IONIC LIQUID BASED AQUEOUS TWO PHASE SYSTEMS

by

Muzakkir Bin Aziz

Dissertation submitted in partial fulfilment of

the requirement for the

Bachelor of Engineering (Hons)

Chemical Engineering

DECEMBER 2011

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

IONIC LIQUID BASED AQUEOUS TWO PHASE SYSTEMS

by

Muzakkir Bin Aziz

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved:

(PROF. THANABALAN MURUGESAN)

Prof. Dr. T. Murugesan
Chemical Engineering Department
Universiti Teknologi PETRONAS

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

DECEMBER 2011

ABSTRACT

Aqueous two phase systems provide an alternative and efficient approach for the extraction, recovery and purification of biomolecules through their partitioning between two liquid aqueous phases. Throughout this project, the ability of hydrophilic ionic liquid to form aqueous two phase systems with aqueous K_3PO_4 solutions will be evaluated. Phase diagrams, tie-lines and tie-lines length will be measured. The studied of ionic liquid have shown more effective in promoting aqueous two phase systems compare to volatile organic solvents. The composition of each ionic liquid and aqueous salt solution will be identified at bottom and top phase at each point respectively. Densities and viscosities of both aqueous phases will also be determined.

ACKNOWLEDGEMENTS

My deepest appreciation goes out to my supervisor, Professor Thanabalan Murugesan for this guidance and assistance throughout the entire duration of Final Year Project I and II. Without him, I would certainly not be able to progress smoothly and complete the project within the time given.

Special thanks go to the course coordinator for their systematic approach and timely arrangement for this project. Genuine gratitude goes to the examiners and evaluators, both internal and external.

Last but not least, I would like to thank my parents for their support and encouragement all through my life.

Thank you,

With Utmost Gratitude,

MUZAKKIR BIN AZIZ

Undergraduates of Chemical Engineering Faculty,

Universiti Teknologi PETRONAS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 CHAPTER 1: INTRODUCTION

1.1 PROJECT BACKGROUND

Aqueous two phase systems, introduced in 1956 Albertesson, [1] have been recognized as an economical and efficient downstream processing method. An aqueous two phase system usually composed of two or more polymers, a polymer and a salt where it is considered to be environmentally friendly because there is no use of traditional volatile organic solvents in the process.

Aqueous two phase systems have been widely used in the separation, concentration and fractionation of biological solutes and particles such as cells and proteins. It also has been studied for application including the selective distribution and separation of metal ion species, nano and microsolid particulates and as green reaction media. In recent years, room temperature ionic liquids, as a class of potential green solvent have found wide application in chemistry and biochemistry including chemical synthesis, biocatalytic transformation, electrochemical device design, and analytical and separation process. A new type of aqueous two phase system need to be investigated more.

A new type aqueous two phase system [2] replace polymer with ionic liquid have been successfully has been investigated since Gutowski and co workers demonstrated that the addition of potassium phosphate to an aqueous solution of a hydrophilic ionic liquid produces aqueous two phase system. Water-immiscible organic solvents have long been commonly used in industrial applications. Nevertheless, environmental concerns about the use of volatile organic has increased in the past few years, and there is an emergent interest for the development of "green" solvents for separation processes. In the context, ionic liquid have appeared as possible nonhazardous candidates. Their particular characteristics, including high salvation abilities and coordination properties, general inflammability, high thermal and chemical stabilites and negligible vapour pressures, make them suitable candidates for a large range of industrial and biotechnologyical applications. Moreover, the possibility of controlling their inherent physicochemical properties by a wise combination of the cation and anion make possible the manipulation of the extraction phase properties for enhanced yield of product recovery. In addition, ionic liquid based aqueous system offer the opportunity to combine the purification process of active biocatalysts with the improved performance of some enzymes in the presence of ionic media.

This new aqueous two phase system has been successfully [2] used to separate testosterone, epitestosteron, opium alkaloids, and bovine serum albumin. The ionic liquid two phase system also have been demonstrated for extraction of antibiotics such as penicillin G, amoxicillin and ampicillin.

1.2 PROBLEM STATEMENT

Liquid-liquid extractions that involve environmentally benign phase forming polymers in aqueous solution have gained increased importance of late, due to their ability to replace the conventional volatile organic solvents, which are a major source of environmental pollution. They can be classified as:

1. Cloud point extraction (CPE)
2. Aqueous two phase extraction (ATPE)
3. Reverse micellar extraction (RME)
4. Extraction using thermo-separating polymer

A new type of aqueous two phase system based on ionic liquid has been investigated and successfully used to separate several compounds including proteins and antibiotics. It is important to design ionic liquid aqueous two phase system for separation and concentration using the phase diagram.

The behaviour of two phase system based ionic liquid is determined throughout this project. The concentration of ionic liquid and inorganic salt solution at bottom phase and top phase are identified. Nevertheless, there are several factors [1] that affect the nature of aqueous two phase system including:

1. The nature and concentration of the polymer.
   These include molecular weight and hydrophobicity of the polymer and its concentration. Experiments have shown that the higher the molecular weight of the ionic liquid, the lower the concentration required for phase separation, the larger the difference in the molecular size between the two phases forms components, the more asymmetrical is the binodial. Also, the higher the

hydrophobic difference between two phases forms components, the higher is the tendency towards phase formation.

2. Temperature.

   Ionic liquid-inorganic salt aqueous phase systems separate into individual phases at relatively higher ionic compound concentration at lower temperatures. Polymer-polymer systems behave in the opposite way which requiring a higher polymer concentration for phase separation at lower temperature.
3. Salt type and concentration. Due Zaslaysky (1995), type of salt and its concentration are reported to have a considerable effect on the phase system.

1.3 OBJECTIVE

The objectives of the project are:

1. To study the behaviour of addition of inorganic salts to aqueous solutions of ionic liquids.
2. To assess the composition of ionic liquid and inorganic salt at top and bottom phase of aqueous two phase system.

1.4 SCOPE OF WORK

The scope of work for the project has been divided into three categories as below:

1. Determine bimodal curves of the compound using cloud point method. Bimodal curve is determined in order to get the composition of the mixture for each point on the two phase system diagram.
2. Determine tie lines at phase diagram. Tie lines are determined by gravimetric method originally proposed by Merchuck. Tie line length is verified as to identify the concentration of ionic liquid and salt concentration at top and bottom phases.

The phase diagram provides information about the concentration of phase-forming components required to form two phases, the concentration of phase components in the top and bottom phases and the ratio of phase volumes.

2.0 CHAPTER 2: LITERATURE REVIEW

2.1 AQUEOUS TWO PHASE EXTRACTION

Aqueous two phase extraction which is a special cased of liquid-liquid extraction involves transfer of solute from one aqueous phase to another. The two immiscible aqueous phases are generated by addition of substances such as polymers and salts to an aqueous solution. For this project, the polymer will be replaced with ionic liquid. However, there are three types of aqueous two phase systems are commonly used [3]:

1. Polymer-polymer two phase system
2. Polymer-salt two phase system
3. Salt-salt two phase system

A polymer-polymer two phase system can for instance be obtained by mixing Dextran and PEG [2] at a certain composition. By adding specific amounts of these polymers to an aqueous feed phase which contains the solute, two aqueous phases, one rich in PEG and the other rich in dextran can be obtained. Aqueous two-phase systems can also be generated using polymers and a salt such as sodium or potassium phosphate. Aqueous two phase separations take place at certain composition only.

