

CHAPTER 3: Methodology

3.1 Introduction

Experimental procedures and data analysis used in this research are explained in this chapter.

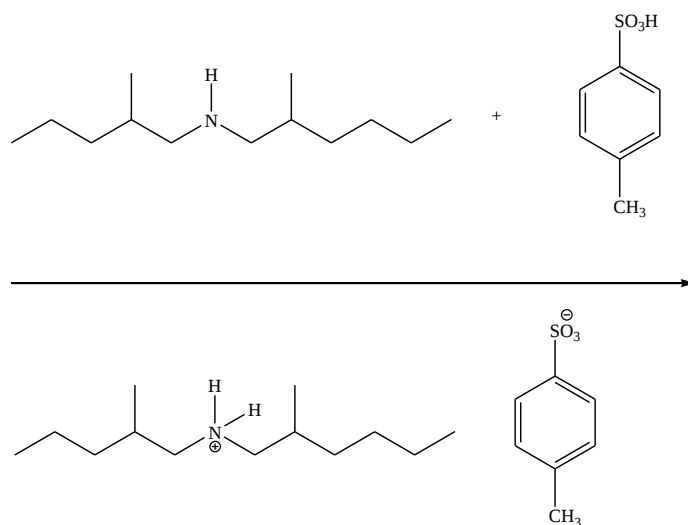
3.2 Materials

Bis-(2-ethylhexyl)amine (97.0 % purity) and tris-(2-ethylhexyl) amine (97.0 % purity) were purchased from Sigma-Aldrich and used as received. On the other hand, ρ -toluenesulfonic acid (98.5 % purity) and isopropyl alcohol (98.0 %) were purchased from Pierce Chemical and Merck, respectively and were also used as received.

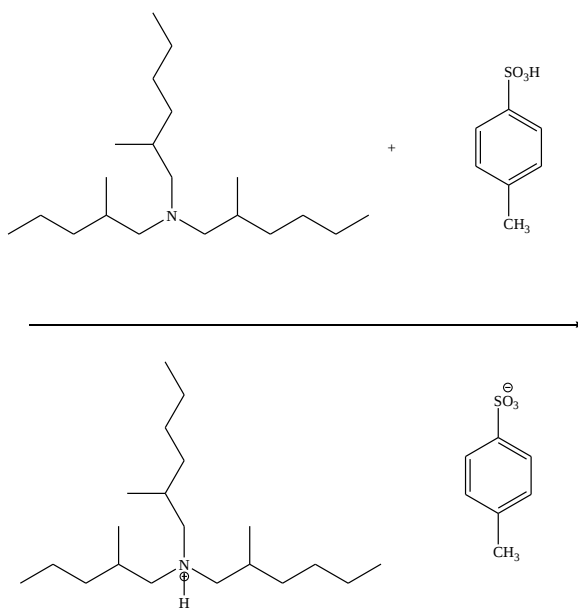
3.2.1 Synthesizing ionic liquids

The 3:1 mixtures of amine and acid were prepared using a simple neutralization reaction by adding drop by drop stoichiometric amount of acid to the base. Schemes 3.1(a) and 3.1(b) display the neutralization reaction between bis-(2-ethylhexyl)amine and ρ -toluene sulfonic acid and tris-(2-ethylhexyl) amine and ρ -toluenesulfonic acid, respectively.

The protic ionic liquid was further purified by distillation over dichloromethane. The unreacted cation or anion was confirmed using mass spectroscopy. The water content for bis-(2-ethylhexyl)ammonium tosylate [BEHA tosylate] and tris-(2-ethylhexyl) ammonium tosylate [TEHA tosylate] were also determined using Karl-Fisher and it was found to be less than 0.3 % wt. for all.



Scheme 3.1(a). Neutralization reaction between bis-(2-ethylhexyl)amine and *p*-toluenesulfonic acid to yield bis-(2-ethylhexyl)ammonium tosylate.



Scheme 3.1(b). Neutralization reaction between tris-(2-ethylhexyl)amine and *p*-toluenesulfonic acid to yield tris-(2-ethylhexyl) ammonium tosylate.

3.3 Solutions preparation

BEHA tosylate or TEHA tosylate, water and isopropanol mixtures (ratio 1:1:1.2) were all prepared gravimetrically with a precision of ± 0.0001 g, using analytical balance (GR 200, A&D, Tokyo, Japan). Prepared mixtures were stirred until homogenized and stored inside screwed cap bottle to avoid the evaporation of isopropanol.

3.3.1 Phase-type changes observation

After homogenization of the solutions occurred, the mixtures were left undisturbed at room temperature ($T \approx 298$ K) until two layers were observed. These two layers are organic and aqueous rich phases. For better observation, the ionic liquid-rich phase was coloured using Nile Red. These mixtures were heated steadily with some stirring and then cooled after formation of homogeneous phase using Heidolph MR-Hei Standard magnetic stirrer with heating. Figure 3.1 depicts the temperature controlling method of the solutions.



Figure 3.1. Temperature controlling technique.

