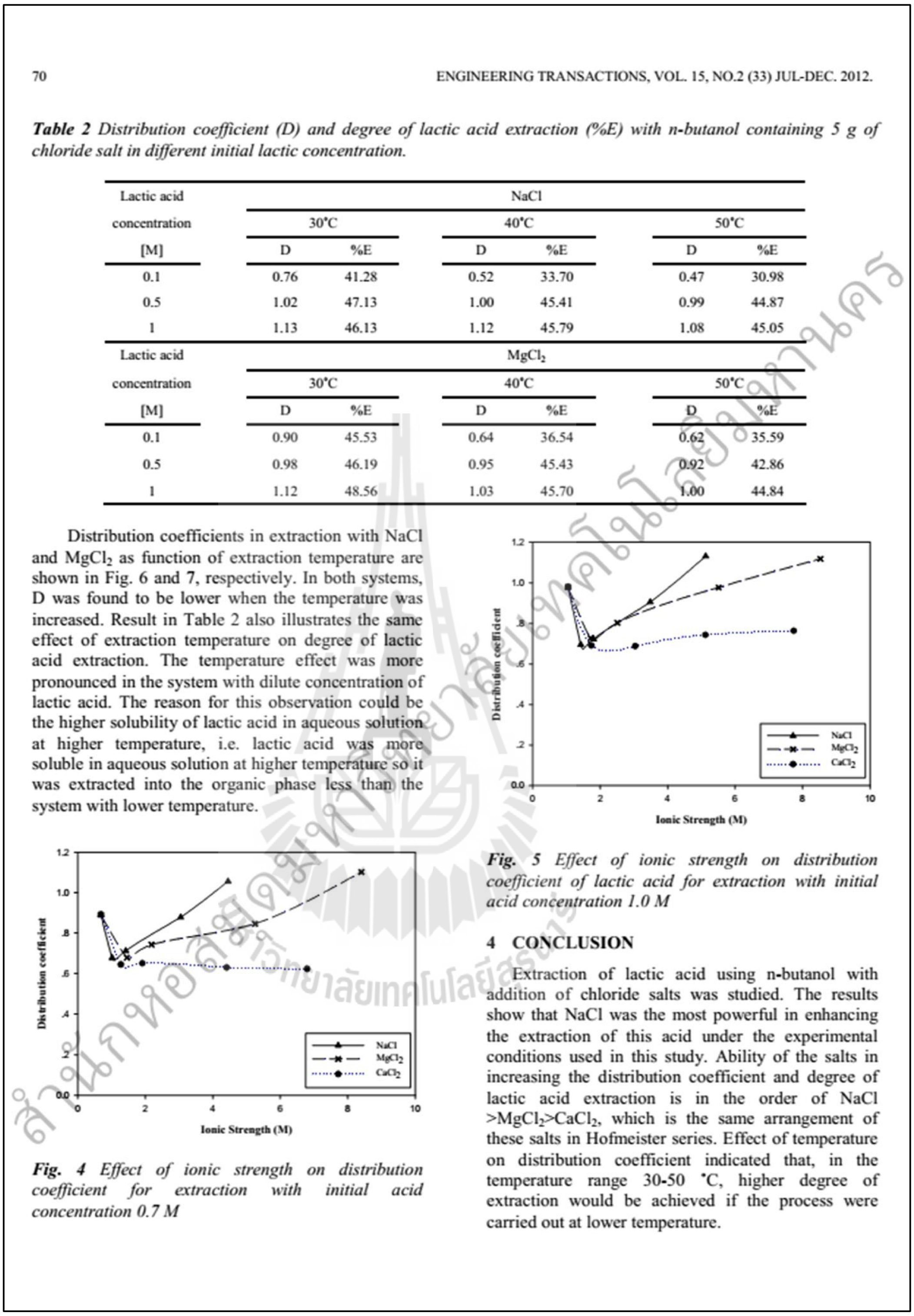


***Table 2** Distribution coefficient (D) and degree of lactic acid extraction (%E) with n-butanol containing 5 g of chloride salt in different initial lactic concentration.*

Lactic acid	NaCl					
concentration	30°C		40°C		50°C	
[M]	D	%E	D	%E	D	%E
0.1	0.76	41.28	0.52	33.70	0.47	30.98
0.5	1.02	47.13	1.00	45.41	0.99	44.87
1	1.13	46.13	1.12	45.79	1.08	45.05
Lactic acid	$MgCl_2$					
concentration	30°C		40°C		50°C	
[M]	D	%E	D	%E	D	%E
0.1	0.90	45.53	0.64	36.54	0.62	35.59
0.5	0.98	46.19	0.95	45.43	0.92	42.86
1	1.12	48.56	1.03	45.70	1.00	44.84

Distribution coefficients in extraction with NaCl and $MgCl_2$ as function of extraction temperature are shown in Fig. 6 and 7, respectively. In both systems, D was found to be lower when the temperature was increased. Result in Table 2 also illustrates the same effect of extraction temperature on degree of lactic acid extraction. The temperature effect was more pronounced in the system with dilute concentration of lactic acid. The reason for this observation could be the higher solubility of lactic acid in aqueous solution at higher temperature, i.e. lactic acid was more soluble in aqueous solution at higher temperature so it was extracted into the organic phase less than the system with lower temperature.

***Fig. 4** Effect of ionic strength on distribution coefficient for extraction with initial acid concentration 0.7 M*

***Fig. 5** Effect of ionic strength on distribution coefficient of lactic acid for extraction with initial acid concentration 1.0 M*

4 CONCLUSION

Extraction of lactic acid using n-butanol with addition of chloride salts was studied. The results show that NaCl was the most powerful in enhancing the extraction of this acid under the experimental conditions used in this study. Ability of the salts in increasing the distribution coefficient and degree of lactic acid extraction is in the order of NaCl >$MgCl_2$>$CaCl_2$, which is the same arrangement of these salts in Hofmeister series. Effect of temperature on distribution coefficient indicated that, in the temperature range 30-50 °C, higher degree of extraction would be achieved if the process were carried out at lower temperature.

สำนักหอสมุด มหาวิทยาลัยเทคโนโลยีสุรนารี

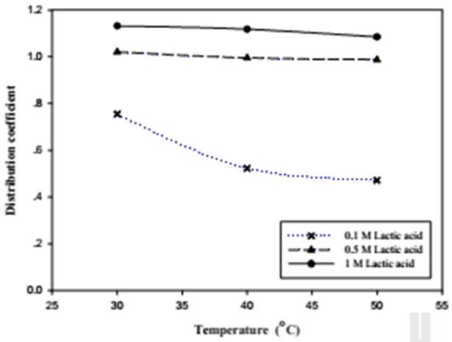


***Fig. 6** Effect of temperature on distribution coefficient of lactic acid for extraction with addition of 5g NaCl*

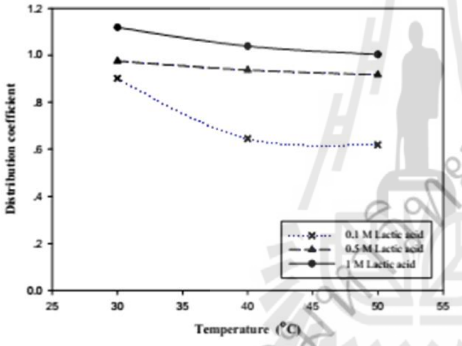


***Fig. 7** Effect of temperature on distribution coefficient of lactic acid for extraction with addition of 5g* $MgCl_2$

วิทยาลัยเทคโนโลยีสุรนาร

5. ACKNOWLEDGEMENTS

This research is financially supported by the National Innovation Agency, Ministry of Science and Technology, Thailand.

REFERENCES

[1] P. Borgardts, W. Krischke, W. Trosch, & H. Brunner, "Integrated bioprocess for the simultaneous production of lactic acid and dairy sewage treatment", *Bioprocess Eng*, vol.19, pp. 321–329, 1998.

