

# CHAPTER 1: Introduction

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## 1.1 Background

Exclusive ions called ionic liquids have become a major topic of research in chemistry because of their special characteristics such as non-volatile, non-flammable, thermally and chemically stable salt [1-3]. Owing to these advantages, ionic liquids have been used in many applications for example, as a catalyst [4-5], reaction media [6-7] and extraction medium [8-10].

Because ionic liquids consist of cations and anions, this unique chemical architecture can potentially contribute to the development of various types of ionic liquids. Two major groups of ionic liquid are protic and aprotic ionic liquids. Protic ionic liquids are an interesting class of ionic liquids which is designed by donation of proton from Brønsted acid, AH, to a Brønsted base, B to yield a  $[BH^+][A^-]$  type [11-13]. The cation from protic ionic liquid has the capability for hydrogen-bond donation and the anion has the functionality to accept the hydrogen-bond.



Gabriel and Weiner [14] reported the first protic ionic liquids, ethanolanmonium nitrate in 1888. Even though the norm of using ionic liquids in research world has emerged vastly since past centuries, their importance towards science application is undeniably useful. Because of their unique properties, many papers have been published especially in the area of physico-chemical studies [15-17], reaction media [18-19] and catalysis [20-21].

Regardless of many publications on protic ionic liquids, aprotic ionic liquids were still widely studied by researchers [22-26]. Due to large irregular organic cation with a monoatomic or polyatomic inorganic anion, aprotic ionic liquids have more physical characteristics compared to protic ionic liquids. Therefore, physical chemistry researchers are keener to choose aprotic ionic liquids in their studies [27-30]. However, both aprotic and protic ionic liquids contribute their own special characteristics toward chemical industries. Various combinations of cations and anions make ionic liquid alterable physico-chemically. For instance, by changing the anion the solubility of ionic liquid in water can be varied from very miscible to almost miscible.

Traditionally, distillation is the most common method in organic solvents separation process. However, there are few reasons that can make this method ineffective or difficult such as two or more chemicals can become an azeotrope or the mixture components have a common boiling point that cannot be separated. Therefore, alternative methods need to be considered. Extraction is a process where an extractor will selectively dissolve one or more of the mixture components. However, in order for the process to be selective, designated extractor must be miscible in either one of the two solvents that were mixed, and one of these two solvents that is to be extracted out must be insoluble to the other solvent. Two separate solvent layers will then be produced. Hence, the desired compound can be easily collected from one of the two layers.

The understanding of liquid-liquid phase behaviour of protic ionic liquids interacting with other solvents is substantially important in separation process studies. There are numerous liquid-liquid equilibria studies introducing ionic liquid that have been published [30-34].

For ternary mixtures, whenever two components are not miscible or moderately miscible as observed, the third component may cause the solubility of the mixture to be increased or decreased. In liquid-liquid extraction, ionic liquids have been very appealing to most researchers for the reason they are potentially recoverable and reused [35-39]. Yet, not all ionic liquids are well-suited with the separation process. Hence, knowledge of solubilities of ionic liquid is important to ensure the most compatible separation agent is used.

Upper critical solution temperature (UCST) and lower critical solution temperature (LCST) are two types of phase separation which are temperature dependent. Whenever the mixture is miscible at higher temperatures and separates gradually at lower temperature it behaves as UCST. Oppositely for LCST, the mixture forms a single phase at lower temperatures and biphasic at higher temperatures [40]. Extracting components from the mixture is common, but being able to control phase separation from the start of the reaction to separation of the mixtures is a big advantage. Therefore, temperature is the most adequate and easiest parameter to consider.

## **1.2 Problem statement**

### **1.2.1 Isopropanol and water mixture**

Alcohols are widely used organic liquids in chemical industry, and, isopropanol is not excluded. The main uses of isopropanol are as a purification agent for organic material, disinfectant in cosmetic and pharmaceutical industry and solvents for resins in paints [41].

Binary mixture of isopropanol and water has served much purpose in many areas, especially, solvent media for separation process. The mixture can be in various type of form, from solvent to waste. Despite their importance, recycling and re-purifying isopropanol with less effort and processing time can be a great improvement to the research world and industries promoting greener environment.

