CHAPTER 4: Results and Discussions

4.1 Synthesis of new protic ionic liquids

Two new types of protic ionic liquids were successfully synthesized using simple neutralization reaction between an amine as the base and *ρ*–toluenesulfonic as the acid. The synthesized protic ionic liquids are named bis–(2-ethylhexyl)ammonium tosylate (BEHA tosylate) and tris–(2-ethylhexyl)ammonium tosylate (TEHA tosylate). Figure 4.1 (a) and (b) represent the two protic ionic liquids that have never been reported in any publication. As can be seen from both structures, the hydrogens attached to nitrogen in bis-(2-ethylhexyl)ammonium cation are less guarded by the 2-ethylhexyl groups compared to tris-(2-ethylhexyl)ammonium cation. The hindrance effect towards the separation process will be discussed further in later part of this thesis. The physical properties of these protic ionic liquids were analyzed using a viscometer and a densitometer. The purification characterizations were confirmed using ^{1}HNMR spectroscopy and electrospray mass spectroscopy.

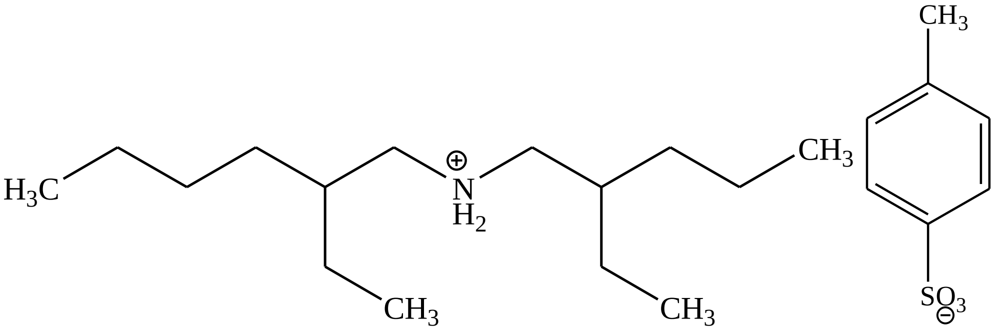


Figure 4.1 (a). Chemical structure of bis–(2-ethylhexyl)ammonium tosylate.

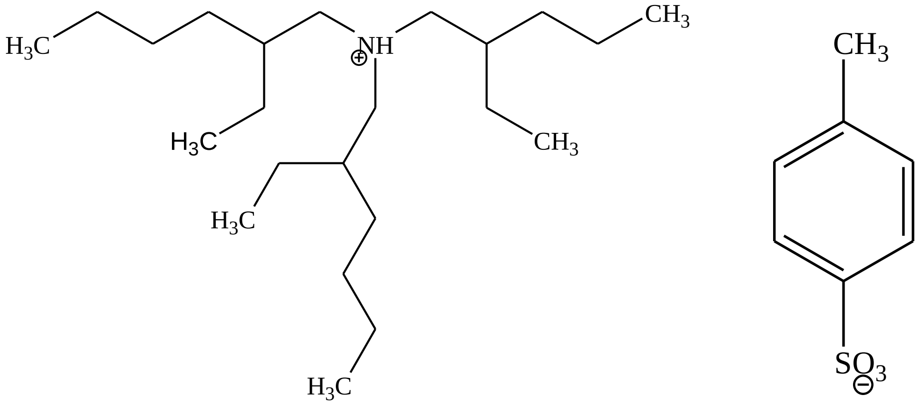


Figure 4.1 (b). Chemical structure of tris–(2-ethylhexyl)ammonium tosylate.

4.2 Physical properties of the protic ionic liquids

Figure 4.2 shows samples of the hydrophobic ionic liquids with two different tones of yellow. BEHA tosylate's colour is darker compared to TEHA Tosylate where the colour is brighter. It is likely that the colour difference is related to the rate of neutralization reaction.

Figure 4.2. Samples of the synthesized new protic ionic liquids.

Molecular weight, viscosity and density values for both protic ionic liquids are represented in Table 4.1. The viscosity and density results for both new protic ionic liquids at room temperature were not reliable due to the viscous nature of the protic ionic liquids. Therefore, the density and viscosity were conducted at temperature of 313 K, in order to get constant readings. From the values, viscosity values for BEHA tosylate seems smaller compared to TEHA tosylate.

Khupse and Kumar [82] mentioned in a review paper written by them that the contribution of weaker, non-associating, dispersion forces also enhances viscosity. The justification put forward by Bonhôte *et. al* [83]. The team synthesized low melting points hydrophobic ionic liquids, based on 1,3-dialkyl imidazolium {bis(trifluorosulfonyl)}amide (alkyl = methyl, ethyl, butyl and isobutyl) and one part of their study was to look at the viscosity of these ionic liquids, how it is affected by the alkyl chain length. They have mentioned in their study that the viscosities of the ionic liquid salts were governed by van der Waal's interaction, where, alkyl chain lengthening make the salt more viscous due to increase of the van der Waal's interaction. They have also reported viscosity value for 1,3-diisobutylimidazolium {bis(trifluorosulfonyl)}amide was slightly higher compared to 1,3-dibutylimidazolium {bis(trifluorosulfonyl)}amide due to the reduction of rotation freedom. This findings was also proved by Hamill *et. al.* [84] where the viscosity for [1-alkyl-3-methylimidazolium][tetrafluoroborate] (alkyl = ethyl, butyl, hexyl) at temperature 293 K increased from 66.5 to 314 mPa.s . Hence, both findings verified the observation seen in this viscosity study for these new protic ionic liquids.

In this study, BEHA tosylate is reportedly denser compared to TEHA tosylate. Tokuda *et. al.* [85] justified this finding by preparing a series of 1-alkyl-3-methylimidazolium {bis(trifluorosulfonyl)}amide based room temperature ionic liquids (alkyl = methyl, ethyl. butyl, hexyl and octyl). The density for these room temperature ionic liquids was measured over a wide range of temperature (280 – 320 K). They have found the density decreased linearly with increasing temperature. On top of that, at constant temperature, decrease trend in the density and increase in the formula weight with increasing carbon atoms in the alkyl chain length causes a subsequent decrease in the density value. Marsh *et. al.* [86] has also reported density of imidazolium ionic liquid decreases with increases of the alkyl chain length. Hence, this agrees with the decreases of density value on an addition of 2-ethylhexyl group in the ionic liquid cation.