[2] G. Raya-Tonetti, P. Cordoba, J. Bruno-Barcena, F. Sineriz, & N. Perotti, "Fluidized bed ion exchange for improving purification of lactic acid from fermentation", *Biotechnoly Tech.*, vol.13, pp. 201–205, 1999.

[3] M. M. Hossain, "Mass transfer investigation of organic acid extraction with trioctylamine and Aliquat 336 dissolved in various solvent", http://cdn.intechweb.org/pdfs/13542.pdf

[4] Ş. S. Bayazit, H. Uslu and İ. İnci, "Comparison of the efficiencies of amine extractants on lactic acid with different organic solvents", *J. Chem. Eng. Data.*, vol. 56, pp. 750-756, 2011.

[5] Y. K. Hong and W.H., Hong, "Reactive extraction of lactic acid with mixed tertiary amine extractants", *Biotechnol. Tech.*, vol. 12, pp. 915-918, 1999.

[6] K. L. Wasewar, A. A. Yawalkar, J. A. Moulijn and V.G. Pangarkar, "Fermentation of glucose to lactic acid coupled with reactive extraction: A Review", *Ind. Eng. Chem. Res.*, vol. 43, pp. 5969-5982, 2004.

[7] B. Choudhury and T. Swaminathan, "Lactic acid extraction with trioctyl amine", *Biopro. Eng.*, vol. 19, pp. 317-320, 1998.

[8] A. Labbaci, G. Kyuchoukov, J. Albet and J. Molinier, "Detailed investigation of lactic acid extraction with tributylphosphate dissolved in dodecane", *J. Chem. Eng. Data.*, vol. 55, pp. 228-233, 2010.

[9] G. Kyuchoukov, M. Marinova, J. Albet and J. Molinier, "New method for the extraction of lactic acid by means of a modified extractant (Aliquat 336)", *Ind. Eng. Chem. Res.*, vol. 43, pp. 1179-1184, 2004.

[10] K. Chawong, and P. Rattanaphanee. "n-Butanol as an Extractant for Lactic Acid Recovery", *World Acad. Sci. Eng. Tech.*, vol. 80, pp. 239-242, 2011.

[11] B. Ghalami-Choobar, A. Ghanadzadeh and S. Kousarimehr. "Salt effect on the liquid-liquid equilibrium of (water + propionic acid + cyclohexanol) system at T = (298.2, 303.2, and 305.2) K", *Chin. J. Chem. Eng.*, vol 19, no.4, pp. 565-569, 2011.

Kanungnit Chawong, Biography not availablea at the time of publication.

Panarat Rattanaphanee, Biography not availablea at the time of publication.

Liquid-liquid equilibrium of 1-butanol + water + $(NH_4)_2SO_4$ and its application in lactic acid extraction

Kanungnit Chawong*, Panarat Rattanaphanee

School of Chemical Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand

*Author for correspondence; E-Mail: kanungnit.cha@hotmail.com, Tel. +66 8160 11435

Abstract: Liquid-liquid equilibrium (LLE) of mixed solvent electrolyte systems containing 1-butanol, water and ammonium sulfate, ($(NH_4)_2SO_4$), at temperatures of 303.15, 313.15 and 323.15 K under atmospheric pressure have been studied experimentally and theoretically. The salt appeared to decrease mutual solubility between water and 1-butanol and enlarge area of two-phase region of the mixture, particularly at high salt concentration. Temperature in the range studied here was found to have minor effect on LLE behavior of this system. Experimental LLE data were correlated by a modified extended UNIQUAC model, which is generally used for describing phase behaviour in water-organic solvent mixtures containing inorganic salts. The model was found to satisfactory agree with the measured LLE data with an average absolute deviation of less than 0.75% between the calculated and measured mass fractions of the mixture components. Salt-modified LLE behaviour of water-butanol mixture was applied in extraction of lactic acid from its aqueous solution using 1-butanol. $(NH_4)_2SO_4$ effectively showed salting out effect that led to decrease in concentration of the acid and 1-butanol in the aqueous phase thus increase in their concentrations in the organic phase. Distribution coefficient and degree of extraction increased with increasing salt concentration. It is concluded in this study that LLE behaviour of water-butanol mixture was significantly affected by $(NH_4)_2SO_4$. The salt enhanced the heterogeneity of the system in a way that favoured the extraction of lactic acid from its aqueous solution using 1-butanol.

1. Introduction

The modelling of electrolyte systems and more specifically, mixed solvent-electrolyte systems is important in chemical engineering because this type of mixture is found in many processes such as extractive crystallization and liquid-liquid extraction for mixtures containing of salt [1]. Salt mainly affects the solubility of organic component in an aqueous-organic solvent mixture. Distribution of the solute between the two liquid phases mainly depends upon the concentration of electrolyte. Specifically, adding salt to an aqueous solution can result in either decrease or increase in solubility of the solute in the solution [2]. These effects can significantly change its equilibrium composition. Experimental as well as theoretical knowledge about phase equilibrium of mixed solvent electrolyte systems is a prerequisite for process design in such systems. Experimental Several thermodynamic theories have been developed to represent in LLE of mixed solvent containing electrolytes systems such as electrolyte NRTL model and extended UNIQUAC model [3-5].

Pirahmadi et al. [7, 8] presented a modified extended UNIQUAC model by explicitly taking into account effect of mixed solvent on liquid-liquid equilibrium of 1-butanol/water/$NaNO_3$ and NH_4Cl system. In this model the excess Gibbs energy is used by taking into account mixed solvent theories. The model consists of three terms, the original UNIQUAC term, Pitzer–Debye–Hückel term and Born term. The model has been found to give a satisfactory description of LLE data.

In addition to their effect on mutual solubilities of mixed-sovent components, inorganic salts were found to influence distribution characteristic of other solutes between the partial miscible phases in the system. Chawong and Rattanaphanee [9] studied effect of chloride salts: NaCl, $MgCl_2$ and $CaCl_2$ on extraction of lactic acid from its aqueous solution. It was observed that, when the salt concentration was sufficiently high, the distribution coefficient increased with increasing salt concentration

This work, therefore, aims to investigate LLE behavior of 1-butanol-water system in a presence of $(NH_4)_2SO_4$ and its application in extraction of lactic acid from its aqueous solution. The LLE behavior is elucidated by correlating experimental data with modified extended UNIQUAC model. Effect of the salt concentration on distribution coefficient of lactic acid between water-rich phase and 1-butanol-rich phase is also reported.

2. Materials and Methods

2.1 Materials

Lactic acid with concentration of 88 %wt and 1-butanol with 99.9% purity were purchased from Acros. Anhydrous $(NH_4)_2SO_4$ was from CARLO ERBA and deionized water was used in the experiments.

2.2 Apparatus and procedure

Weighted quantity of $(NH_4)_2SO_4$ was added into 10 ml DI water. Equal volumes of 1-butanol was then mixed with the prepared solution in 125 ml of Erlenmeyer flask and shaken in a temperature-controlled shaking bath for 12 h. The two phases were separated after the mixture was left to settle for 12 h. Finally, the samples of top and bottom phases were taken for analysis. For extraction study, aqueous

solution of lactic acid at desired concentration was used in place of DI water.

2.3 Methods of analysis

Mass fractions of 1-butanol were analyzed by gas chromatograph (GC) equipped with 30m x 0.53 mm x 0.5 µm TR-FFAP capillary column and flame ionization detector (FID) using helium as the carrier gas. The samples are diluted with deionized water before analysis.

Water content was analyzed by GC equipped with thermal conductivity detector (TCD) using helium as carrier gas. A 2m x 1/8 in. stainless steel column packed with Chromosorb 102 80/100 was used to separate the components. All samples were diluted with absolute ethanol before the analysis.

Lactic acid concentration was determined by HPLC using Hypersil BDS C18-column 4.0×100 mm, 3-Micro (Agilent). Sulfuric acid solution with concentration of 0.005 M of H_2SO_4 and flow rate of 0.35 ml/min was used as a mobile phase. The UV wavelength was set at 210 nm, and the injection volume was 10 µL.

Salt contents were analyzed by drying the samples at 120°C for 12 h to completely remove all the liquid.