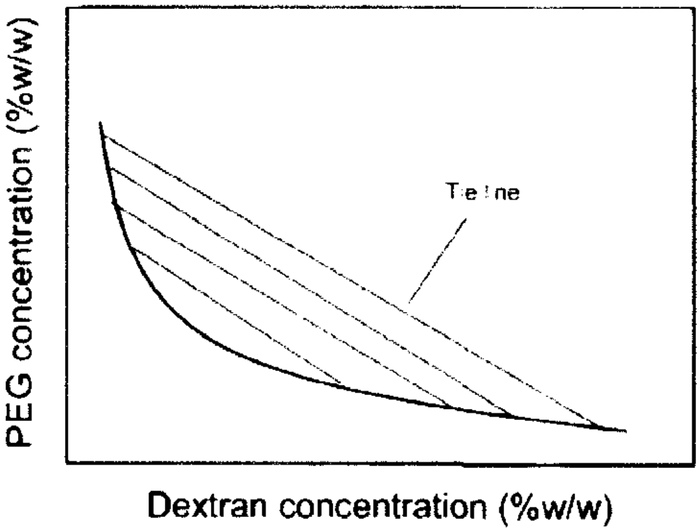


Figure 2.1: Phase diagram for aqueous two phase system.

Figure 2.1 shows a PEG-Dextran phase diagram where a solubility curve separates the two phase region (above the curve) from the single phase region (below the curve). Such binary phase diagrams which are based on the composition of the two polymers (or polymer and salt) only are used for determining the concentrations needed for an extraction process. These phase diagrams also predict the polymer or salt content of the raffinate and the extract phases. The composition of the individual phases generated can be obtained using tie-lines as shown in the figure.

The partition of a solute between the two aqueous phases depends on its physicochemical properties as well as those of the two polymers (or ionic liquid and salt). The partition coefficient of a biological macromolecule in an aqueous two phase system formed by two polymers A and B can be determined using equations of the form shown below [5]:

$$\ln K = a_A(C_{A1}-C_{A2})+a_B(C_{B2}-C_{B1})+b \qquad (1)$$

Where

K = partition coefficient (-)

a_A = association constant for the macromolecule and polymer A

a_B = association constant for the macromolecule and polymer B

b = system constant

C_{A1} = polymer A concentration in extract (kg/m^3)

C_{A2} = polymer A concentration in raffinate (kg/m^3)

C_{B1} = polymer B concentration in extract (kg/m^3)

C_{B2} = polymer B concentration in raffinate (kg/m^3)

In PEG/dextran aqueous two phase extraction of proteins, the partition behaviour depends to a great extent on the relative polymer composition. It also depends on the solution pH and the molecular weight of the protein. Generally speaking, protein partitioning into the PEG rich phase is favoured. When a polymer-salt is used to generate the aqueous two phase system, a protein favourably into the polymer rich phase.

2.2 ADDITION OF INORGANIC SALTS TO AQUEOUS SOLUTIONS OF IONIC LIQUIDS

Aqueous two phase systems are usually formed by polymer-polymer, polymer-salt and salt-salt combinations in an aqueous solution. Nevertheless, in the past few years, Gutowski demonstrated that the addition of inorganic salts to aqueous solutions of ionic liquids can cause liquid-liquid demixing and induce aqueous two phase system. In addition, Abraham showed that both aqueous solutions of ionic liquids and aqueous two phase system might be regarded as novel liquid partitioning systems. As a result, ionic liquid can be virtually used as replacement of the polymeric-rich phase in typical aqueous two phase system. Ionic liquid, salts that are liquid below the temperature of 373K, were originally suggested as alternative solvents [4] for the replacement of the noxious volatile organic compounds currently used in industrial processes. Ionic liquid present extremely low volatility under atmospheric conditions, exhibit good thermal and chemical stability as well as low flammability. These properties that have contributed to their widespread recognition as ambient-friendly media. The valuable properties ionic liquid has improved their use in areas ranging from organic synthesis, catalysis, extraction and separation processes, among others. Moreover, the wide range of potential combinations between cations and anions allows a high degree of tenability of the ionic liquid properties, and thus, ionic liquid can be considered tailor-made compounds for specific tasks.

Research regarding the use of ionic liquid based two phase system has been, so far mostly centred on the influence of several inorganic salts, or in the use of carbohydrates or amino acids, using exclusively imidazolium-based ionic liquid. Therefore in this work, the influence of 1-Butyl-3-methylimidazolium Tetrafluoroborate based ionic liquid in promoting aqueous two phase system maintaining the same inorganic salt (K_3PO_4) will be evaluated.

2.3 DETERMINATION OF PHASE DIAGRAM AND TIE-LINES

Tie-lines were determined by a gravimetric method originally proposed by Merchuck. For the determination of tie-lines, a mixture from the biphasic region was selected, vigorously agitated and allowed to reach the equilibrium, by the separation of both phases, for 12 h and at 298K. After a careful separation step, both top and bottom phases were weighed. Finally, each individual tie-lines was determined by application of the lever rule to the relationship between the top mass phase composition and the overall system composition. The experimental bimodal curves were fitted using equation below:

$$Y = A \exp [(BX^{0.5}) - (CX^{3})] \tag{2}$$

Where Y and X, are respectively, the ionic liquid and salt weight percentages, and A, B and C are constant obtained by regression.

For the tie-lines determination [6] the following system of four equations as below and four unknown values (Y_T, Y_B, X_T and X_B) was solved.

$$Y_T = A \exp [(BX_T^{0.5}) - (CX_T^{3})] \tag{3}$$

$$Y_B = A \exp [(BX_B^{0.5}) - (CX_B^{3})] \tag{4}$$

$$Y_T = (Y_M/\alpha) - ((1-\alpha)/\alpha)Y_B \tag{5}$$

$$X_T = (X_M/\alpha) - ((1-\alpha)/\alpha)X_B \tag{6}$$

Where subscripts M, T and B denote respectively the mixture, the top phase and bottom phase, X is the weight fraction of inorganic salt, Y the weight fraction of ionic liquid and α is the ratio between mass of the top phase and the total mass of the mixture. The system solutions results in the concentration of the ionic liquid and inorganic salt in the top and bottom phases, and thus, tie lines can be simply represented.

For the calculation of the tie-lines length, equation below was used:

$$TLL = \sqrt{(X_T - X_B)^2 - (Y_T - Y_B)^2} \tag{7}$$

Where subscripts T and B denote respectively the top and bottom phases, and X and Y are the weight fraction of inorganic salt and ionic liquids, respectively. It should be pointed out that the top phase is the ionic liquid rich phase, while the bottom phase is the salt rich phase.

2.4 ABILITY OF IONIC LIQUID FOR PHASE SEPERATION

2.4.1 Phase Diagram

The experimental phase diagram for several ionic liquids and salt, (K_3PO_4) at 298K and atmospheric pressure are presented in figure below [6]. All data are presented in molality units for a more detailed understanding of the ionic liquid aptitude for aqueous two phase system formation. These results also show for a deeper inspection of the cation influence in promoting aqueous two phase system.

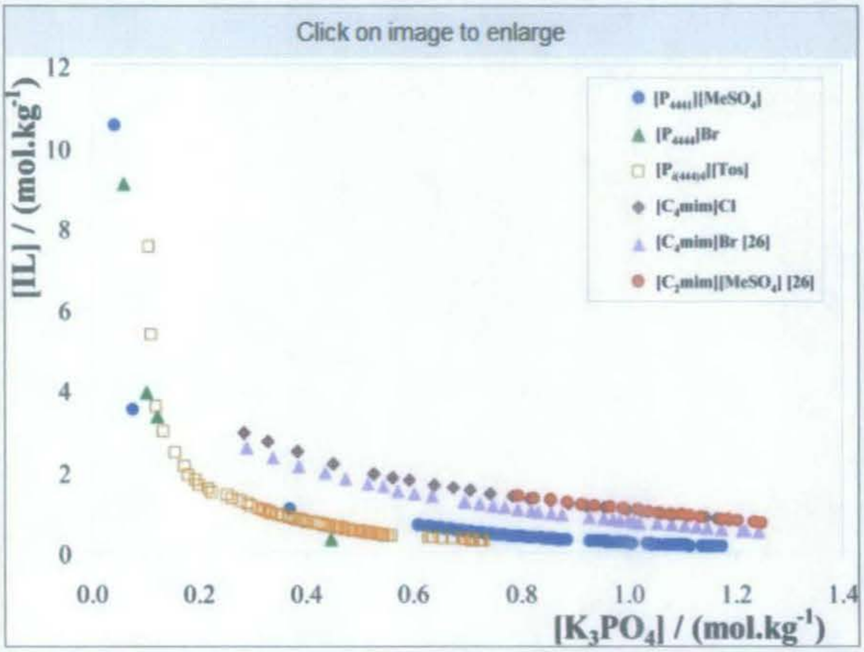


Figure 2.2: Binodal curve with difference salt.