Table 4.1. Molecular weight, density, viscosity values for both protic ionic liquids.

Protic ionic liquid	Molecular weight (g/mol)	Density (g/cm^3)	Viscosity (mPa.s)
BEHA tosylate	413.68	0.9980	850.2
TEHA tosylate	525.89	0.9615	1264.0

4.3 Purification characterization of the protic ionic liquids.

4.3.1 Proton Nuclear Magnetic Resonance (^{1}HNMR)

Table 4.2 shows the ^{1}HNMR integration values corresponding to the chemical shift of the spectra for BEHA tosylate protic ionic liquid that was synthesized in this study [refer Appendix I for full image of the spectra]. The ^{1}HNMR spectrum showed eight signals from a total of 42 hydrogen (H) atoms. Four methyl ($–CH_3$) groups, resonated as a two triplets signal at δ 0.7485 ppm [refer Appendix II for close up image of the peak]. The most right triplet signal is contributed by H-(a), and the second triplet peak is belong to H-(b). A cluttered signal resonating at δ 1.2212 ppm is from a redundant multiplet signals from methylene ($–CH_2$) that is attached to ethylhexyl group of BEHA cation, H-(c), [refer Appendix III for close up image of the peak]. A triplet peak signal at δ 1.6678 ppm is belongs to methine (C-H) that is attached in between ethyl and hexyl of the cation, H-(d). A quite distinct single peak was observed at δ 2.8280 ppm contributed from methyl group from the tosylate anion, H-(e). The doublet ^{1}HNMR signal at δ 2.7741 ppm belongs to methylene ($–CH_2$) nearest to the nitrogen in ethylhexyl chain of the cation, H-(f). Two doublet peaks observed at δ 7.0828 ppm and δ 7.6710 ppm are owned by C-H of tosylate ring near the methyl group H-(g) and SO_3^- H-(h), respectively [refer Appendix IV for close up image of the peaks]. Finally, the most far down broad peak of the ^{1}HNMR spectra, δ 8.1620 ppm, belongs to the most shielded hydrogen atom that are attached to the nitrogen, H-(i) [refer Appendix IV for close up image of the peak].

Table 4.2. Proton Magnetic Nuclear Resonance (^{1}HNMR) of neat bis-(2-ethylhexyl)ammonium tosylate.

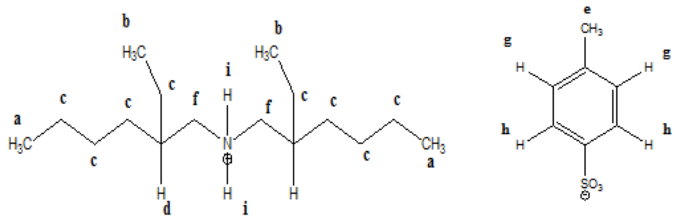
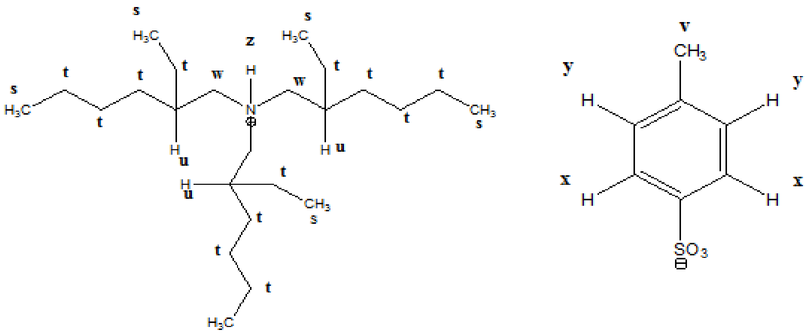
Proton	Chemical Shift (ppm)	Relative Integration (%)
H (a) - H (b)	0.7485	12.21
H (c)	1.2212	16.12
H (d)	1.6678	1.92
H (e)	2.8280	2.87
H (f)	2.7741	4.06
H (g)	7.0828	2.00
H (h)	7.6710	2.03
H (i)	8.1620	1.25
		

Table 4.3. Proton Magnetic Nuclear Resonance (^{1}HNMR) of neat tris-(2-ethylhexyl)ammonium tosylate.

Proton	Chemical Shift (ppm)	Relative Integration (%)
H (s)	0.8080	18.82
H (t)	1.2258	25.38
H (u)	1.7018	2.90
H (v)	2.2740	3.75
H (w)	2.9435	6.01
H (x)	7.0645	2.00
H (y)	7.7038	2.03
H (z)	9.3147	0.90
		

^{1}HNMR integration values of TEHA tosylate protic ionic liquid are represented in Table 4.3 [refer Appendix V for full image of the spectra]. Similar to BEHA tosylate, there were also eight signal observed. These signals consist of sixty hydrogen atoms. Due to signals overlapping of eighteen hydrogen atoms from methyl (-CH_3) group attached to the three 2-ethylhexyl groups, H-(s), a theoretical three triplet peaks at δ 0.8080 ppm become broad [refer Appendix VI for close up image of the peak]. The same observation happened in H-(c) in BEHA tosylate ^{1}HNMR spectra, -CH_2 attached to the TEHA tosylate cation, H-(t), contributed to a disorganized multiplet peak at δ 1.2258 ppm [refer Apendix VII for close up image of the peak]. A peak at δ 1.7018 ppm is owned by –CH that attached in between ethyl and hexyl of the cation, H-(u). The signal for hydrogens attached to methyl group of tosylate anion, H-(v) was observed at δ 2.2740 ppm. A peak resonated at δ 2.9435 ppm belongs to the six hydrogen atoms nearest to nitrogen of the cation H-(w). Two doublet peaks at δ 7.0645 ppm and δ 7.7038 ppm belong to H-(x) and H-(y) of tosylate ring. Finally, a broad peak was observed at the lower field, δ 9.3147 ppm which belonged to the most shielded hydrogen in TEHA tosylate ionic liquid, H-(z) [refer Appendix VIII for close up image of the peak].

The peaks were easily correlated based on the structural features. It is clear from both spectra the protic ionic liquids were synthesized with minimal impurities. The peaks at 7.2 ppm in the pure ionic liquids spectra are due to the deuterated chloroform ($CDCl_3$) that the ionic liquids were dissolved in for the scans.