3. Results and Discussion

3.1 Experimental LLE data

LLE data for water+1-butanol system were measured at temperature 303.15, 2313.15 and 323.15 K under atmospheric pressure and are presented as mass percent of each component in Tables 1-3, respectively. The data are also depicted by ternary diagrams in Figure 1-3. Decreasing mass fraction of water in 1-butanol-rich phase and of 1-butanol in water-rich phase indicated that the mutual solubility between the two components was diminished as the salt concentration increased. This led to the enlarged heterogeneous region of the mixture in the ternary diagrams. Similar LLE behavior is observed at all the temperature studied here. Effect of temperature in this range on phase composition was slightly observed.

3.2 Model correlation and parameters evaluation

The modified extended UNIQUAC models were used to correlate the experimental LLE data. The model consists of three terms contributing to the excess Gibbs free energy. The first contribution is an original UNIQUAC term as given by Abrams and Pranusnit [10] for short range interaction. The second one is a Pitzer-Debye-Hückel term [11] for considering long range interaction. For the last contribution, a Born term is added to the model in order to explain energy associated with the transfer of ionic species from an infinite dilution state in the mixed solvent to an infinitively dilute aqueous phase [12]. Water and 1-butanol are considered as the solvent, where their activity coefficients are defined by symmetrical convention. The activity coefficients of caionic and anionic species from dissociation of the salt are defined using asymmetric convention.

All adjustable parameter have been determined by minimizing differences between the experimental and calculated mass fraction using the following objective function (OF).

$$OF = \sum_{j=1}^{M}\sum_{i=1}^{N}\left[\left(w_{ij}^{calc}-w_{ij}^{\exp}\right)_I^2 - \left(w_{ij}^{calc}-w_{ij}^{\exp}\right)_{II}^2\right] \qquad (1)$$

where j and i refer to solvent and ions. M and N are number of tie-lines and number of components. w^{calc} and w^{exp} signify mass fraction calculated by model and experimental data, while I and II represent the equilibrium phase.

The correlated results together with the experimental data for these ternary systems were plotted and are shown in Figure 1-3. All the binary interaction parameters (a_{ij}) were estimated from model optimization using experimental result from this work. The values are given in Table 4.

It should be noted that values of a_{12} and a_{21} obtained in this work are appreciably diverse from those reported for system of water+1-butanol+NH_4Cl and water+1-butanol+$NaNO_3$, which were estimated from the original UNIQUAC model [7, 8].

Table 1: Mass percent of water (1), 1-butanol (2) and $(NH_4)_2SO_4$ (3) in the ternary system at 303.15 K

Water rich phase			1-Butanol rich phase		
$\%w_1$	$\%w_2$	$\%w_3$	$\%w_1$	$\%w_2$	$\%w_3$
92.98	7.02	0	20.71	79.29	0
93.93	5.14	0.93	8.24	91.76	0.01
93.50	4.31	2.19	7.87	92.12	0.01
92.25	3.62	4.13	7.73	92.25	0.02
88.66	2.33	9.01	6.34	93.65	0.01
83.53	0.94	15.53	5.85	94.14	0.01
76.92	0.58	22.50	5.36	94.62	0.01

Table 2: Mass percent of water (1), 1-butanol (2) and $(NH_4)_2SO_4$ (3) in the ternary system at 313.15 K

Water rich phase			1-Butanol rich phase		
$\%w_1$	$\%w_2$	$\%w_3$	$\%w_1$	$\%w_2$	$\%w_3$
93.23	6.77	0	22.47	77.53	0
92.41	6.35	1.24	14.24	85.76	0.00
92.19	5.02	2.79	14.25	85.75	0.01
90.09	3.96	5.94	9.18	90.80	0.01
86.14	2.76	11.10	9.21	90.78	0.01
80.22	1.17	18.61	7.08	92.92	0.01
75.55	0.87	23.58	6.17	93.81	0.01

Table 3: Mass percent of water (1), 1-butanol (2) and $(NH_4)_2SO_4$ (3) in the ternary system at 323.15 K

Water rich phase			1-Butanol rich phase		
$\%w_1$	$\%w_2$	$\%w_3$	$\%w_1$	$\%w_2$	$\%w_3$
93.41	6.59	0	23.87	76.13	0
92.14	6.65	1.21	11.02	88.98	0.00
91.39	5.57	3.04	10.27	89.72	0.01
90.19	4.23	5.58	9.94	90.05	0.01
86.53	2.78	10.70	8.55	91.43	0.02
79.96	1.24	18.80	7.56	92.42	0.02
74.49	0.35	25.16	6.81	93.17	0.02

Table 4: Binary interaction parameters and average absolute deviation of the modified extended UNIQUAC model for water (1) + 1-butanol (2) + NH_4^+ (3) + SO_4^{2-} (4) system obtain using experimental data from this work

		303.15 K		313.15 K		323.15 K	
i	***j***	a_{ij} **(K)**	a_{ji} **(K)**	a_{ij} **(K)**	a_{ji} **(K)**	a_{ij} **(K)**	a_{ji} **(K)**
1	2	168.81	207.71	126.71	215.08	180.10	159.41
1	3	-18851.29	-763.87	-31691.33	-865.72	-9379.17	-891.55
1	4	-12327.69	4501.49	-4156.87	37038.94	-3670.75	9255.00
2	3	21150.88	24839.89	36754.21	34784.97	10831.30	11516.91
2	4	14521.12	23224.39	9754.03	17494.97	3583.56	10150.93
3	4	-2239.18	-870.54	-5643.68	-1980.42	-5221.33	-541.60
%Δw		0.6815		0.7257		0.7476	

Different thermodynamic models as well as dissimilar inorganic salt presented in the system could be the main reasons for this variation in these parameters.

Quality of the correlation in this work is evaluated by root mean square absolute deviation of component mass fraction in both phases:

$$\%\Delta w = 100\left[\frac{\sum_{j=1}^{M}\sum_{i=1}^{N}\left(\left(w_{ij}^{I,\exp}-w_{ij}^{I,calc}\right)^2+\left(w_{ij}^{II,\exp}-w_{ij}^{II,calc}\right)^2\right)}{2MN}\right]^{1/2} \quad (2)$$

Values of $\%\Delta w$ in the correlation by modified extended UNIQUAC model for the systems studied are also shown in Table 4. As seen, the average absolute

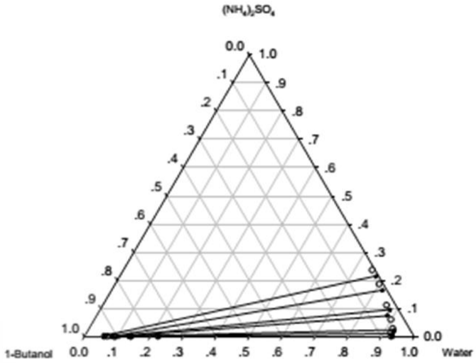


Figure2. Experimental (○) and calculated (-★-) LLE tie-lines for water(1), 1-butanol(2) and $(NH_4)_2SO_4$(3) at 313.15 K.

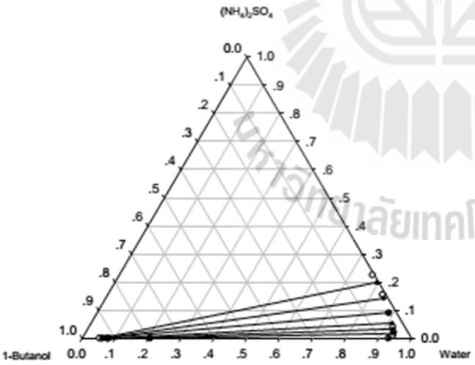


Figure1. Experimental (○) and calculated (-★-) LLE tie-lines for water(1), 1-butanol(2) and $(NH_4)_2SO_4$(3) at 303.15 K.