### **1.2.2 Alcohol-water separation methods**

Over the past decade, researchers have focused on the most environmental friendly technique reproducing alcohols from waste or renewable resources. However, current methods to separate alcohol-water mixtures, such as distillation and metal halides extraction are not as sustainable and easy as demanded. Distillation is the lowest-cost technique that has been used for over a decade now. Nonetheless, most alcohol-water mixtures form azeotropes, which makes simple distillation as not the most suitable process to be used [42]. In extraction, a solvent that is not miscible and does not form an azeotrope with the mixture is being introduced into the mixture. It is crucial to choose a suitable separation solvent in this technique. The solvent need to be less volatile and should be easily separated and does not react with all the components in the mixture. These two methods have been widely used in most industries, commonly, gas-fuel, pharmaceutical and paint industries. As the world is getting modernized, researchers are battling with each other to find unconventional alcohol-water mixtures separation techniques which are low cost, less time consuming and greener.

Green salt or to be specific ionic liquid has been proven to be able to separate alcohol-water mixture. Upon adding salt (in this case protic ionic liquid) into the alcohol-water mixture, the solubility of the two components decreases and as a result the mixture formed two layers which are salt-rich phase and aqueous rich phase. This phenomenon helps the separation process to be less elaborate.

### **1.3 Scope and research objectives**

The increasing number of scientific studies using ionic liquid shows a great awareness amongst researchers towards sustainable environment [43-45]. Amongst all explored field, separation studies have gained many interest from industries. Therefore, the aim for this work is to investigate protic ionic liquids that can successfully transport organic solvent from one phase to another without cross-contamination.

The cation of this new protic ionic liquid consists of an amine ion interacting with anion, *p*-toluenesulfonate ion. These protic ionic liquids are easily synthesized using simple neutralization method between acid (cation) and base (anion). The separations were conducted at various temperatures depending on the phase change behaviour. Physical and chemical changes of the phase separation at each temperature were observed. In order to have a better understanding on the separation process, compositions for each component were determined at all temperatures at which the mixture exists in bilayers. These composition data were used to construct a ternary phase diagram which shows the solubility curve of the mixture.

Hence, the objectives for this research are as follows:

- i) To investigate the chemical behaviour during phase miscibility and phase separation.
- ii) To comprehend the effect of cation and molecular weight of new protic ionic liquids toward miscibilities of the ternary mixtures.
- iii) To determine temperature dependence of efficiency new protic ionic liquids in extraction of isopropanol from water.

#### **1.4 Outline of thesis**

With the intention to fulfill and accomplish the objectives above, a few steps and studies are needed, which are explained in the following six chapters:

##### *Chapter 1: Introduction*

This chapter is an overview of this project that includes the importance of separation process for alcohol-water mixture. The problem statement, scope and objectives were also covered in this section.

##### *Chapter 2: Literature review*

In this chapter, a brief background of the separation process including selection of ionic liquid and solvent, suitable temperature range used and behaviour of temperature dependence phase changes was discussed.

### *Chapter 3: Methodology*

This chapter covers the chemicals used, sample preparation and experimental procedures. Details on the technique of sampling for  $^1\text{H}$ NMR and composition studies were covered. The experimental set up for the separation process to occur at different temperatures were thoroughly explained.

### *Chapter 4: Results*

This section reports  $^1\text{H}$ NMR spectrums during phase miscibility and phase separation. The experimental composition data for isopropanol, water and protic ionic liquid at each temperature involved were also reported. The chemical behaviour during phase separation and phase miscibility were thoroughly discussed. The test was conducted at the temperature when the mixture formed both phase behaviour. Variations on the integration value of hydrogen that sits on nitrogen in the protic ionic liquid were explained. On the other hand, the two-axis graphs for each mixture provides an overview on which condition is the best resulting the separation to be well-executed.

### *Chapter 6: Conclusion*

This chapter summarizes the findings of this research and the future application that can be useful adopting from this work.