4.3.2 Electrospray Mass Spectra (MS)

Electrospray mass spectra was carried out to confirm both protic ionic liquids formed consisted of related cations and anions. Refering to Table 4.4, a molecular ion peak with m/z value 242.3 was observed due to the presence of bis-(2-ethylhexyl)ammonium cation $[CH_3\ (CH_2)_3CH\ (C_2H_5)\ CH_2]_2H_2N^+$. From the same sample of protic ionic liquid, a very distinct peak, m/z = 171.0 is the peak for tosylate anion, $C_7H_7O_3S^-$**.** On the other hand, for mass spectra of tris-(2-ethylhexyl) ammonium cation, $[CH_3\ (CH_2)_3CH\ (C_2H_5)\ CH_2]_3HN^+$ the m/z = 354.5. Similar to tosylate anion mass spectra in BEHA tosylate, m/z = 171.0, belongs to the tosylate anion in TEHA tosylate ionic liquid. Table 4.4 shows the mass spectra values for both new protic ionic liquids that were used in this study. Hence from all the observations, both protic ionic liquids that were prepared are completely formed. Kindly refer Appendix IX – XII for the full mass spectra.

Table 4.4. Electro mass spectra values for both neat protic ionic liquids.

Cation / Anion	Relative molecular Weight (g/mol)	Mass spectra value (m/z)
BEHA tosylate		
bis-(2-ethylhexyl)ammonium	242.6	242.3
ρ-toluenesulfonate	171.2	171.0
TEHA tosylate		
tris-(2-ethylhexyl)ammonium	354.7	354.5
ρ-toluenesulfonate	171.2	171.0

4.4 Observation on the thermo-responsive ternary mixtures

As mentioned in chapter 3 of this thesis, the preparation of both ternary mixtures *i.e* BEHA tosylate / water/ isopropanol and TEHA tosylate / water/ isopropanol were made at a ratio of 1:1:1.2, respectively, based on weight per weight basis. In order to understand the efficiency of both protic ionic liquids in extracting isopropanol from water, the ratio of IL : water was fixed at 1:1. The appropriate ratio was based on the observation where two different compositions were also prepared. Refer Table 4.5 for the range of ratio prepared and its observation.

Table 4.5. Composition of BEHA tosylate/ water/ isopropanol and TEHA tosylate/ water/ isopropanol ternary mixtures.

Ratio (ionic liquid:water:isopropanol) (% wt)	**Observation**
1:1:1.0	bilayers observed even at full range of temperatures (no UCST/LCST type phase changes)
1:1:1.1	bilayers observed even at full range of temperatures (no UCST/LCST type phase changes)
1:1:1.2	UCST type phase changes observed
1:1:1.3	homogeneous mixture observed even at full range of temperatures (no UCST/LCST type phase changes)

Note; ionic liquid:water:isopropanol = BEHA tosylate or TEHA tosylate:water:isopropanol

As reported in Table 4.5, for ternary mixtures with 1:1:1.0 and 1:1:1.1 ratios, bilayers were observed at all times and temperatures due to the hydrophobicity of the ionic liquid. Nevertheless, at where excess of isopropanol (ratio 1:1:1.3) were prepared, both mixtures were totally miscible to each other, this might be due to the “like-dissolve-like” effect in protic ionic liquid:isopropanol and water:isopropanol. In determining the correct ratio for both mixtures, we could also observe that isopropanol improved the solubility between both protic ionic liquids and water. Hence, ternary mixtures with 1:1:1.2 ratio were selected for further study.

4.4.1 Bis-(2-ethylhexyl)ammonium tosylate/ water/ isopropanol system

Figure 4.3 shows images of a graded series in a two-phase system (upper: ionic liquid rich phase; lower: isopropanol rich phase) for BEHA tosylate + water + isopropanol system. Upon heating of the two phases for this system, the volume of the ionic liquid rich phase increased steadily until a monophase mixture appeared at 313 K. This shows that BEHA tosylate, water and isopropanol are miscible to each other above 313 K. As soon as temperatures were decreased, the phase separation produced a cloudy suspension then separated. Ionic liquid rich phase and isopropanol rich phase were clearly observed at 285 K. The cloud point temperature in this particular system is at 308 K at which a cloudy mixture was observed, where at this temperature, the mixture initially change from one phases to two phase. From the observation, it is definite that the mixture exhibits upper critical solution temperature type phase changes (UCST) at temperature between 285 to 308 K.