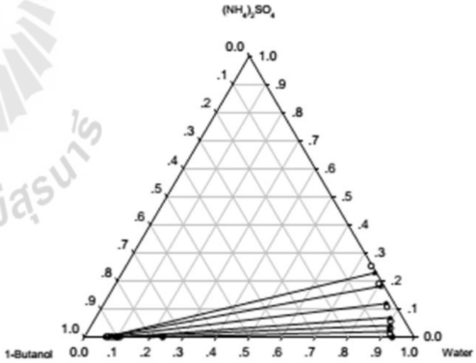


Figure3. Experimental (○) and calculated (-★-) LLE tie-lines for water(1), 1-butanol(2) and $(NH_4)_2SO_4$(3) at 323.15 K.

3.3 Effect of $(NH_4)_2SO_4$ on extraction of lactic acid

It has been reported that addition of inorganic salt to an aqueous solution of addition of salt to aqueous solution of an organic acid can result in either decrease or increase in solubility of the acid in the solution [13, 14]. If the acid solubility is increased upon addition of salt, the effect is called "salting in". On the other hand, if its solubility is diminished when the salt is added, the effect is called "salting out".

In this study, effect of $(NH_4)_2SO_4$ content in lactic acid aqueous solution on extraction of the acid using 1-butanol was investigated. Lactic acid extraction

มหาวิทยาลัยเทคโนโลยีสุรนารี

without $(NH_4)_2SO_4$ is used as a controlled experiment in order to reveal effect of this salt on the process performance. Efficiency of lactic acid extraction was represented by the distribution coefficient (D) and the degree of extraction (%E), shown in Table 5. As water and 1-butanol are partially miscible, volumes of water- and 1-butanol-rich phase after extraction differed from initial volumes of aqueous solution and 1-butanol. For that reason, D and %E, in this study were defined as follows.

$$D = \frac{C_{org}V_{org}}{C_{aq}V_{aq}} \tag{3}$$

$$\%E = \frac{C_0V_0 - C_{aq}V_{aq}}{C_0V_0} x100 \tag{4}$$

where C_0 is the concentration of lactic acid in the starting solution, C_{org} and C_{aq} are equilibrium concentration of lactic acid in the organic and aqueous phase, respectively. V_0 is the volume of starting solution; V_{aq} and V_{org} is volume of the aqueous phase and organic phase after extraction.

Table 5: Distribution coefficient (D) and degree of lactic acid extraction (%E) with 1-butanol containing $(NH_4)_2SO_4$

Salt concentration (g/L)	**D**	**%E**
0	1.14	60.27
0.10	1.03	56.56
0.19	1.17	60.31
0.26	1.30	62.94
0.40	1.41	63.18

It can be seen from Table 5 that both D and %E of lactic acid extraction were lower when small concentration of $(NH_4)_2SO_4$ was presented in its aqueous solution. This observation signified that lactic acid preferred to be in aqueous phase containing low salt concentration rather than the organic phase. In other word, the acid was more soluble in the aqueous phase with low concentration of salt, which could be considered as "salting-in" effect of $(NH_4)_2SO_4$ on lactic acid in this system. With further addition of salt until its concentration was sufficiently high, "salting-out" effect was observed when both D and %E increased with the salt concentration. It should be noted that, although D changed significantly with the salt concentration, only slight increase in %E was observed. This could be due to the partial miscibility between the two phases that resulted in larger volume of organic phase and smaller volume of aqueous phase after the extraction. Relative value between lactic acid quantity in organic and aqueous phase, equation (3) for D, is consequently higher than that between organic phase and starting solution.

4. Conclusions

Experimental liquid-liquid equilibrium data of mixed solvent electrolyte systems containing 1-butanol, water and $(NH_4)_2SO_4$ has been measured at temperatures of 303.15, 313.15 and 323.15 K. The results show that $(NH_4)_2SO_4$ is less soluble in organic phase as compared to the water aqueous phase. Salting out effect, i.e. reduced mutual solubility between the two solvents was observed at all temperature in the range studied. The process temperature, however, was found to have minor effect on equilibrium phase compositions.

The modified extended UNIQUAC model was used to correlate the experimental LLE data. The corresponding optimized UNIQUAC binary interaction parameters were also reported here. The model gave good agreement between the experimental and the calculated data. Application of salt-modified LLE behavior of water and 1-butanol mixture in extraction of lactic acid from its aqueous solution showed that $(NH_4)_2SO_4$ was able to enhance the extraction of this acid under the experimental conditions used in this study.

References

[1] K. Thomsen, M. C. Iliuta and P. Rasmussen, *Chem. Eng. Sci.* **59** (2004) 3631-3647.

[2] B. Ghalami-Choobar, A. Ghanadzadeh and S. Kousarimehr, *Chin. J. Chem. Eng.* **19** (2011) 565–569.

[3] C. C. Chen, Y. Song, *AIChE J.* **50** (2004) 7788-7797.

[4] G. H. van Bochove, G. J. P. Krooshof and Th. W. de Loos, *Fluid Phase Equilibria.* **171** (2000) 45-48

[5] B. Sander, A. Fredenslund and P. Rasmussen, *Chem. Eng. Sci.* **41** (1986) 1171-1183.

[6] E. A. Macedo, P. Skovborg and P. Rasmussen, *Chem. Eng. Sci.* **45** (1990) 875-882.

[7] F. Pirahmadi, M. R. Deghani, B. Behzadi, S. M. Seyedi and H. Rabiee, *Fluid Phase Equilibria.* **299** (2010) 122-126.

[8] F. Pirahmadi, M. R. Deghani and B. Behzadi, *Fluid Phase Equilibria.* **325** (2012) 1-5.

[9] K. Chawong, P. Rattanaphanee, *Engineering Transaction.* **15** (2012) 66-71.

[10] D. S. Abrams and J. M. Prausnitz, *AIChE J.* **21** (1975) 116-128.

[11] K. S. Pitzer, *J. Am. Chem. Soc.* **102** (1980) 2902-2906.

[12] Y. Marcus, *Ion Solvation*, Wiley, New York, (1985).

[13] B. C. Roy, M. R. Awual and M. Goto, *Journal of applied Sciences.* **7** (2007) 1053-1060.

[14] H. N. Sólimo, C. M. Bonatti, J. L. Zurita and M. B. Gramago de Doz, *Fluid Phase Equilibrium,* **137** (1997) 163-172.

GPE – 4th International Congress on Green Process Engineering 7-10 April 2014 – Sevilla (Spain)
Récents Progrès en Génie des Procédés, Numéro 106 - 2014
ISSN: 1775-335X ; ISBN: 978-2-910239-80-0, Ed. SFGP, Paris, France

EXTRACTION OF LACTIC ACID IN MIXED SOLVENT ELECTROLYTE SYSTEM CONTAINING WATER, 1-BUTANOL AND AMMONIUM SULFATE

K. CHAWONG(1), C. RAYABSRI(2), P. RATTANAPHANEE(3),

- School of Chemical Engineering, Institute of Engineering
  Suranaree University of Technology, Suranaree, Muang District
  Nakhon Ratchasima 30000 THAILAND
  e-mail : kanungnit.cha@hotmail.com

- (2) School of Chemical Engineering, Institute of Engineering
  Suranaree University of Technology, Suranaree, Muang District
  Nakhon Ratchasima 30000 THAILAND
  e-mail : chanita1813@yahoo.com

- (3) School of Chemical Engineering, Institute of Engineering
  Suranaree University of Technology, Suranaree, Muang District
  Nakhon Ratchasima 30000 THAILAND
  e-mail : panarat@sut.ac.th

Abstract. Extraction of lactic acid from its aqueous solution was carried out at 30.0°C in a mixed solvent electrolyte system containing water, 1-butanol and ammonium sulfate ($(NH_4)_2SO_4$). In the presence of this salt, the mutual solubility between water and 1-butanol (which is a partially miscible system) was reduced resulting in an enlarged two-phase region for the mixture. The effect was more pronounced at high salt concentration. In view of the extraction, $(NH_4)_2SO_4$ effectively salted-out 1-butanol and lactic acid leading to a reduced concentration of these two components in the aqueous phase, while increasing their concentration in the organic phase. The distribution coefficient and degree of lactic acid extraction were significantly improved with increasing concentration of the salt in the system. Additionally, $(NH_4)_2SO_4$ appeared to lessen the transfer of one solvent into the other, which is the problem normally encountered in extraction when partially miscible solvents are employed. In extraction of lactic acid without addition of $(NH_4)_2SO_4$, a substantial portion of the aqueous phase was incorporated into the 1-butanol-rich phase. Although the acid was conveyed out of the aqueous phase, a large amount of water remained in 1-butanol-rich phase could complicate the following purification steps and inhibit efficient solvent recovery and recycle. Moreover, enhancing lactic acid recovery by performing the extraction at a high 1-butanol-to-aqueous phase volume ratio was not feasible since the aqueous phase nearly disappeared. The presence of $(NH_4)_2SO_4$ advantageously allowed the extraction to be carried out at a high 1-butanol-to-aqueous phase volume ratio, where large recovery of the acid was achieved while the volume of the aqueous phase was only slightly reduced. Extraction of lactic acid in this mixed solvent electrolyte system could be further improved by operating it in a stage-wise mode rather than a batch one.