The studied phosphonium-based ionic liquid display a greater ability for aqueous two phase system formation than imidazolium-based ionic liquid when evaluating both classes with similar anions. The higher the affinity for water and hydrophilic nature of the ionic liquid, the less effective is the ionic liquid in prmoting phase separation. Therefore, the studied phosphonium-based ionic liquid present lower affinity for water, and are thus more hydrophobic than imidazolium-based ionic liquid. The quaternary phosphonium cations present four alkyl chains and no aromatic character, which is result for their lower affinity for aqueous phases. Their water miscibility essentially derives from the polar water hydrogen bonding to the anions.

Due to the figure 2.2, the ability of the aionic liquid for phase separation can be described by the following order:

$[P_{4444}]Br > [P_{i(444)4}][Tos] > [P_{4441}][MeSO_4]$.

Thus, at such an ionic liquid concentration, $[P_{4444}]Br$ has the higher ability to induce phase separation in ionic liquid with additional of salt K_3PO_4 system. Indeed this ionic liquid is the one with four straight butyl chains enhancing therefore the aqueous two phase system formation ability. On the other hand, $[P_{4441}][MeSO_4]$ presents a shorter alkyl chain coupled to a salting-out inducing anion that consequently decreases the miscibility region of the ternary phase system which including water inside the system. In addition, the aromatic ring in $[P_{i(444)4}][Tos]$ is certainly the main responsible for its enhanced water affinity when compared to $[P_{4444}]Br$. The result presented in figure above show that, in general $[P_{4441}][MeSO_4]$ is the strongest salting-out inducing phosphonium-based ionic liquid studied while $[P_{4444}]Br$ is the strongest salting-in inducing ionic liquid.

2.4.2 Tie-Lines

From phase diagram result [6], it is observed that the empirical equation correlates satisfactorily with the experimental data for the $[P_{i(444)4}]$[Tos, water and salt (K_3PO_4) system.

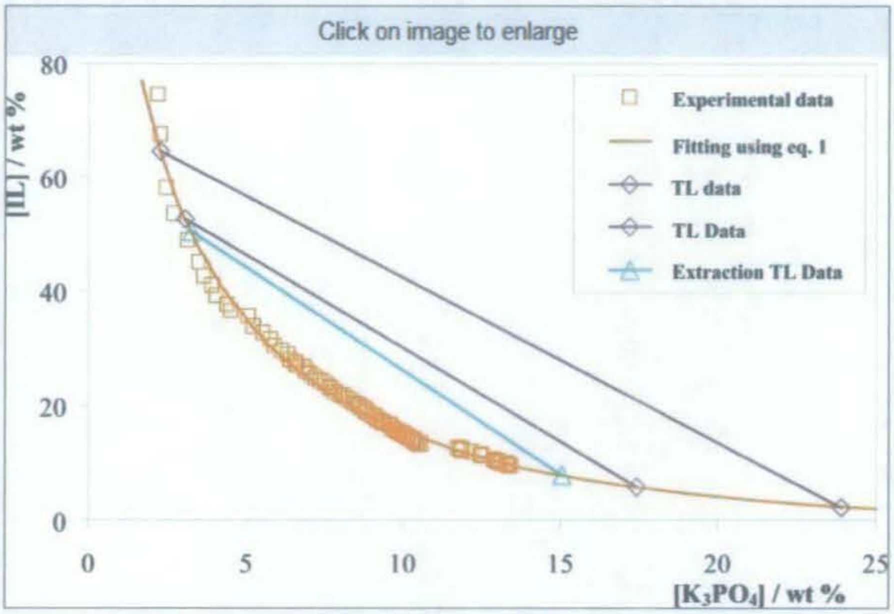


Figure 2.3: Tie lines

As an example, the results obtained for [$P_{i(444)4}$][Tos, water and salt (K_3PO_4) system are showed as figure 2.3. Since the tie line length represents the difference between the ionic liquid and inorganic salt concentrations in the top and bottom phases, the higher the tie line length, the higher is the ionic liquid concentration in the top phase and the salt concentration at the bottom phase.

2.4.3 Density and Viscosity

As for wide range of processes, the properties like density and viscosity need to be evaluated in order to identify the behaviour of composition of phase forming systems. Therefore, density and viscosity measurements were performed on both the top and bottom phases for selected mass fraction composition at the biphasic region. [6]

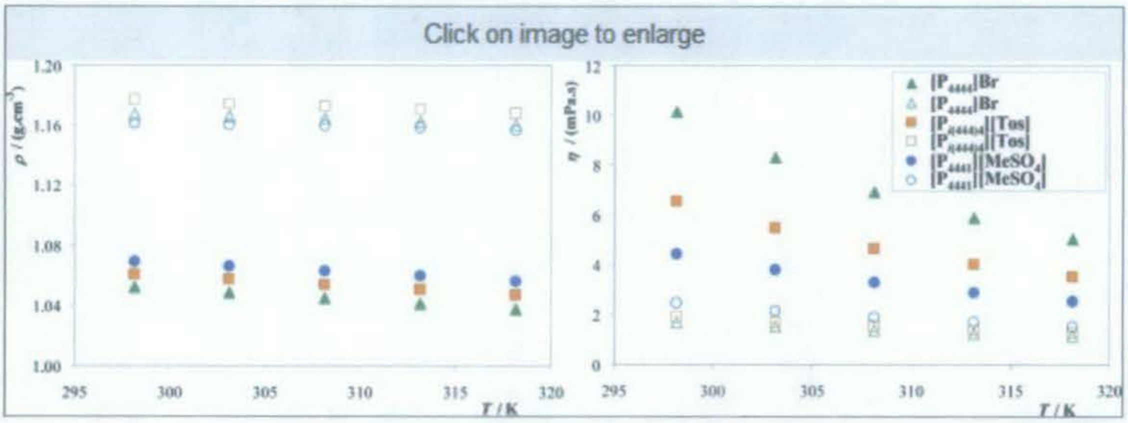


Figure 2.4: Experimental density and viscosity.

Both density and viscosity for ionic liquid and inorganic salt rich phases are found to decrease as the temperature decreased. From the results depicted in figure 2.4, no significant differences in density values between ionic liquid based aqueous two phase system and typical polymer-inorganic salt aqueous two phase system are observed. Similarly, the bottom phase is the inorganic salt-rich phase while the top phase is the polymer or ionic liquid rich phase, with density values ranging from 1.0 to 1.2 g.cm^{-3}.

However, larger differences are observed in viscosity values between ionic liquid based and polymer based aqueous two phase system. Ionic liquid rich phases are far less viscous (4-11 Mpa.s) than typical PEG-rich phases (39 MPa.s) at mass fraction compositions close to those measured in this work. Therefore, since ionic liquid based aqueous two phase systems are less viscous it constitutes a major advantage for the mass transfer process between the phases and phase handling. The lower the viscosity of ionic liquid based aqueous two phase system compared with polymer based aqueous two phase system is thus very important from an industrial point of view.