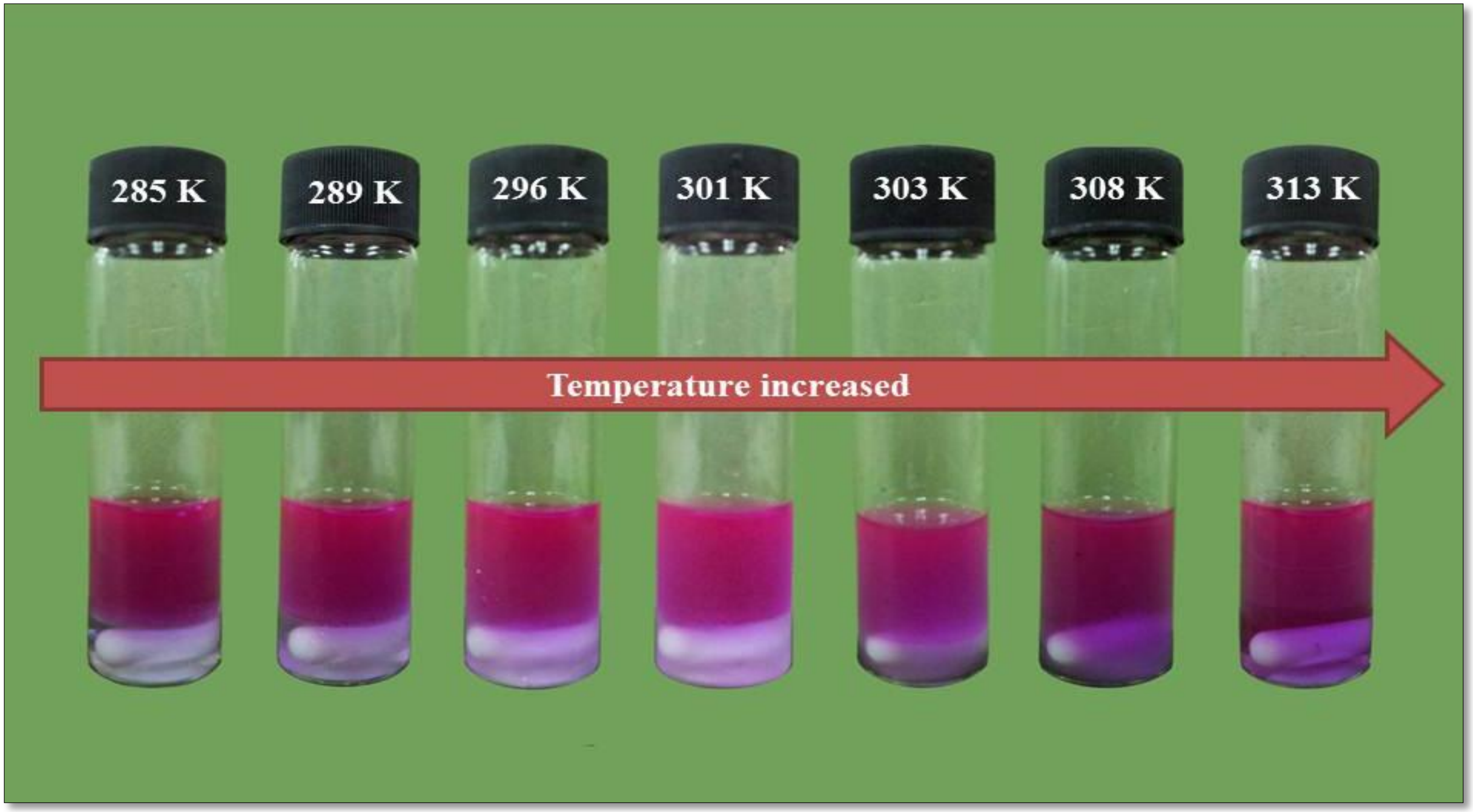


Figure 4.3. Phase behaviour of bis-(2-ethylhexyl)ammonium tosylate/ water/ isopropanol system.

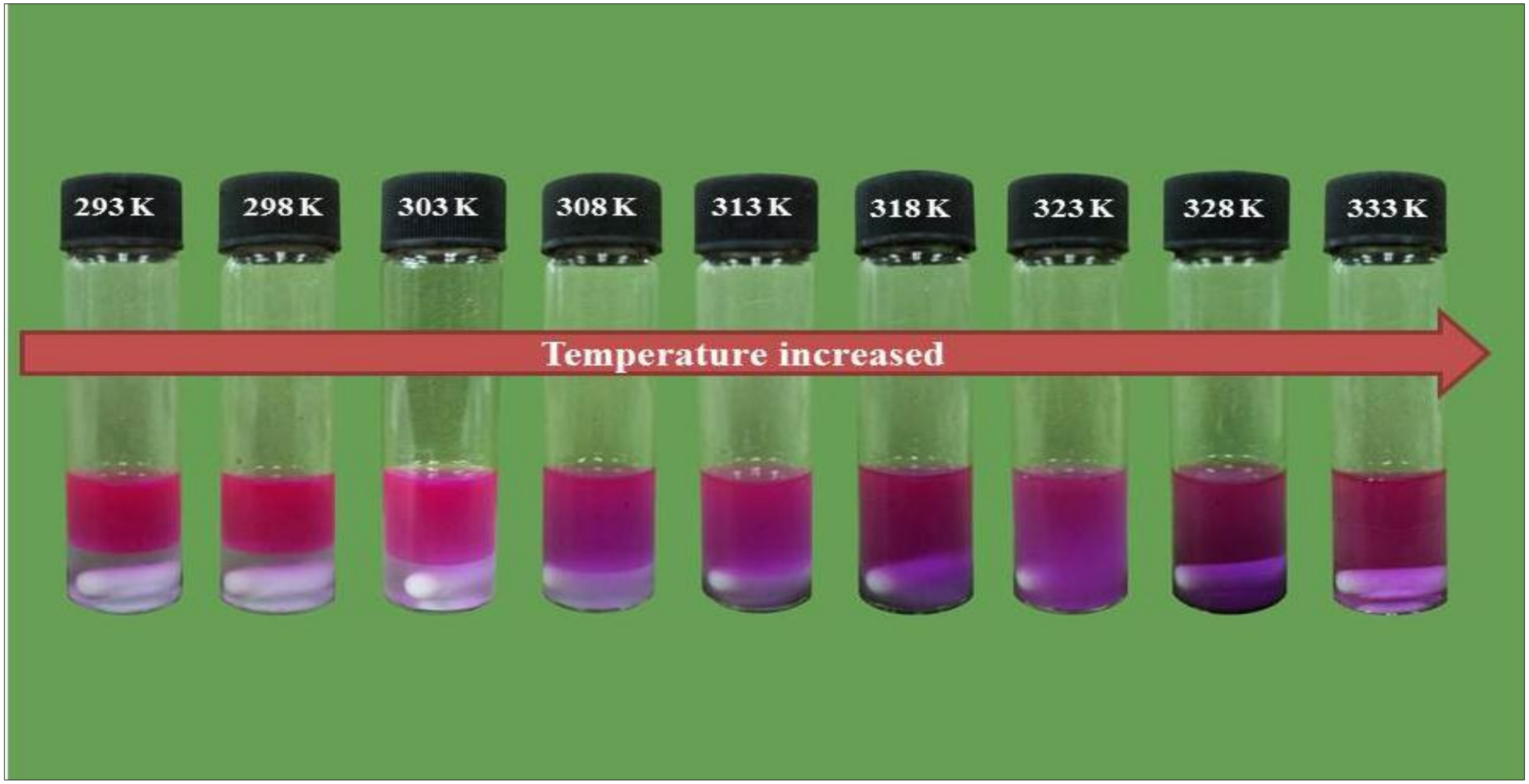


Figure 4.4. Phase behaviour of tris-(2-ethylhexyl)ammonium tosylate/ water/ isopropanol system.