Key-words. lactic acid, extraction, liquid-liquid equilibrium; 1-butanol, ammonium sulfate

Lactic acid is one of important carboxylic acids in chemical industries. It is primarily produced biologically through fermentation of sugars or starch and is widely used as acidulates and preservatives in food industry. It also has a potential of becoming an important feedstock for production of biodegradable plastics and other environmental-friendly green compounds. The production requires highly purified lactic acid. Consequently, recovery of lactic acid from an aqueous solution or a fermentation broth where it is biologically produced is a crucial step in fermentation-based lactic acid production, and the cost for separation and purification processes was reported to account for up to 50% of the total production costs of lactic acid[1].

Number of proceses for recovery of lactic acid from the aqueous solution or fermentation broth have been proposed. Among those, liquid-liquid or solvent extraction is one of the promising techniques for this purpose. With proper choice of solvent or extractant, this technique can achieve satisfactory selective separation of desired solutes. As extraction is not as enery-intensive as evaporation or distillation, further advantage of this method lies on its suitability for large capacity processing with low energy consumption.

Common extractants for lactic acid recovery include organic bases or amine such as tri-n-octylamine (TOA), alkyl phosphate esters, such as tributyl phosphate (TBP) and trioctyl phosphine oxide

(TOPO), and the extractants that function as ion exchangers such as quaternary ammonium salts like the commercial extractant Aliquat 336 or methyltrialkyl(C_8-C_{10})ammonium chloride. Despite the high distribution coefficient obtained from the extraction, some of the extractants are expensive and might inherit some toxicity. Specifically, major disadvantages in solvent extraction using amine are large initial investment on extractant supply due to a large amount of the amine is needed as well as difficulties in removing the acids from the ammonium lactate intermediate and regeneration of the amine solvent after extraction. As a result, recovery of lactic acid by extraction with more economical and environmental friendly solvents is still needed[2].

With an aim to recover lactic acid from its aqueous solution using aliphatic alcohols as extracting solvent, LLE data and extraction efficiency of water-lactic acid-alcohols have been investigated[3,4]. For the system of water-lactic acid-1-butanol, it was reported that the process efficiency was significantly decreased with increasing pH of the aqueous solution, especially in the pH range less than 1. Consequently, degree of lactic acid extraction was higher in extraction of more concentrated, thus lower pH, lactic acid solution, which would facilitate the acid extraction at large capacity. Disadvantage of lactic acid extraction with 1-butanol, however, is the fact that water and 1-butanol are partially miscible. Water in aqueous phase was fractionally transferred into 1-butanol phase, and vice versa, leading to an incorporation of both phases and, in turn, incomplete solvent recovery and complicated the subsequent purification processes[5].

Inorganic salts or electrolytes have been reported to affect the solubility of organic solute in its aqueous solution. Particularly, addition of the salts into to an aqueous solution can result in either decrease or increase in solubility of the solute in the solution and influence the distribution characteristic of the solute between the partial miscible phases in the system[6]. In the study concerning the effect of chloride salts such as NaCl, $MgCl_2$ or $CaCl_2$ on the extraction using 1-butanol to recover lactic acid from its aqueous solution, it was found that, when the salt concentration was sufficiently high, the extraction efficiency was increased with increasing salt concentration[7].

In this study, effect of the inorganic sulphate salt $(NH_4)_2SO_4$ on extraction of lactic acid from its aqueous solution with 1-butanol was investigated. Liquid-liquid equilibrium (LLE) data of water-1-butanol-lactic acid system with and without $(NH_4)_2SO_4$ were investigated. Efficiency of extraction process was evaluated from the distribution coefficient and degree of lactic acid extraction.

MATERIALS AND METHODS

Lactic acid with concentration of 88 %wt and 1-butanol with 99.9% purity were purchased from Acros. Anhydrous $(NH_4)_2SO_4$ was from CARLO ERBA and deionized water was used in the experiments.

Weighted quantity of $(NH_4)_2SO_4$ was added into 10 ml DI water. Equal volumes of 1-butanol was then mixed with the prepared solution in a 125 ml of Erlenmeyer flask. The mixture was shaken in a temperature-controlled shaking bath for 12 h before being transferred to a separatory funnel and was left for phase separation in the bath for another 12 h. The samples of top and bottom phases were taken for analysis. Mass fractions of 1-butanol were analyzed by gas chromatograph (GC) equipped with TR-FFAP capillary column and flame ionization detector (FID) using helium as the carrier gas. Water content was analyzed by GC equipped with thermal conductivity detector (TCD) using helium as carrier gas. A stainless steel Chromosorb$^{(R)}$ packed-column was used to separate the components.

Lactic acid concentration was determined by HPLC using Hypersil BDS C18-column 4.0×100 mm, 3-Micro (Agilent). Sulfuric acid solution with concentration of 0.005 M was used as a mobile phase. The UV wavelength of the detector was set at 210 nm. The salt contents were analyzed by drying the samples at 120°C for 12 h to completely remove all the liquid.

RESULTS AND DISCUSSION

Effect of $(NH_4)_2SO_4$ on LLE of Water-1-butanol System

Effect of $(NH_4)_2SO_4$ on LLE data for water-1-butanol system at 30.0°C was measured. The results are is given in Table 1. The LLE data for binary mixture between 1-butanol and water, i.e., when

Table 1. Mass percent of water(1), 1-butanol(2) and $(NH_4)_2SO_4$(3) in the ternary system at 30.0 °C

Water-rich phase			1-Butanol rich phase		
%w1	%w2	%w3	%w1	%w2	%w3
92.50	7.50	0	12.95	87.05	0
93.93	5.14	0.93	8.24	91.76	0.01
93.50	4.31	2.19	7.87	92.12	0.01
92.25	3.62	4.13	7.73	92.25	0.02
88.66	2.33	9.01	6.34	93.65	0.01
83.53	0.94	15.53	5.85	94.14	0.01
76.92	0.58	22.50	5.36	94.62	0.01

no salt was added to the mixture, was presented in the first row of the table. Water and 1-butanol mixture naturally separate into two phases: the top 1-butanol rich or organic phase and the bottom water-rich or aqueous phase. Due to its partial miscibility, water is fractionally transferred into the organic phase and a portion of 1-butanol is transferred into the aqueous phase. Under the experimental conditions used in this work, the aqueous phase contained 7.5% of 1-butanol while the organic phase contained approximately 13% of water. The result showed higher solubility of water in 1-butanol than that of 1-butanol in water, which agreed with the results observed in other works concerning LLE of water-butanol system[9,10].

When $(NH_4)_2SO_4$ was presented in the system, mass percent of water in 1-butanol-rich phase decreased from 12.95 to 5.36% and the mass percent of 1-butanol in water-rich phase decreased from 7.50 to 0.94% upon increasing $(NH_4)_2SO_4$ concentration. This indicates that the mutual solubility between the two components was reduced as the salt concentration increased. In other words, $(NH_4)_2SO_4$ salted out 1-butanol from water, and, as expected, the salt preferred to be in water-rich phase so only trace concentration of it was found in 1-butanol-rich phase.