The density of the inorganic salt-rich phase is higher than the corresponding equilibrated ionic liquid rich phase. $[P_{4441}][MeSO_4$ is the ionic liquid studied with smaller differences in density values among both phases. The density differences among phases generally increase with the increase of the tie line length since larger differences in the mixture composition are occurring. Indeed for $[P_{4441}][MeSO_4$ the tie lines length, at the mixture composition selected, is the shorter one. On the other hand, viscosities of the ionic liquid rich phase, and at the mass fraction compositions evaluated, decrease in the rank:

$[P_{4444}]Br > [P_{i(444)4}][Tos] > [P_{4441}][MeSO_4]$

Nevertheless, the opposite order is verified for the inorganic salt rich phases. Both differences in viscosities and densities at the K_3PO_4 rich phase indicate that there is some ionic liquid migration for this phase contributing for these deviations. However, differences among the inorganic salt-rich phases are significantly smaller than differences between distinct ionic liquid rich phases.

2.4.4 Effect of Temperature on Binodal Curves

For the $[Bmim]BF_4 + Na_3C_6H_5O_7$ + water aqueous two phase systems [9], the effect of temperature on the equilibrium phase composition for investigated systems is showed in fugure 2.5 for the temperature, T = (298.15, 308.15, and 323.15) K:

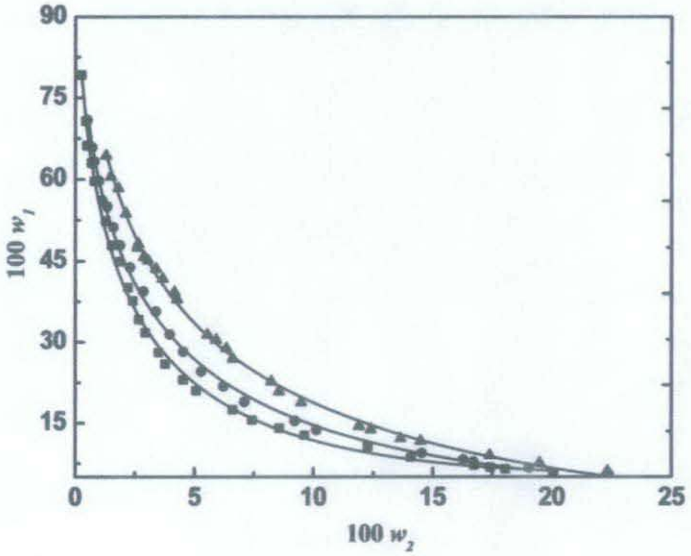


Figure 2.5: Binodal curve with difference temperature: ■, 298.15 K; ○, 308.15; ▲ , 323.15 K

The locus for the experimental binodals demonstrates that the two phase area is expanded with a decrease in temperature, which attribute to the decrease in solubility of ionic liquid or the increase in the phase forming ability in studied system. The reason is the effect of a decrease in temperature on the structure of water is quantitively similar to that structure making ion and therefore can promote the phase forming ability in the investigated system as a favourable factor for salting-out of ionic liquid.

2.4.5 Effect of Temperature on Tie Lines.

For the [Bmim]BF_4 + $Na_3C_6H_5O_7$ + water aqueous two phase systems [9], the effect of temperature on the equilibrium phase composition for investigated systems is showed as below for the temperature, T = (298.15, 308.15, and 323.15) K:

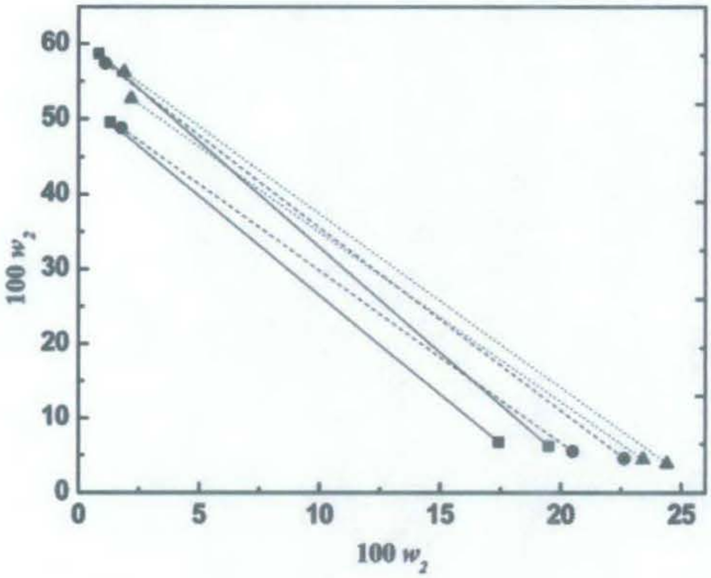


Figure 2.6: Tie lines with difference temperature: ■, 298.15 K; ○, 305.15 K ▲, 323.15 K

In figure 2.6, it was found than the slopes of the tie lines slightly decrease with an increase in temperature. This trend means that when the temperature is decreased, water is driven from the [Bmim]BF_4 rich phase to the salt rich phase, so the [Bmim]BF_4 concentration at the [Bmim]BF_4 rich phase increases, whereas the salt rich phase will be somewhat more diluted. In other words, water becames a poorer solvent for [Bmim]BF_4 as the temperature decreased.

Thus, throughout the experiment, the temperature needs to be controlled as constant as to avoid error to the values of bimodal curve data. The system must be conducted within thermostated bath as to make sure the temperature is constant throughout the experiment is conducted.

2.5 SALTING-OUT EFFECT IN AQUEOUS SOLUTIONS OF IONIC LIQUIDS AND AQUEOUS SALT.

The phenomenon of inorganic salt precipitation associated with aqueous two phase systems was previously reported [12] in studies involving the hydrophilic ionic liquid [C_4mim][Cl] and the inorganic salt K_3PO_4. Throughout the research, inorganic salt precipitation is present in the (K_3PO_4 + [C_4mim]Cl + H_2O) sytem and ubiquitously in the (K_3PO_4 + [C_4mim][$MeOSO_3$] + H_2O) system.

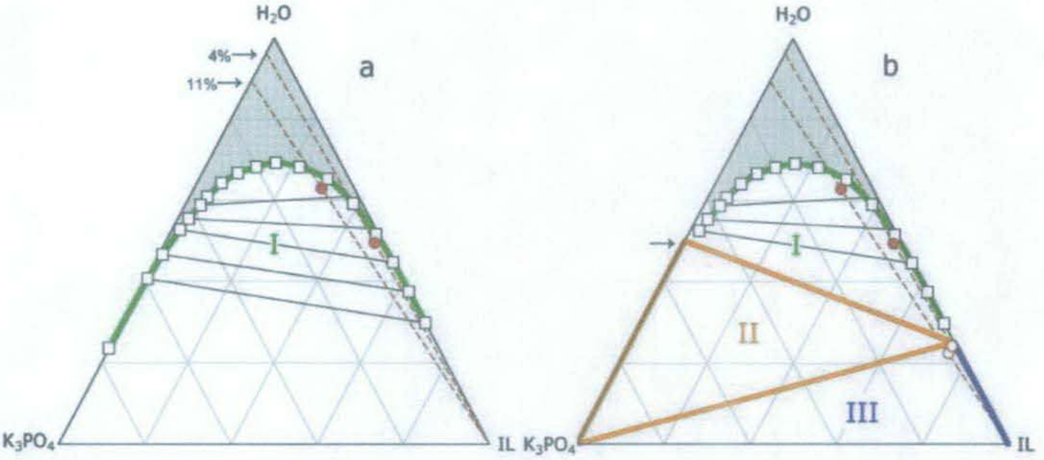


Figure 2.7: Ternary diagram of (K_3PO_4 + [C_4mim]Cl + H_2O) system

Note that the fair symmetry of the diagram indicates that the salting out effect corresponds to a mutual exclusion of the two salts, the inorganic salt and ionic liquid as they compete for being solvated by water molecules. Ionic liquids with non-bulky ions significantly inherited a good portion of what makes common inorganic salts different from other compounds.