4.4.2 Tris (2-ethylhexyl) ammonium tosylate / water / isopropanol system

Phase behaviour for TEHA Tosylate + water + isopropanol mixture is depicted in Figure 4.4. Similar to BEHA tosylate / water/ isopropanol system, this ternary mixture is also observed exhibiting upper critical solution temperature type phase changes (UCST). However, the temperature when it formed a clear single phase and bilayers are slightly higher compared to BEHA tosylate/ water/ isopropanol ternary system. At 333 K, this ternary mixture becomes monophasic. On the other hand, clear bilayers mixtures were observed when the temperature is at 293 K and a cloudy suspension was observed at 323 K.

4.4.3 Comparison aspects based on the observation of both thermo-responsive ternary systems.

It is well observed that there were slight temperature differences at when the mixture turned miscible or separated. The miscibility temperature for BEHA tosylate / water/ isopropanol system was 20 K lower compared to TEHA tosylate / water/ isopropanol system where the mixture shows miscibility at 333 K. Wu *et. al.* [33] studied on the few measurements on 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquid (alkyl = butyl, pentyl, hexyl, heptyl and octyl) with 1-butanol over a composition and temperature range. The “cloud point” was used in determining the bimodal curves of the mixtures. The temperature was adjusted starting from 275 – 350 K. They reported the bimodal curves on the mixtures were found to have an UCST. Decreasing clear trends on UCST were observed for the ionic liquid with shorter alkyl chain with butyl at 373 K and octyl at 326 K. The same declination trend was observed in Heinz *et. al.*study [87].

Even with their remarkable findings, the length of the cation alkyl chain does not play a significant role in this study. However, we do observed an increase in UCST trend for the more highly branched ionic liquid's cation *i.e.* TEHA tosylate. This decrease trend observation indicating that the van der Waals interactions between ionic liquid's cation and isopropanol or water is weaker in TEHA tosylate/ water/ isopropanol system compared to BEHA tosylate/ water/ isopropanol system. Despite of the temperature differences, both systems shows upper critical solution temperature (UCST) type phase behaviour.

Arce *et al.* [88] synthesized hydrophobic ionic liquids with the common anion {bis(trifluoromethyl)sulfonyl}amide. They studied on the mutual miscibility between pairs of ionic liquids that they have synthesized. It was found that the miscibility of these pairs of ionic liquids was temperature dependent, following UCST behaviour. Recently, by using dynamic method, Królikowska and Karpińska [89] studied phase equilibria of binary liquid + liquid for eight systems containing N-octylquinolinium thiocyanate [C_8iQuin][SCN] and aliphatic hydrocarbon, aromatic hydrocarbon or thiophene. The main purpose of their research was to continue searching for the best ionic liquid for the separation of aliphatic from aromatic hydrocarbons. The experiment was carried out from room temperature to the boiling point of the solvents. They have found {ionic liquid + aliphatic hydrocarbon or thiophene} binary systems exhibit the mutual immiscibility with an

UCST while {ionic liquid + aromatic hydrocarbon} binary mixture shows immiscibility gap with LCST.

UCST is the more common temperature responsive behaviour on mixture compared to LCST. However, it does not mean that LCST type phase changes were not found and reported in journals. Kohno and Ohno [81] synthesized twenty different amino acid based ionic liquids. In the other study [90], previously synthesized amino acid derived ionic liquids were then mixed with water and the phase separation was determined using common “cloud point method” at temperature range 293 K to 363 K °C. The solubility of these amino acid derived ionic liquids in water was studied. They have found all mixtures showed phase separation with LCST. As an example reported by them, tetrabutylphosphonium N-trifluoromethanesulfonyl leucine/ water mixture showed a two phase system at 298 K and complete miscibility at 295 K. As all the ionic liquids used in their study exhibited LCST type phase behaviour with water, they have concluded the LCST type phenomenon does not depend on specific structure of the side chain on the anion. However, an increase in hydrophobicity of the side chain caused the phase separation temperature to fall.

On the other aspect, Zhang *et. al*. [91] mentioned in their findings that, ionic liquid with lower freezing point and viscosity enhances the relative volatility, which means, the separation process is much more effective. We have also found that BEHA tosylate/ water/ isopropanol mixture frozen into solid at 283 K compared TEHA tosylate/ water/ isopropanol mixture frozen at temperature 288 K. Hence, in this particular case, BEHA tosylate/ water/ isopropanol mixture does have a lower freezing point. Therefore, at this point BEHA tosylate is predictably having better ability than TEHA tosylate to separate isopropanol from water.

As mentioned in chapter 3, the ionic liquid rich phase was coloured using Nile Red, which was insoluble in aqueous phase [81]. From the images provided in Figure 4.3 and 4.4, it can be seen that the nile-coloured phase was the upper layer. Reported density values for both ionic liquids were lesser than the density of water. Therefore, this clarifies the “arrangement” of both phases. The viscosity readings for BEHA tosylate are lower than TEHA tosylate, hence, this partially explained the temperature for mutual solubilities in TEHA tosylate/ water/isopropanol ternary system was slightly higher compared to BEHA tosylate / water/ isopropanol mixture. At lower temperature, the ionic liquid particles are mainly touching or perhaps may have few gaps in between particles. However, as the temperature arises, the forces that held the particles together are weaken and causing more gaps to be appeared. Hence forward, this occurrence causing the viscosity value of both protic ionic liquid decreases and therefore it is easier for isopropanol to penetrate into ionic liquid rich phase from aqueous rich phase.

4.5 Proton nuclear magnetic resonance of the thermo-responsive ternary mixtures.

In order to have a better understanding on the chemical behaviour of these thermo-responsive ternary systems, both ternary mixtures were analyzed for hydrogen bonding activity at temperature where it formed a monolayer mixture and a biphasic mixture. Up until today there were no published works that study on proton exchange involving protic ionic liquid in UCST type phase ternary system. Hence, few samples were prepared in NMR tubes in order to observe the hydrogen bonding activity. Table 4.6 represents the NMR integration values for all prepared samples. In order to understand this, the most deshielded peak which is belonging to nitrogen attached to ionic liquid's cation was focused. Since the samples were prepared based on weight per weight basis, with some advice and guidance from ^{1}HNMR experts from Monash University, a calculation was needed to determine the value per N-H proton. The formula for stated calculation is shown in equation (4.1) – (4.3) (refer Appendix XIII for calculation details and values). The value of N-H proton was divided into no deprotonation, mostly deprotonated and slightly deprotonated. We have made this classification based on the small changes of the N-H integrated values, therefore, we are finally decided that as when the calculated value is the same as integrated value, we assumed that no proton loss is observed. Most of the protons were deprotonated when the integrated value is half or more than the amount of calculated proton value. Opposite from that, when the integrated value is less than half from the calculated one, the classification falls under slight deprotonation.