Extraction of lactic acid in Water-1-Butanol-$(NH_4)_2SO_4$ System

It has been reported that addition of inorganic salt into the aqueous solution of an organic acid can result in either decrease or increase in solubility of the acid in the solution[8]. If the acid solubility is increased upon addition of salt, the effect is called "salting in". On the other hand, if its solubility is diminished when the salt is added, the effect is called "salting out". In this study, effect of $(NH_4)_2SO_4$ on solubility of lactic acid in the aqueous and organic solution as well as the LLE behavior of water-1-butanol-lactic acid system were investigated. The results are depicted as ternary diagrams on salt-free basis as shown in Fig. 1, 2 and 3 for system with 0, 2 and 5 g of $(NH_4)_2SO_4$ respectively.

In the system with an absence of $(NH_4)_2SO_4$, Fig.1, the tie lines in the diagram were mostly horizontal indicating the even distribution of the acid between both phases. In Fig. 2 and 3 where $(NH_4)_2SO_4$ was added to the system, the tie-lines became inclined with the mass fraction of lactic acid in 1-butanol-rich phase higher that that in water-rich phase, which suggested that the acid preferred to be in 1-butanol-rich phase under the presence of $(NH_4)_2SO_4$. Dependency of the LLE behavior of this system on $(NH_4)_2SO_4$ quantities can be elucidated by comparing the LLE behavior of this system in Fig. 2 and 3. Similar to the previously presented LLE data in Table 1, the mass fraction of water in 1-butanol-rich phase and of 1-butanol in water-rich phase were reduced with increasing quantities of the salt in the system. This is evidenced by the longer tie-lines and the larger two-phase region in the ternary diagram for the system with 5 g $(NH_4)_2SO_4$ when compared to the system with 2 g of the salt. It should also be noted that the slope of the tie-lines increased with increasing lactic acid concentration in the system.

Equilibrium mass fractions of lactic acid in aqueous and organic phase with and without the presence of $(NH_4)_2SO_4$ were graphically shown in Fig. 4. The ratio of lactic acid mass fraction in the organic phase to that in the aqueous phase was higer in system with salt, which confirmed that the acid extraction with 1-butanol was promoted when the $(NH_4)_2SO_4$ was added to the system.

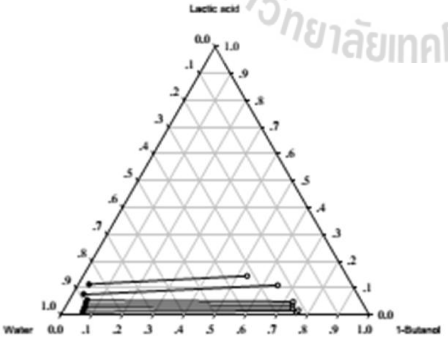


Fig. 1 Salt-free basis LLE of water-1-butanol-lactic acid system at 0 g $(NH_4)_2SO_4$

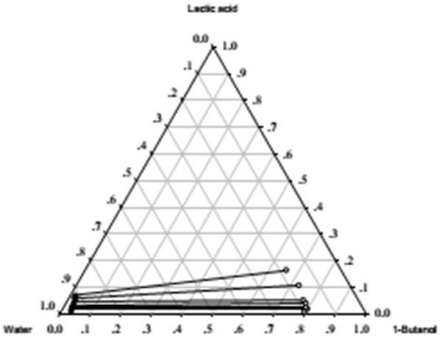


Fig. 2 Salt-free basis LLE of water-1-butanol-lactic acid system at 2 g $(NH_4)_2SO_4$

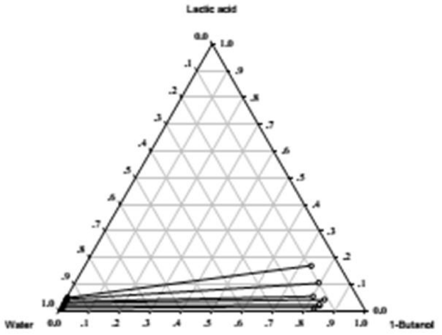


Fig. 3 Salt-free basis LLE of water-1-butanol-lactic acid system at 5 g $(NH_4)_2SO_4$

Efficiency of lactic acid extraction was evaluated from the distribution coefficient (D) and degree of lactic acid extraction (%E). Due to the partially miscible nature of water and 1-butanol, which leads to unequal volume of each phase after extraction, the distribution coefficient of lactic acid in this study is defined as the ratio between number of moles of lactic acid in the organic phase to that in the aqueous phase and can be calculated as shown in eq. (1). The degree of lactic acid extraction is expressed as percent of the acid recovered into the organic phase in relative with its initial amount in the aqueous phase and can be calculated as shown in eq. (2). C is the molar concentration of lactic acid, V is the volume of each phase, subscript 0, 1 and 2 refer to the starting solution, the aqueous phase and the organic phase, respectively.

$$D = \frac{C_2V_2}{C_1V_1} \qquad (1)$$

$$\%E = \frac{C_0V_0 - C_1V_1}{C_0V_0} \times 100 \qquad (2)$$

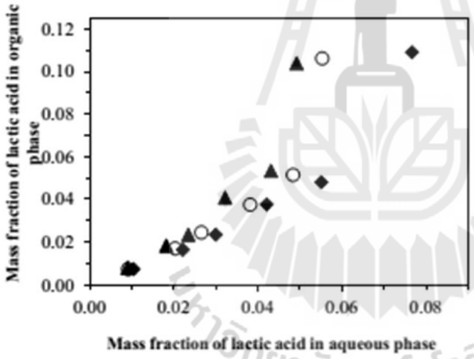


Fig. 4 Equilibrium mass fraction of lactic acid in organic and aqueous phase in extraction with 0 g (◆), 2 g (○) and 5 g (▲) $(NH_4)_2SO_4$

The distribution coefficient and degree of extraction of lactic acid in system with and without $(NH_4)_2SO_4$ are given in Table 2. The presence of $(NH_4)_2SO_4$ clearly promoted the extraction of lactic acid. It should be noted that D and %E was enhanced with increasing lactic acid concentration in the starting aqueous solution. This result was expectable and was similar to the observation reported in the previous study[5]. Elevated extraction efficiency at higher lactic acid concentration in the aqueous solution is the process characteristic that can facilitate its application in recovery of the acid from its concentrated solution. It implies that the process intensification is feasible as the dilute lactic acid solution or fermentation broth could be concentrated prior to the extraction, which could help in reducing the size of process equipments and easing the process stream handling in actual operation.

Effect of the volume ratio between 1-butanol and starting aqueous solution on lactic acid extraction was also investigated in this study. The result shown in Table 3 indicated that the extraction efficiency was increased significantly when higher volume ratio between both phases was employed. For example, about 62.4% of lactic acid was recovered in extraction with the initial phase volume ratio of 1:1, but the recovery was raised to approximately 83.4% when the ratio of 3:1 was used.