Due to figure 2.7, the three-phase region (II) bounded by the orange triangle simply acknowledges the fact that although the K_3PO_4 is extremely soluble in water but there is a solubility limit where one cannot move down indefinitely on the left side of triangles without reaching a point where water becomes saturated in K_3PO_4 and the salt starts to precipitate. The arrow in Figure 2.7 indicates the approximate position of the solubility limit at 298K. The point identified by the arrow and the one corresponding to solid K_3PO_4 define two of the orange triangle tips.

The other fact is that when more ionic liquid is added to the aqueous two phase system where it moving further down the dashed line eventually one starts to see the precipitation of K_3PO_4. This means that one has entered a three-phase region and the compositions of each phase become fixed. The three phases in presence (liquid-liquid-solid equilibrium) are a saturated K_3PO_4 aqueous solution, solid K_3PO_4 and an ionic liquid-rich aqueous solution.

If more ionic liquid is added to the system then the amount of K_3PO_4 rich aqueous solution starts to diminish until it disappears. This means that the system exhibits again only two phases (liquid-solid equilibrium) which consist of precipitated K_3PO_4 and an ionic liquid-rich aqueous solution (region III).

The fluid phase behaviour of the other studied (inorganic salt + ionic liquid + water) systems can now be discussed in terms of the relative positions of regions I which is aqueous two phase system, region II which is liquid-liquid-solid systems and region III which is liquid-solid systems.

CHAPTER 3: METHODOLOGY

3.1 CHEMICAL AND TOOLS

Tables below show chemicals and tools involved throughout the project:

Table 3.1: Tools involved.

No	Tools	Purpose
1	Thermostated Bath	To control temperature of the systems
2	Stirrer	To mix the liquids
3	Thermometer	To measure the temperature
4	Buret	Titration process for separation of two phase
5	Rotational viscometer-densimeter	To measure the viscosity and density of the mixture
6	Vessel	Medium for the process take place

Table 3.2: Chemicals involved

No	Chemicals	Purpose
1	1-Butyl-3-methylimidazolium Chloride	As a medium for ionic liquid
2	Sodium Hydroxide	As a medium for inorganic salt
3	Ultrapure water	To get a clear one-phase system during separation of two phases.

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Overall Procedure

Flow chart below is the overall procedures for the project:

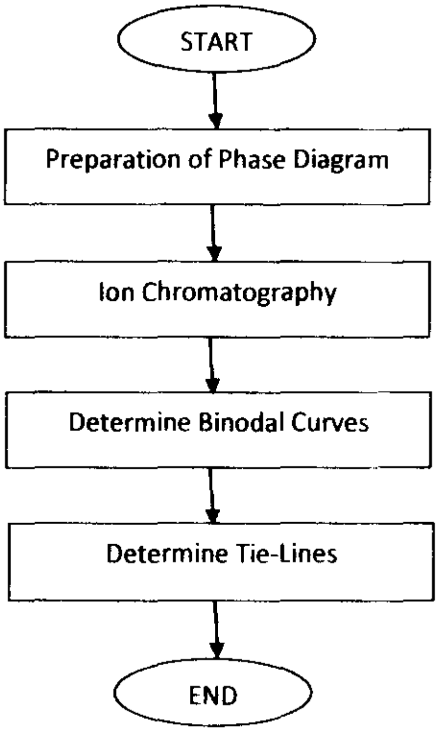


Figure 3.1: Flow Chart for Overall Procedure

3.2.2 Preparation of Phase Diagram

Phase diagram for two phase aqueous system is conducted by using cloud point method. The procedures are showed as below:

Cloud Point method [8]

1. Put 10 g ionic liquid, [C_4mim]Cl solution of 50% into a vessel.
2. Immersed the vessel in a jacketed vessel.
3. Measure the temperature of the system.
4. Add a salt solution of sodium hydroxide 40% dropwise to the vessel until the mixture become turbid or cloudy.
5. Add water dropwise to the vessel to get a clear oone-phase system.

6. The system compositions are determined by the weight quantitification of all components added.

Binodal curve is the plotted due to data collected after weight quantification.

3.2.3 Tie-Line Procedure

Tie-lines for two phase aqueous system is determined by using gravimetric method. The procedures are showed as below:

Gravimetric method [8]

1. Mix 10 g amounts of [C_4mim]Cl with 10 g amounts of sodium hydroxide 40% aqueous solution.
2. Stir the system vigorously for at least 1 hour.
3. Wait till the system reaches equilibrium for at least 12h and at constant temperature (298.15K).
4. Separate both phases using small ampoules via titration process.
5. Determine the concentration of ionic liquid at both phases using Ionic Chromatography.

Each individual tie-lines are determined by application of the lever rule to the relationship between the top mass phase composition and the overall system composition. Tie-lines length is determined using equation (7)

3.3 KEY MILESTONE AND GANTT CHART

3.3.1 Final Year Project I

Table 3.3: Gantt Chart for FYPI

No	Activities/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	🟦	🟦												
2	Preliminary Research Work		🟦	🟦	🟦	🟦									
3	Submission of Extended Proposal Defence						🟨								
4	Proposal Defence								🟦	🟦					
5	Project work continue										🟦	🟦	🟦		
6	Submission of Interim Draft Report													🟨	
7	Submission of Interim Report														🟨

🟨 Key Milestone 🟦 Process

3.3.1 Final Year Project II

Table 3.4: Gantt Chart for FYPII

No	Activities/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues	🟦	🟦	🟦	🟦	🟦	🟦	🟦								
2	Progress Report Submission								🟨							
3	Project Work Continues								🟦	🟦	🟦	🟦	🟦			
4	Pre-EDX											🟨				
5	Draft Report Submission												🟨			
6	Dissertation Submission													🟨		
7	Submission of Technical Paper													🟨		
8	Oral Presentation														🟨	
9	Project Dissertation Submission															🟨

🟨 Key Milestone 🟦 Process

CHAPTER 4: RESULT AND DISCUSSION

4.1 DETERMINATION OF TWO PHASE SYSTEMS

The addition of inorganic salts to ionic aqueous systems could lead to ion exchange or ions pairing between the salts present in both aqueous-rich phases. Thus, the ionic liquid itself need to carefully select in order to sufficiently salt out the sodium hydroxide to allow aqueous two phase systems formation.

For first trial, sodium carbonate is used as inorganic salt throughout the experiment. The result indicates that the ionic liquid used, 1-butyl-3-methylimidazolium chloride, the three-phase systems produced which consist of liquid-liquid-solid phases. The inorganic salt used is extremely soluble in water which there is a solubility limit. Sodium carbonate has low solubility in water at 20C. Thus, by adding the aqueous salt with ionic liquid will form three phase systems where salt of sodium carbonate formed in solid form.

For second trial, sodium hydroxide is used replacing sodium carbonate due to higher solubility in water. As the aqueous salt and inorganic salt mix, two phase systems formed. It shows that the ionic liquid is sufficiently salted out by inorganic salt which lead to two phase systems formation.

Besides that, it appears that aqueous two phase systems can be formed with ionic liquid only by adding appropriate amount of alkali or alkaline salts, such as KOH, NaOH, or K_3PO_4 whereas acidic or neutral salts, such as KH2PO4, $(NH_4)_2SO_4$, NaCl or KCl did not create biphasic system.

The result by adding sodium hydroxide with 1-butyl-3-methylimidazolium chloride has formed two phase systems and further procedure is conducted in order to determine the concentration of ionic liquid at top and bottom phase.