$$\begin{array}{l} \text{N-H per proton value} \\ \text{(calculated)} \end{array} = \frac{\text{Percentage of ionic liquid inside the mixture}}{\text{Relative molecular weight of ionic liquid}} \tag{4.1}$$

$$\text{Water per proton value} = \frac{\text{Percentage of water inside the mixture}}{\text{Relative molecular weight of water}} \tag{4.2}$$

$$\begin{array}{l} \text{Isopropanol} \\ \text{per proton value} \end{array} = \frac{\text{Percentage of isopropanol inside the mixture}}{\text{Relative molecular weight of isopropanol}} \tag{4.3}$$

4.5.1 Bis-(2-ethylhexyl)ammonium tosylate/ water/ isopropanol system

From the integration values referred in Table 4.6, it is detected that total hydrogen loss were observed during phase separation at 289 K. On the other hands, during phase miscibility at 313 K, the N-H peak was still appeared unreacted, where, the integrated N-H proton value was almost the same as the N-H calculated value *i.e.* 0.0742, therefore, no deprotonation was observed in this case. It is assumed that, deprotonation is driving the mixture to separate. The organic rich phase and aqueous rich phase were also been analyzed. Both phases were extracted out and filled in the NMR tubes. The integration values, 0.0000, for both samples shows that the hydrogen attached to nitrogen were fully deprotonated. As the per proton value for ionic liquid is ten times smaller compared to water's and isopropanol's per proton value, 1.200 and 0.8330 (refer Appendix XIII for calculation details and values) , respectively, by looking at the ^{1}HNMR spectrum, the destination of protons that were deprotonated cannot be located. However, based on composition studies made, the proton is most probably attached to –OH group from isopropanol. As an addition to this study, a sample containing pure BEHA tosylate and isopropanol (ratio 1:1) with and without the presence of water were prepared and another sample using the same tube was added a trace of water. Both samples were analyzed for ^{1}HNMR. From the integration values of 0.0000 for both samples, it shows that deprotonation happened rapidly with or without water inside the binary mixture. Appendix XIV to XIX represents the ^{1}HNMR spectra for all samples mentioned above.

4.5.2 Tris-(2-ethylhexyl)ammonium tosylate/ water/ isopropanol system

The integration value, 0.0583, at when the sample formed a homogenous mixture (333 K) was observed to be the same as the per proton calculated value, 0.0588, indicates, no new hydrogen bonding involving N-H was observed. In contrast, at when the mixture formed bilayers (293 K), the intensity of the N-H peak seems to be smaller, N-H peak integration value is 0.0351, This concludes that, a slight deprotonation is observed during phase separation. Both upper and lower layers were analyzed for ^{1}HNMR, the integration values show that protons were mostly deprotonated. Similar to BEHA tosylate/ water/ isopropanol system, the deprotonated proton(s) is hard to be located due to the same reason mentioned in section 4.5.1. The same samples as previous system were prepared, which are samples containing pure TEHA tosylate and isopropanol (ratio 1:1) with and without the presence of water. From the ^{1}HNMR integration values, it shows that without any presence of water inside the mixture, there was no deprotonation occurred. However, when a trace of water was added into the same sample and analyzed for ^{1}HNMR, a slight deprotonation was observed, the N-H peak integration value was almost half reduced compared to the per proton calculated value. Therefore, it can be concluded, for this particular system, an optimum amount of water is needed in order to encourage deprotonation hence for making sure the mixture separates. Refer Appendix XIV to XIX for the ^{1}HNMR spectra for all samples involved.

Table 4.6. Calculation and classification of Proton Nuclear Magnetic Resonance (^{1}HNMR) spectral data for all samples analyzed.

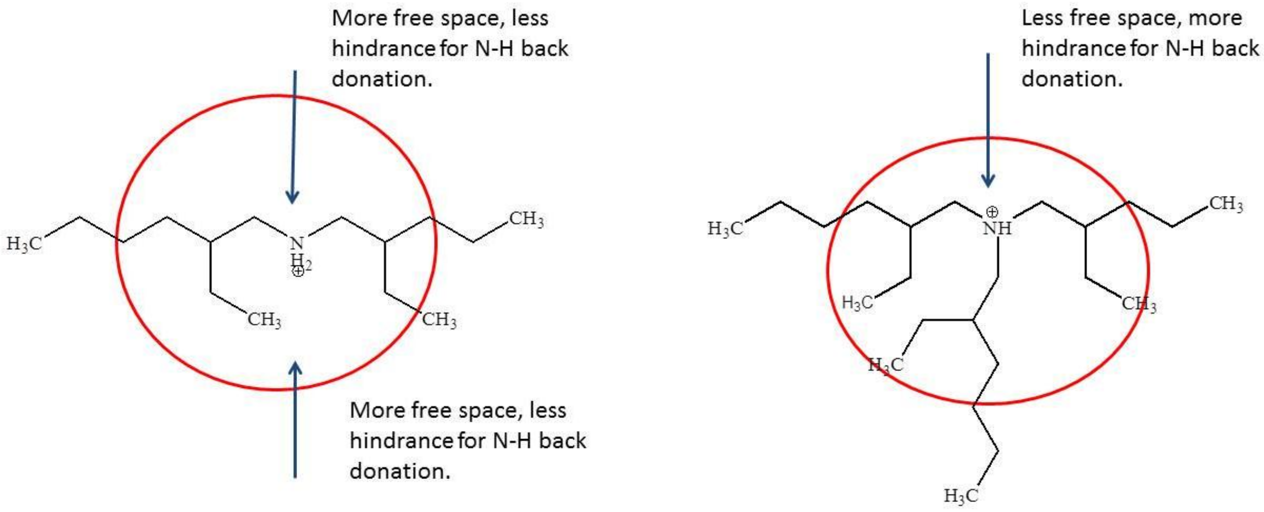
Appendix no: ^{1}HNMR spectrum	**Sample content**	**Temperature (K)**	**N-H (calculated value per proton), %w/w**	**N-H (integration value per proton), %w/w**	**Classification**
XIV	BEHA Tos + water + isopropanol (phase separated)	283	0.0741	0.0000	deprotonated
XV	BEHA Tos + water + isopropanol (phase miscibility)	313		0.0742	not deprotonated
XVI	BEHA Tos + water + isopropanol (aqueous rich phase)	298		0.0000	deprotonated
XVII	BEHA Tos + water + isopropanol (organic rich phase)	298		0.0000	deprotonated
XVIII	BEHA Tos + isopropanol	298	0.1066	0.0000	deprotonated
XIX	BEHA Tos + isopropanol + trace of water	298	0.1019	0.0000	deprotonated
XXI	TEHA Tos + water + isopropanol (phase separated)	293	0.0588	0.0351	slight deprotonation
XXII	TEHA Tos + water + isopropanol (phase miscibility)	333		0.0583	not deprotonated
XXIII	TEHA Tos + water + isopropanol (aqueous rich phase)	298		0.0220	mostly deprotonated
XXIV	TEHA Tos + water + isopropanol (organic rich phase)	298		0.0284	mostly deprotonated
XXV	TEHA Tos + isopropanol	298	0.0864	0.0862	not deprotonated
XXVI	TEHA Tos + isopropanol + trace of water	298	0.0827	0.0452	slight deprotonation