In order to clarify the effect of $(NH_4)_2SO_4$ in extraction of lactic acid with high 1-butanol-to-aqueous phase volume ratio, degree of lactic acid extraction in the process without salt obtained from our previous study[5] was also given in Table 3. The problem encounterred in extraction without salt was that a

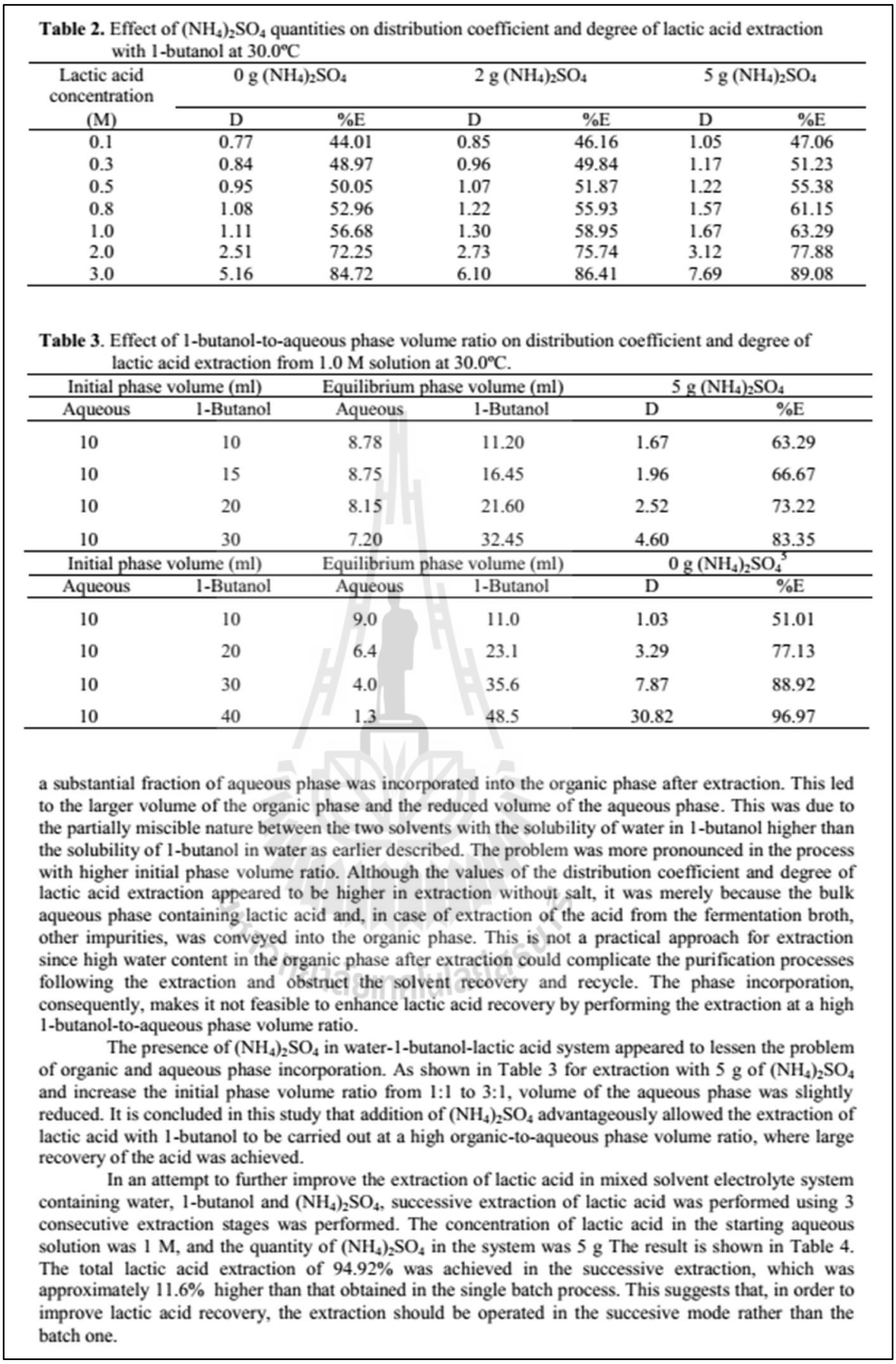


Table 2. Effect of $(NH_4)_2SO_4$ quantities on distribution coefficient and degree of lactic acid extraction with 1-butanol at 30.0ºC

Lactic acid concentration	0 g $(NH_4)_2SO_4$		2 g $(NH_4)_2SO_4$		5 g $(NH_4)_2SO_4$	
(M)	D	%E	D	%E	D	%E
0.1	0.77	44.01	0.85	46.16	1.05	47.06
0.3	0.84	48.97	0.96	49.84	1.17	51.23
0.5	0.95	50.05	1.07	51.87	1.22	55.38
0.8	1.08	52.96	1.22	55.93	1.57	61.15
1.0	1.11	56.68	1.30	58.95	1.67	63.29
2.0	2.51	72.25	2.73	75.74	3.12	77.88
3.0	5.16	84.72	6.10	86.41	7.69	89.08

Table 3. Effect of 1-butanol-to-aqueous phase volume ratio on distribution coefficient and degree of lactic acid extraction from 1.0 M solution at 30.0ºC.

Initial phase volume (ml)		Equilibrium phase volume (ml)		5 g $(NH_4)_2SO_4$	
Aqueous	1-Butanol	Aqueous	1-Butanol	D	%E
10	10	8.78	11.20	1.67	63.29
10	15	8.75	16.45	1.96	66.67
10	20	8.15	21.60	2.52	73.22
10	30	7.20	32.45	4.60	83.35

Initial phase volume (ml)		Equilibrium phase volume (ml)		0 g $(NH_4)_2SO_4^{5}$	
Aqueous	1-Butanol	Aqueous	1-Butanol	D	%E
10	10	9.0	11.0	1.03	51.01
10	20	6.4	23.1	3.29	77.13
10	30	4.0	35.6	7.87	88.92
10	40	1.3	48.5	30.82	96.97

a substantial fraction of aqueous phase was incorporated into the organic phase after extraction. This led to the larger volume of the organic phase and the reduced volume of the aqueous phase. This was due to the partially miscible nature between the two solvents with the solubility of water in 1-butanol higher than the solubility of 1-butanol in water as earlier described. The problem was more pronounced in the process with higher initial phase volume ratio. Although the values of the distribution coefficient and degree of lactic acid extraction appeared to be higher in extraction without salt, it was merely because the bulk aqueous phase containing lactic acid and, in case of extraction of the acid from the fermentation broth, other impurities, was conveyed into the organic phase. This is not a practical approach for extraction since high water content in the organic phase after extraction could complicate the purification processes following the extraction and obstruct the solvent recovery and recycle. The phase incorporation, consequently, makes it not feasible to enhance lactic acid recovery by performing the extraction at a high 1-butanol-to-aqueous phase volume ratio.

The presence of $(NH_4)_2SO_4$ in water-1-butanol-lactic acid system appeared to lessen the problem of organic and aqueous phase incorporation. As shown in Table 3 for extraction with 5 g of $(NH_4)_2SO_4$ and increase the initial phase volume ratio from 1:1 to 3:1, volume of the aqueous phase was slightly reduced. It is concluded in this study that addition of $(NH_4)_2SO_4$ advantageously allowed the extraction of lactic acid with 1-butanol to be carried out at a high organic-to-aqueous phase volume ratio, where large recovery of the acid was achieved.

In an attempt to further improve the extraction of lactic acid in mixed solvent electrolyte system containing water, 1-butanol and $(NH_4)_2SO_4$, successive extraction of lactic acid was performed using 3 consecutive extraction stages was performed. The concentration of lactic acid in the starting aqueous solution was 1 M, and the quantity of $(NH_4)_2SO_4$ in the system was 5 g The result is shown in Table 4. The total lactic acid extraction of 94.92% was achieved in the successive extraction, which was approximately 11.6% higher than that obtained in the single batch process. This suggests that, in order to improve lactic acid recovery, the extraction should be operated in the succesive mode rather than the batch one.