Figure 4.1: Two phase systems after left for 18 hours

4.2 PREPARATION OF PHASE DIAGRAMS

Different concentration of aqueous salt is mixed with constant concentration of ionic liquid. After a careful separation step, both top and bottom phases were separated into different test tubes.

Figure 4.2: Titration method is used to separate top and bottom phase

All the samples of top and bottom phases are tested using ionic chromatography in order to determine the ionic liquid concentration at both phases.

Figure 4.3: Samples with different concentration of aqueous salt

Below is the weight for both top and bottom phases measured at different concentration of aqueous salt solution.

Table 4.1: Experimental data for weight measurement

Ionic liquid (wt%)	Salt (wt%)	Top Phase (g)	Bottom Phase (g)
50	20	9.81	0
50	25	7.15	2.76
50	30	7.03	2.89
50	35	6.51	3.38
50	40	5.01	4.88
50	50	4.63	5.23

The data collected in the table above simplify in the graph below.

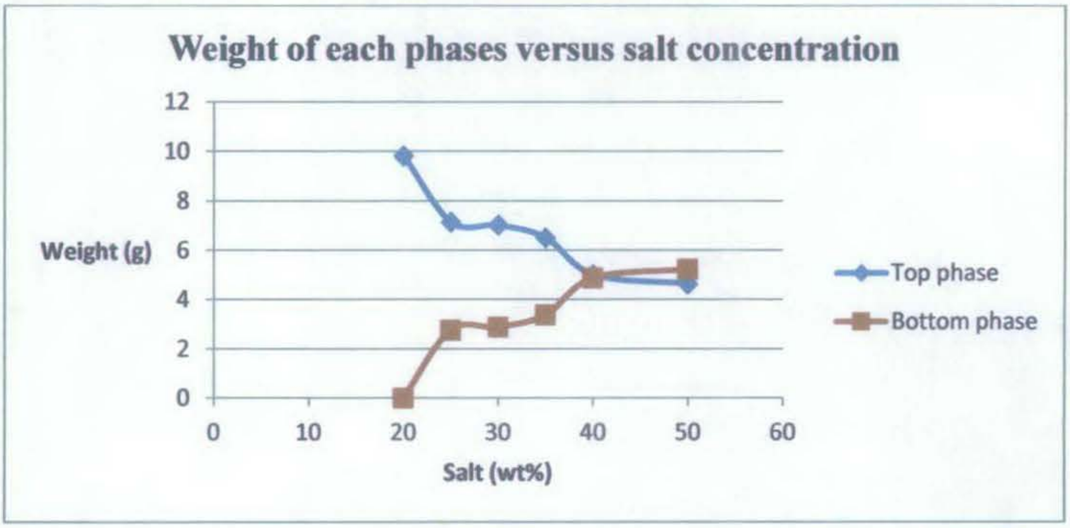


Figure 4.4: Weight of each phase versus salt concentration

The graph above shows that the weight measurement for top and bottom phases. At 20 wt% of sodium hydroxide, there is bottom phase formation as all the feeds are reacted. As the concentration of sodium hydroxide increases, the formation of bottom phase is increasing. Due to literature review that had studied, top phase is ionic liquid-rich phase while bottom phase is salt-rich phase.

For further analysis, the concentration of ionic liquid at top and bottom phase is verified using ion chromatography. Below is the experimental data for ionic liquid concentration for different aqueous salt concentration used.

Table 4.2: Experimental data for ionic liquid concentration

Ionic liquid (wt%)	Salt (wt%)	Top Phase (ppm)	Bottom Phase (ppm)
50	20	0.052	0.000
50	25	0.058	0.118
50	30	0.068	0.128
50	35	3.496	0.547
50	40	6.723	0.623
50	50	9.887	6.452

The data collected in the table above simplify in graph below:

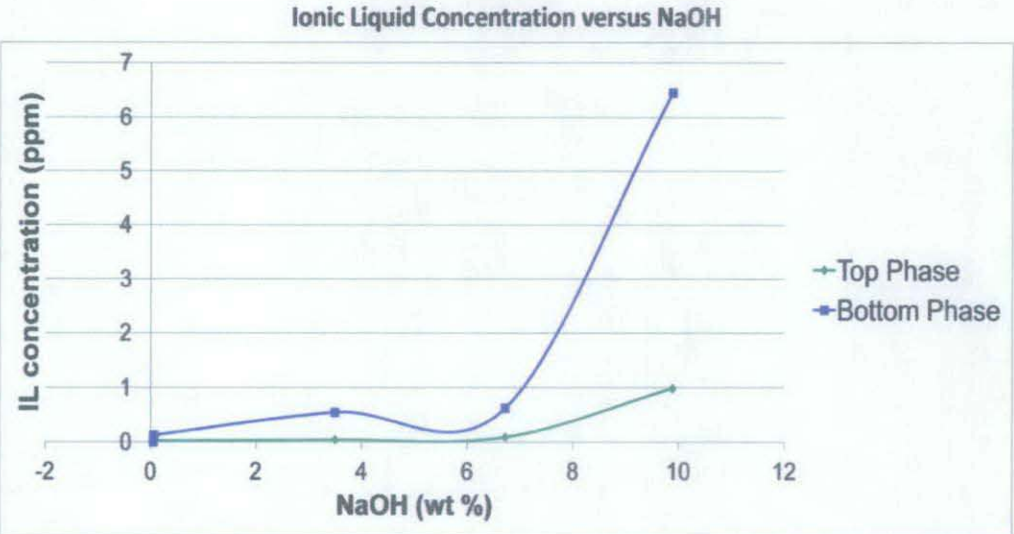


Figure 4.5: Ionic liquid concentration versus different aqueous salt concentration

In a recent work, the project focus on salting-out effects produced by the addition of inorganic salt, sodium hydroxide to aqueous solution of water-miscible ionic liquid, namely 1-butyl-3-methylimidazolium chloride.

From a molecular point of view, salting-out effects can be understood as a delicate balance between the interactions between two solutes and the solvent. Throughout my project, the solutes are the inorganic salt, sodium hydroxide and the ionic liquid while the solvent is water. The salting-out effect corresponds to a mutual exclusion of the two solutes, sodium hydroxide and ionic liquid, they compete for being solvated by water molecules.

The graph shows the concentration of chloride is differed with different concentration of aqueous sodium hydroxide. The chloride concentration at lower concentration of sodium hydroxide is lower as the ionic liquid is sufficiently salted out by the addition of sodium hydroxide. While as the concentration increases, the salting-out effect become the limitation where the water molecules itself is the limitation. Thus the ionic liquid is not sufficiently salted out by the addition of sodium hydroxide which leads to excessive of ionic liquid concentration at higher concentration of sodium hydroxide. Thus, concentration of ionic liquid is higher at higher salt concentration.

From the graph also shows that the concentration of ionic liquid at top phase is higher that bottom phase as based on theoretically, top phase is ionic liquid-rich phase while bottom phase is salt-rich phases.

Therefore, the addition of inorganic salts to ionic aqueous systems leads to ion exchange or ion pairing between the salt presents in both rich phases. the results show that salting out effects produced by the addition of inorganic salt to aqueous solutions of ionic liquid can produce two phase systems. No precipitation of sodium hydroxide was observed in any of the studied solution.

Based on data collected, phase diagram for 1-butyl-3-methylimidazolium chloride, [C_4mim]Cl, sodium hydroxide and water system can be made.

4.3 DETERMINATION OF TIE LINES

The concentration of sodium hydroxide also identified at top and bottom phases. In order to determine tie line length of the system, both concentration of ionic liquid and aqueous salt solution need to be identified as due to the formula given as equation (7):

$$\mathrm{TLL} = \sqrt{(X_T - X_B)^2 - (Y_T - Y_B)^2}$$

Where subscripts T and B denote respectively the top and bottom phases, and X and Y are the weight fraction of inorganic salt and ionic liquids, respectively.