3.3.2 Proton Nuclear Magnetic Resonance (^1H NMR) studies

In order to understand more on chemical activities of the phase separation, ^1H NMR studies were conducted on the mixtures (without Nile red addition) when it formed a single clear phase, clear biphasic layers, ionic-liquid rich phase and aqueous-rich phase. Samples involved were analyzed using Jeol ECA - 400 with temperature controller. The same ratio mixtures were sampled in NMR tube and were put into the sampler at the specific temperatures where it formed single clear layer and clear biphasic layers. At temperature where the mixture formed a clear bilayer, both organic and aqueous-rich phase were taken out using 100 microlitres pipetter and dispensed into two separate NMR tubes.

3.3.3 Composition studies

In this separation studies, it is important to understand the composition changes on each component inside BEHA tosylate or TEHA tosylate with aqueous isopropanol mixture. The purpose of this study is to determine at which temperature is the best for a protic ionic liquid be able to extract isopropanol from water for both systems. Besides temperature, the composition determination would be able to define either BEHA tosylate or TEHA tosylate is the best protic ionic liquid to extract isopropanol from water.

In order to achieve the purpose, composition values for each component in the ternary mixture at each temperature is necessary. The same ratio mixtures were prepared as in the previous section. Known weight of organic rich phase and aqueous rich phase at specific temperatures, refer Table 3.1, were sampled out from the mixture. The composition of isopropanol in each phase was determined using a simple distillation method using rotavapour at 313 K and 35 rpm. This isopropanol percentage value were calculated by subtracting the final weight from the united for each sample.

Using the same sample, both phases were diluted with known amount of methanol and the sample was analyzed using Karl-Fisher (831 KF Coulometer from Metrohm) in order to acquire the water content. From both isopropanol and water composition results, ionic liquid composition was determined using a simple mathematical calculation (equation 3.1). Figure 3.2 illustrates a summary of the method used in this section.

$$\text{Ionic liquid composition (\%)} = 100\% - \text{IPA composition} - \text{water composition} \quad (3.1)$$

Once the compositions for each component in both mixtures were acquired, the results will be plotted into two-axis graphs corresponding to temperature. From the graphs, the best temperature and ionic liquid that able to extract isopropanol from water will be determined.

Table 3.1. Temperatures applied for both ternary mixtures

Mixtures	Temperatures (K)
BEHA tosylate + water + isopropanol	285
	289
	296
	301
	304
TEHA tosylate + water + isopropanol	293
	298
	303
	308
	313

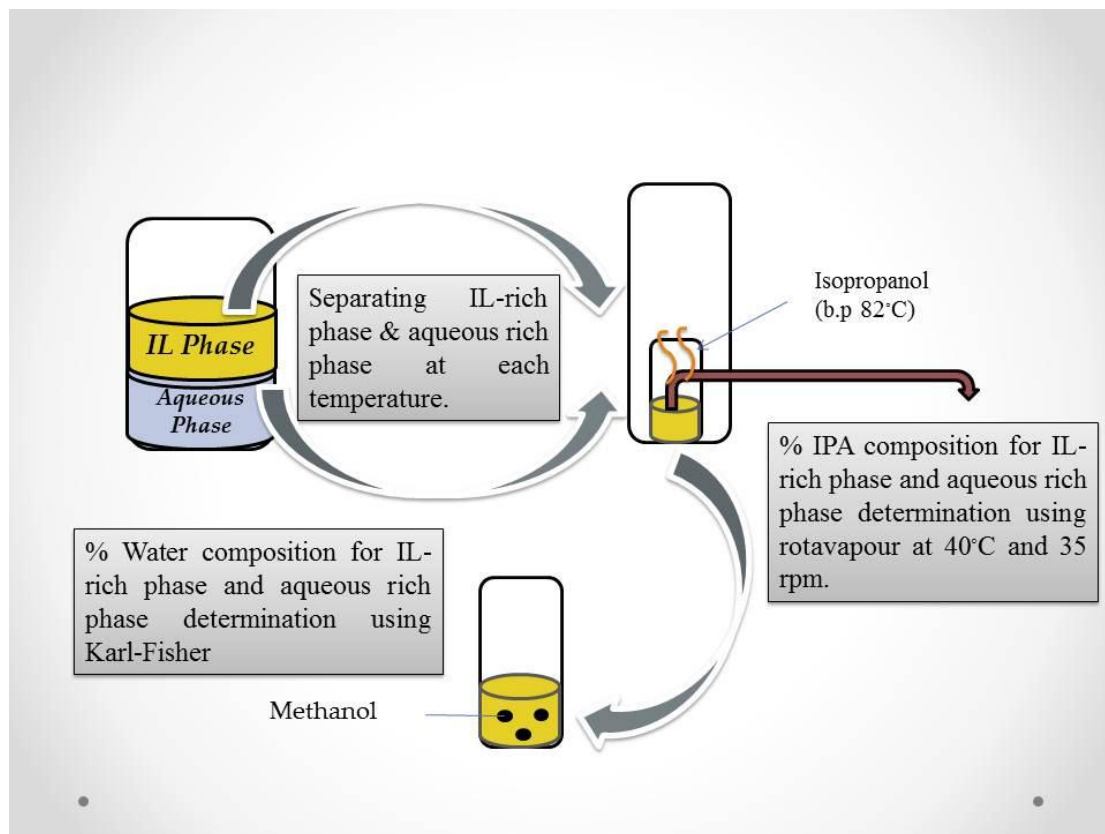


Figure 3.2. Summary of technique used in composition studies