N-H $_{\text{integrated}}$ = N-H $_{\text{calculated}}$; no deprotonation
N-H $_{\text{integrated}}$ = more than 50% N-H $_{\text{calculated}}$; mostly deprotonated
N-H $_{\text{integrated}}$ = less than 50% N-H $_{\text{calculated}}$; slight deprotonation

4.5.3 Comparison between two studied systems based on the ^{1}HNMR data.

It is obvious that the ^{1}HNMR data for both ternary systems were slightly different from each other. This might be due to the structures of protic ionic liquids' cation where bis-(2-ethylhexyl)ammonium are less compact compared to tris-(2-ethylhexyl)ammonium (refer Figure 4.5 for both protic ionic liquid's chemical structure). This makes the N-H proton easier to get rid off from the cation. Yet, the "more free space" and less hindrance structure in BEHA tosylate was causing protic ionic liquid to have rapid proton exchange with aqueous proton or alcohol proton. It was observed that the protons were fully removed in BEHA tosylate / water / isopropanol ^{1}HNMR spectrums in opposite to TEHA tosylate / water / isopropanol ^{1}HNMR spectrums where few samples were observed to be partially or fully deprotonated.

However, despite of the minor dissimilarities represented in Figure 4.6 between both systems in ^{1}HNMR data, both systems show deprotonation of N-H happened during phase separation, which means, deprotonation was driving phase separations. The difference between these two systems was only the rate of proton transfer. In this particular work, it is proved that these systems were not about physical changes but also involved changes in chemical activity. The new hydrogen bonding of N-H proton with either isopropanol –OH group or water –OH group was causing the upper critical solution temperature (UCST) type phase changes in both ternary mixtures.



More free space, less hindrance for N-H back donation.

More free space, less hindrance for N-H back donation.

Less free space, more hindrance for N-H back donation.

Figure 4.5. Chemical structure: hindrance effect on both protic ionic liquids.

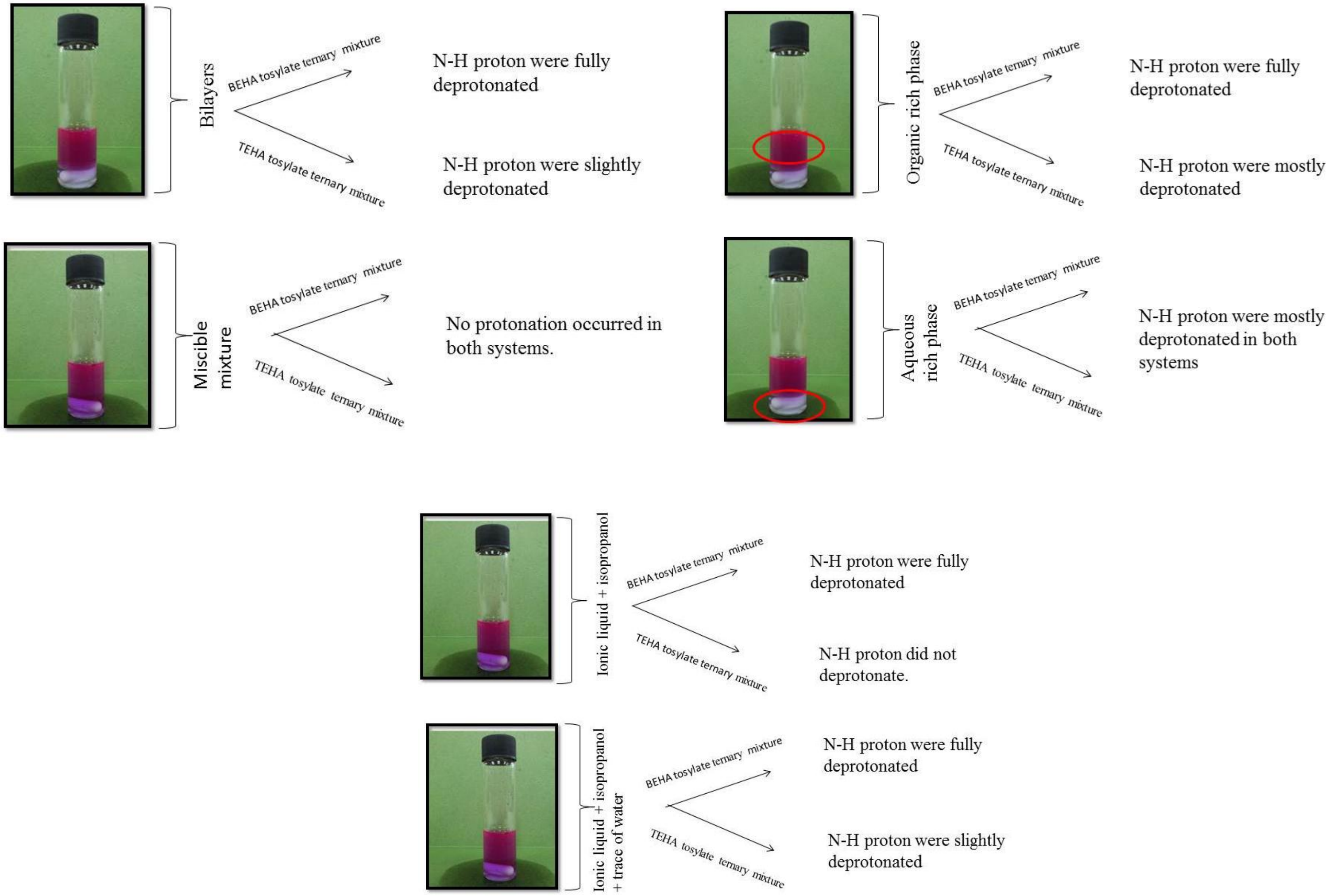


Figure 4.6. Classification of integrated N-H proton observed for both ternary mixtures.