The result collected through experiment for concentration for both compounds at top and bottom phase as shown as below:

Table 4.3: Tie Line Composition

Feed		Top Phase		Bottom Phase		Tie Line Length
IL (wt%)	Salt (wt%)	IL (ppm)	Salt (ppm)	IL (ppm)	Salt (ppm)	
50	20	0.052	0.018	0	0	0.0550
50	25	0.058	0.021	0.118	0.095	0.0953
50	30	0.068	0.026	0.128	0.103	0.0976
50	35	3.496	0.043	0.547	0.122	2.9501
50	40	6.723	0.092	0.623	0.455	6.1108
50	50	9.887	0.981	6.452	1.387	3.4589

The data above are simplified as graph below:

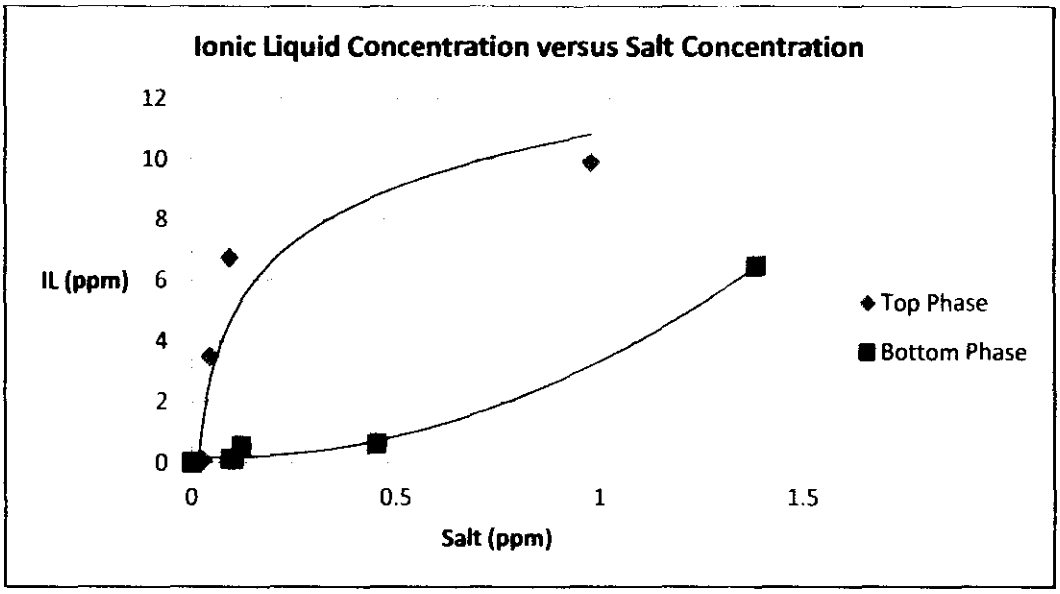


Figure 4.6: Ionic liquid concentration versus salt concentration

Since the tie line length represents the difference between the ionic liquid and inorganic salt concentrations in the top and bottom phases, the higher the tie line length, the higher is the ionic liquid concentration in the top phase and salt concentration at the bottom phase. As the graph shows that as the concentration of aqueous salt solution increase, the tie line length is increased as the concentration of ionic liquid at top phase is increasing and also the concentration of salt at bottom phase is increasing as well. As discussed before, it shows that at higher concentration of aqueous salt solution used, the ionic liquid is not sufficiently salted out by the aqueous salt solution as the water molecules itself become the limitation of the system.

The concentration of salt is higher at bottom phase as bottom phase is salt-rich phase while top phase is ionic liquid-rich phase.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

Addition of inorganic salts to ionic aqueous systems leads to ion exchange between salt present in both aqueous rich phases. Thus, ionic liquid needs to carefully select in order to sufficiently salt out the aqueous salt solution to allow aqueous two phase system to be formed. Besides that, the ability of hydrophilic ionic liquids to form salt-salt aqueous two phase systems allow them to be used in aqueous separation systems. By accessing the concentration of ionic liquid at top and bottom phase, the results presented show that salting out effects produced by the addition of an inorganic salt to aqueous solutions of water-soluble ionic liquid can produces aqueous two phase system.

5.2 RECOMMENDATION

More data should be collected in order to get more precise phase diagram. As the chemical is very limited, thus only 6 samples can be collected throughout the project.

Different types of aqueous salt solution need to be tested as to identify different trend of phase diagram with different type of aqueous two phase systems.

Different types of ionic liquid also need to be tested as to study more about the characteristics of new type aqueous two phase systems.

More sophisticated and accurate graph generating software should be used to ensure the graphs obtained are correct and reliable.

REFERENCES

Boris Y. Zaslavsky, 1995, Aqueous two phase partitioning, New York, pp 342-410.

Chuanxiang Li, Juan Han, Yun Wang, Yongsheng Yan, Jianming Pan, Xiaohui Xu, Zulei Zhang, 2010, Phase behaviour for the aqueous two phase system containing the ionic liquid 1-3Butyl-3-methylimidazolium Tetrafluoroborate and Kosmotropic Salts, J. Chem. Eng. Data, pp 1087-1092.

Claudia :.S. Louros, Ana Filipa M. Claudio, Catarina M. S. S. Neves, Mara G. Freire, Isabel M. Marrucho, Jerome Pauly, Joao A. P. Coutinho, 2010, Extraction of Biomolecules Using Phosphonium Based Ionic Liquids + K_3PO_4 Aqueous Biphasic System, International Journal of Molecular Sciences, published online on 15 April 2010.

Cuilan Yu, Juan Han, Yun Wang, Yongsheng Yan, Shiping Hu, yanfang Li, Xiaohong Zhao, 2011, Liquid-Liquid Equilibrium Composed of Imidazolium Tetrafluoroborate Ionic Liquids + Sodium Carbonate Aqueous Two Phase Systems and Correlation at (288.15, 298.15 and 308.15), Thermochimica Acta, published online 6 June 2011.

Gutowski KE, Broker GA, Willauer HD, Huddleston JG, Swatloski RP, Holbrey JD, Rogers RD., 2003, Controlling the Aqueous Miscibility of Ionic Liquids: Aqueous Biphasic Systems of Water-Miscible Ionic Liquids and Water-Structuring Salts for Recycle, Metathesis, and Separations. *J. Am. Chem. Soc.* pp 6632–6633.

Jolanta Flieger, Anna Czajkowska-Zelazko, 2009, Ionic Liquids in Seperation Techniques, Medical University of Lublin.

Jose C. Merchuk, Barbara A. Andrew, Juan A. Asenjo. 1998, Aqueous two-phase Systems for Protein Seperation Studies on Phase Inversion, Journal of Chromatography B, 711, pp 285-293.

Juan Han, Ru Pan, Xueqiao Xie, Yun Wang, Yongsheng Yan, Guowu Yin, Weixing Guan. 2010, Liquid-Liquid Equilibria of Ionic Liquid 1-Butyl-3-Methyimidazolium tetrafluoroborate + Sodium and Ammonium Citrate

Aqueous Two Phase Systems at (298.15, 308.15 and 323.15K), J. Chem. Eng. Data 2010; pp 3749-3754.

K.S.M.S. Raghavarao, T.V. Ranganathan, N.D. Srinivas, R.S. Barhate, 2003, Aqueous Two Phase Extraction, pp 136-141.

K.S.M.S. Raghavarao, T.V. Ranganathan, N.D. Srinivas, R.S. Barhate, Aqueous two phase extraction, 2010, Clean Techn Environ Policy 5. pp 136-141.