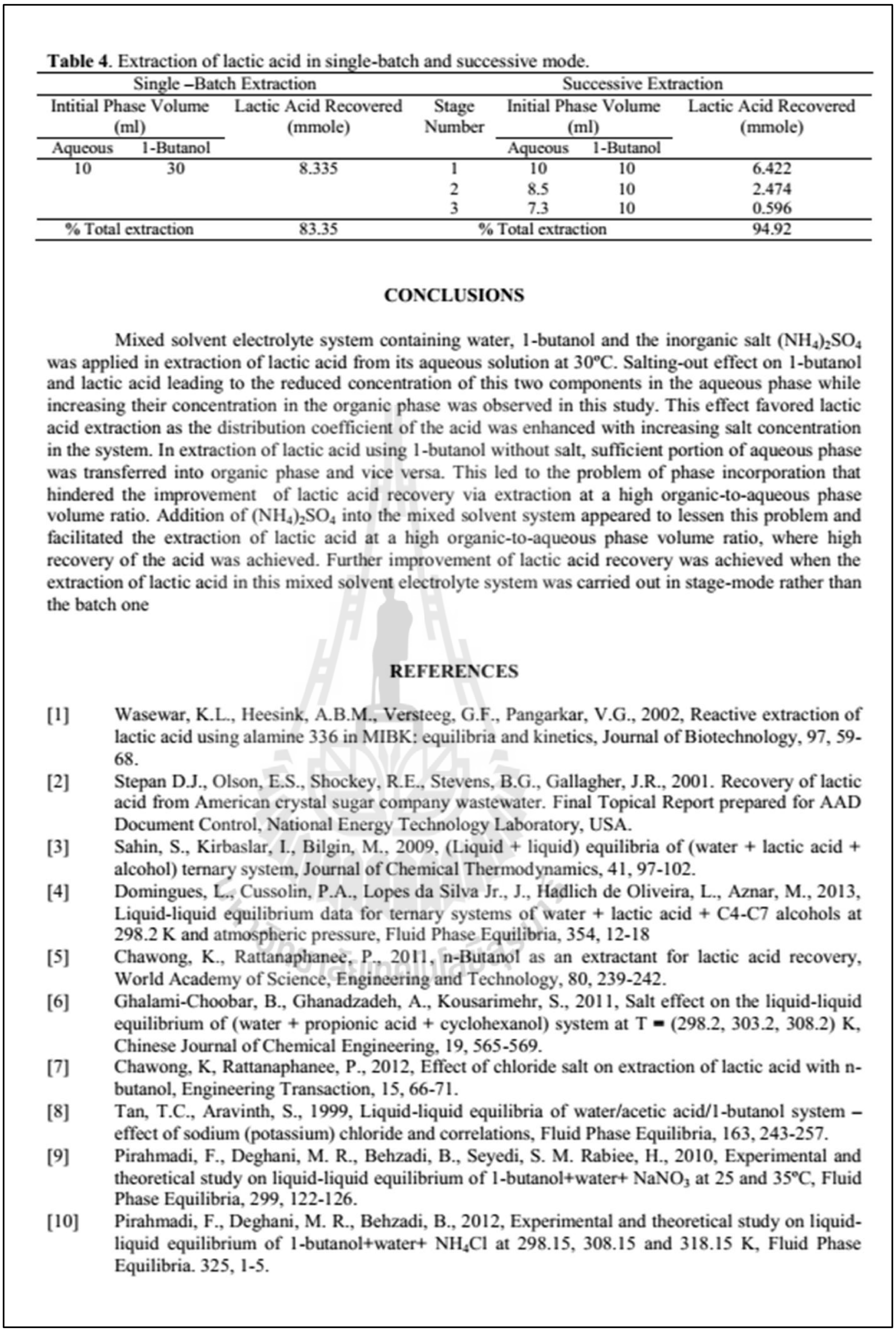


Table 4. Extraction of lactic acid in single-batch and successive mode.

Single –Batch Extraction			Successive Extraction			
Intitial Phase Volume (ml)		Lactic Acid Recovered (mmole)	Stage Number	Initial Phase Volume (ml)		Lactic Acid Recovered (mmole)
Aqueous	1-Butanol			Aqueous	1-Butanol	
10	30	8.335	1	10	10	6.422
			2	8.5	10	2.474
			3	7.3	10	0.596
% Total extraction		83.35	% Total extraction			94.92

CONCLUSIONS

Mixed solvent electrolyte system containing water, 1-butanol and the inorganic salt $(NH_4)_2SO_4$ was applied in extraction of lactic acid from its aqueous solution at 30°C. Salting-out effect on 1-butanol and lactic acid leading to the reduced concentration of this two components in the aqueous phase while increasing their concentration in the organic phase was observed in this study. This effect favored lactic acid extraction as the distribution coefficient of the acid was enhanced with increasing salt concentration in the system. In extraction of lactic acid using 1-butanol without salt, sufficient portion of aqueous phase was transferred into organic phase and vice versa. This led to the problem of phase incorporation that hindered the improvement of lactic acid recovery via extraction at a high organic-to-aqueous phase volume ratio. Addition of $(NH_4)_2SO_4$ into the mixed solvent system appeared to lessen this problem and facilitated the extraction of lactic acid at a high organic-to-aqueous phase volume ratio, where high recovery of the acid was achieved. Further improvement of lactic acid recovery was achieved when the extraction of lactic acid in this mixed solvent electrolyte system was carried out in stage-mode rather than the batch one

REFERENCES

[1] Wasewar, K.L., Heesink, A.B.M., Versteeg, G.F., Pangarkar, V.G., 2002, Reactive extraction of lactic acid using alamine 336 in MIBK: equilibria and kinetics, Journal of Biotechnology, 97, 59-68.

[2] Stepan D.J., Olson, E.S., Shockey, R.E., Stevens, B.G., Gallagher, J.R., 2001. Recovery of lactic acid from American crystal sugar company wastewater. Final Topical Report prepared for AAD Document Control, National Energy Technology Laboratory, USA.

[3] Sahin, S., Kirbaslar, I., Bilgin, M., 2009, (Liquid + liquid) equilibria of (water + lactic acid + alcohol) ternary system, Journal of Chemical Thermodynamics, 41, 97-102.

[4] Domingues, L., Cussolin, P.A., Lopes da Silva Jr., J., Hadlich de Oliveira, L., Aznar, M., 2013, Liquid-liquid equilibrium data for ternary systems of water + lactic acid + C4-C7 alcohols at 298.2 K and atmospheric pressure, Fluid Phase Equilibria, 354, 12-18

[5] Chawong, K., Rattanaphanee, P., 2011, n-Butanol as an extractant for lactic acid recovery, World Academy of Science, Engineering and Technology, 80, 239-242.

[6] Ghalami-Choobar, B., Ghanadzadeh, A., Kousarimehr, S., 2011, Salt effect on the liquid-liquid equilibrium of (water + propionic acid + cyclohexanol) system at T = (298.2, 303.2, 308.2) K, Chinese Journal of Chemical Engineering, 19, 565-569.

[7] Chawong, K, Rattanaphanee, P., 2012, Effect of chloride salt on extraction of lactic acid with n-butanol, Engineering Transaction, 15, 66-71.

[8] Tan, T.C., Aravinth, S., 1999, Liquid-liquid equilibria of water/acetic acid/1-butanol system – effect of sodium (potassium) chloride and correlations, Fluid Phase Equilibria, 163, 243-257.

[9] Pirahmadi, F., Deghani, M. R., Behzadi, B., Seyedi, S. M. Rabiee, H., 2010, Experimental and theoretical study on liquid-liquid equilibrium of 1-butanol+water+ $NaNO_3$ at 25 and 35°C, Fluid Phase Equilibria, 299, 122-126.

[10] Pirahmadi, F., Deghani, M. R., Behzadi, B., 2012, Experimental and theoretical study on liquid-liquid equilibrium of 1-butanol+water+ NH_4Cl at 298.15, 308.15 and 318.15 K, Fluid Phase Equilibria. 325, 1-5.

BIOGRAPHY

Miss Kanungnit Chawong was born on August 20, 1987 in Bangkok, Thailand. She earned her Bachelor's Degree in Chemical Engineering from Suranaree University of Technology (SUT) in 2011. Her senior project was extraction of lactic acid from aqueous solution with n-butanol. She then continued her Master's Degree in Chemical Engineering at School of Chemical Engineering, Institute of Engineering at Suranaree University of Technology under the guidance Asst. Prof. Dr.Panarat Rattanapanee. Her expertise includes the field of Liquid-liquid extraction. During her Master's degree study, she presented one oral presentation entitled of "Effect of Chloride Salt on Extraction of Lactic acid with n-Butanol" in the 22nd Thai Institute of Chemical Engineering and Applied Chemistry Conferrence, Nakhon Ratchasima, Thailand and one poster presentation entitled of "Liquid-liquid equilibrium of 1-butanol + water + $(NH_4)_2SO_4$ and its application in lactic acid extraction" in The Pure and Applied Chemical International Conference 2014, Khon Kaen, Thailand.

มหาวิทยาลัยเทคโนโลยีสุรนารี