Raja Ghosh, 2006, Principles of Bioseperations Engineering, Singapore: World Scientific Publishing Co.

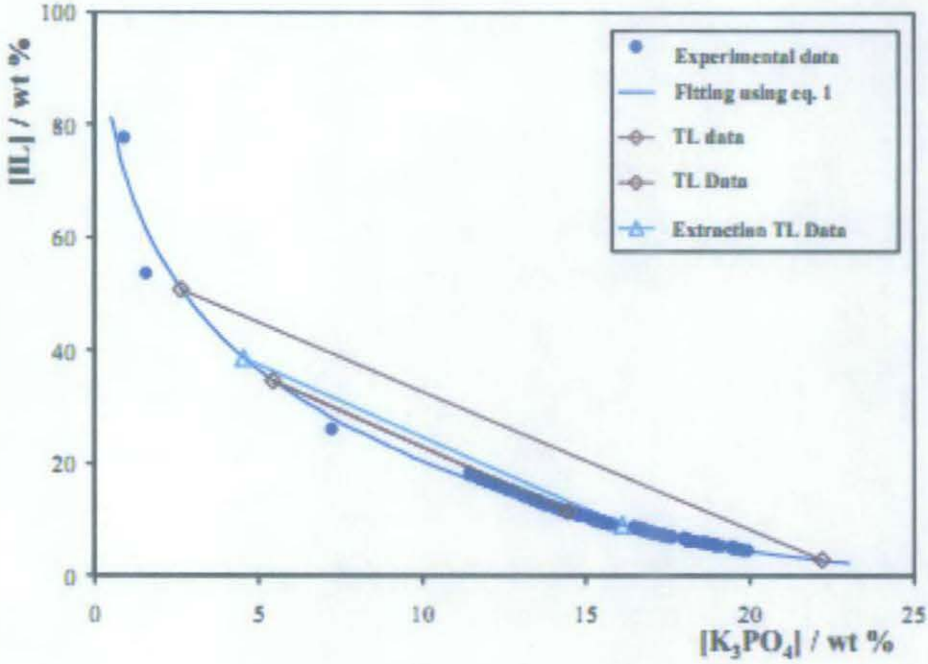
Vesna Najdanovic Visak, Jose N. Canongia Lopes, Zoran P. Visak, J. Trindade and Luis P. N. Rebelo, 2007, Salting-out in Aqueous Solutions of Ionic Liquids and Aqueous Biphasic Systems and Salt Precipitation, International Journal of Molecular Sciences 2007, published online on 31 July 2007.

APPENDIX

Experimental mass fraction data for system [P_{4441}][$MeSO_4$] (1) + K_3PO_4 (2) + H_2O (3) at 298 K

$100\,w_1$	$100\,w_2$	$100\,w_1$	$100\,w_2$	$100\,w_1$	$100\,w_2$
77.5934	0.90771	11.2609	14.4430	7.4775	17.1636
53.4656	1.5792	11.2103	14.5451	7.4469	17.1578
25.9023	7.2379	11.0322	14.6659	7.3744	17.2109
18.2887	11.4349	10.9383	14.7164	7.3094	17.2570
17.9208	11.4616	10.8315	14.7398	7.2174	17.3563
17.4714	11.7238	10.7604	14.7986	7.1409	17.3780
17.1359	11.7926	10.6804	14.8402	7.0842	17.4493
16.9415	11.9064	10.5979	14.8798	7.0141	17.4787
16.7287	11.9991	10.4992	15.0632	6.9281	17.6240
16.5239	12.1081	10.4027	15.0715	6.8851	17.5459
16.3093	12.2274	10.2866	15.2087	6.6925	18.0071
16.0326	12.2485	10.1696	15.1612	6.5704	17.9871
15.8815	12.3688	10.0974	15.1936	6.4922	17.9813
15.7122	12.4548	10.0264	15.2281	6.4232	18.0218
15.5477	12.5460	9.9546	15.2601	6.3594	18.0536
15.3678	12.6077	9.8942	15.3046	6.2947	18.0826
15.2070	12.6873	9.8279	15.3474	6.2293	18.1219
14.9984	12.7611	9.7574	15.3750	6.1590	18.1035
14.8520	12.8584	9.6942	15.3936	6.1033	18.1352
14.5307	13.0061	9.6382	15.4562	6.0215	18.3160
14.3171	13.0385	9.5057	15.5441	5.9277	18.4942
14.1664	13.1165	9.4206	15.5440	5.8285	18.6036
14.0185	13.1889	9.3527	15.5680	5.7511	18.6721
13.8758	13.2791	9.2936	15.6016	5.6735	18.7119
13.7015	13.3035	9.2257	15.6554	5.6080	18.7912
13.558	13.3816	9.1052	15.7240	5.5372	18.8673
13.4310	13.4522	8.9754	15.8082	5.4743	18.9215
13.2930	13.5466	8.6569	16.4467	5.4140	18.9163
13.1275	13.5644	8.5488	16.4900	5.3627	18.9361
12.9994	13.6333	8.4453	16.5391	5.2760	19.0394
12.8554	13.6283	8.3687	16.6413	5.2150	19.1205
12.7437	13.7052	8.2877	16.6178	5.0581	19.4294
12.633	13.7689	8.2414	16.6429	4.9745	19.4137
12.4280	13.8984	8.1978	16.6689	4.8979	19.4868
12.221	14.0268	8.1218	16.7586	4.8186	19.5608
12.0649	14.0426	8.0307	16.8020	4.7515	19.5266
11.8794	14.1976	7.9690	16.8050	4.6646	19.5781
11.739	14.2035	7.8985	16.9016	4.5839	19.6828
11.6482	14.2683	7.8380	16.9003	4.5141	19.7926
11.5457	14.3293	7.7460	16.9424	4.3991	19.9380
11.4515	14.3768	7.6696	17.0048		
11.3520	14.4131	7.5775	17.0471		

Phase Diagram for the ternary system $[P_{4444}]Br + K_3PO_4 + H_2O$ at 298 K



Experimental density for IL + K_3PO_4 + Water Systems

T / K	$[P_{4444}]Br$ (ρ / g·cm^{-3})		$[P_{i(444)1}][Tos]$ (ρ / g·cm^{-3})		$[P_{4441}][MeSO_4]$ (ρ / g·cm^{-3})	
	IL-rich phase	**K_3PO_4-rich phase**	**IL-rich phase**	**K_3PO_4-rich phase**	**IL-rich phase**	**K_3PO_4-rich phase**
298.15	1.0521	1.1676	1.0605	1.1769	1.0689	1.1612
303.15	1.0483	1.1660	1.0571	1.1745	1.0656	1.1599
308.15	1.0446	1.1644	1.0537	1.1727	1.0625	1.1594
313.15	1.0409	1.1624	1.0502	1.1705	1.0592	1.1583
318.15	1.0374	1.1601	1.0467	1.1680	1.0559	1.1566

Experimental viscosity for IL + K_3PO_4 + Water Systems

T / K	$[P_{4444}]Br$ (η / mPa·s)		$[P_{i(444)4}][Tos]$ (η / mPa·s)		$[P_{4441}][MeSO_4]$ (η / mPa·s)	
	IL-rich phase	**K_3PO_4-rich phase**	**IL-rich phase**	**K_3PO_4-rich phase**	**IL-rich phase**	**K_3PO_4-rich phase**
298.15	10.137	1.6851	6.5119	1.8670	4.4083	2.4271
303.15	8.2925	1.5042	5.4527	1.6743	3.7647	2.1356
308.15	6.9087	1.3575	4.6339	1.5108	3.2542	1.8759
313.15	5.8434	1.2451	3.9879	1.3725	2.8439	1.6671
318.15	5.0076	1.1400	3.4693	1.2548	2.5093	1.4940

Experimental procedure applied for the biomolecules partitioning