4.6 Composition analysis of thermo-responsive ternary mixtures.

In separation study, the basic knowledge of knowing the composition of multicomponent mixtures typically involving two phases are crucially important. Hence, the purpose of this study is to examine the temperature dependence of these two protic ionic liquids in separating isopropanol from water at its best. Therefore, from the results and observation, the efficiency of both protic ionic liquids in extracting isopropanol from water will be known. The same ratio *i.e.* 1:1:1.2 of protic ionic liquid, water and isopropanol was prepared respectively. Both organic and aqueous rich phase (refer Figure 4.7) were extracted out at certain temperature and the compositions for each component inside were determined.

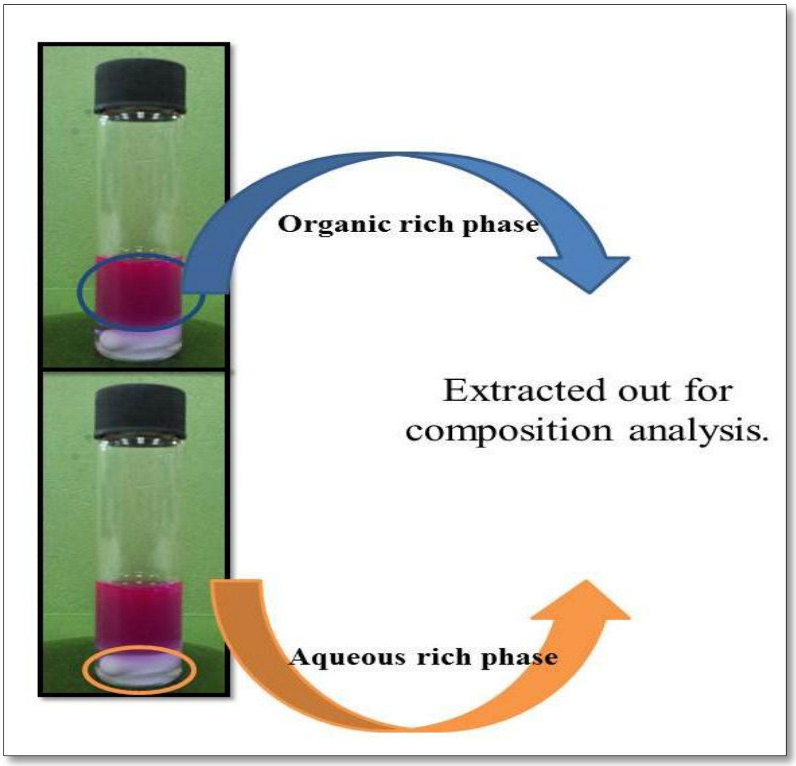


Figure 4.7. General composition analysis method overview.

4.6.1 Bis-(2-ethylhexyl)ammonium tosylate/ water/ isopropanol system

BEHA tosylate and water are partially miscible to each other at 1:1 ratio. However, water and this ionic liquid were very miscible to isopropanol. A bilayer mixture was formed when ionic liquid and water were mixed and upon addition of isopropanol, the mixture becomes cloudy and slowly separates at room temperature (≈ 293 K). Table 4.7 shows compositions of each component of each phases at all observed temperatures where the solution formed a biphasic mixture.

As shown in Figure 4.8 (a) – (c), the data were plotted into two axis graph corresponding to temperature. It was observed from the diagram, the phase compositions that isopropanol was almost extracted out (60.97 %) from water by only 32.86 % of BEHA tosylate at mixture temperature 285 K. It shows that this ternary system separates into an ionic liquid-isopropanol phase and almost pure water phase (0.59 % and 28.29 % w/w of BEHA tosylate and water still existed in isopropanol rich phase, respectively). Increasing trends of ionic liquid content were observed when the temperature for the mixture escalated in both phases. On the other hand, the isopropanol content in organic rich phase and aqueous rich phase were decreasing upon temperature. However, an opposite trend was observed for water composition, where, the water amounts in organic rich phase were slowly increased when temperature increased and a decreasing trend was observed in aqueous rich phase.

We believe the isopropanol will remain in ionic liquid – rich phase at all temperatures studied. It also appears that, at lower temperature (285 K – 296 K), the upper layer is rich with isopropanol and at higher temperature (301 K – 304 K) the layer is rich with ionic liquid, based on the reported composition data in Table 4.7. This occurrence shows that as temperature increased, higher volume of BEHA tosylate was required in order to extract isopropanol from water. Even though at higher temperature BEHA tosylate was predicted to be less viscous, hence, more isopropanol can easily diffused into the organic rich phase because of the 'more free-space' between the molecules and the situation does not assist or affect the efficiency of the extraction.

Table 4.7. Compositions of the phases in BEHA tosylate + water + isopropanol system.

Organic rich phase			
Temperature (K)	BEHA tosylate content (wt %)	Water content (wt %)	Isopropanol content (wt %)
285	32.85	6.18	60.97
289	36.37	6.39	57.24
296	51.70	7.42	40.88
301	55.37	9.44	35.19
304	59.85	10.41	29.74
Aqueous rich phase			
Temperature (K)	BEHA tosylate content (wt %)	Water content (wt %)	Isopropanol content (wt %)
285	0.59	71.12	28.29
289	3.58	70.61	25.81
296	7.55	68.86	23.59
301	11.68	66.56	21.76
304	16.45	64.21	19.34

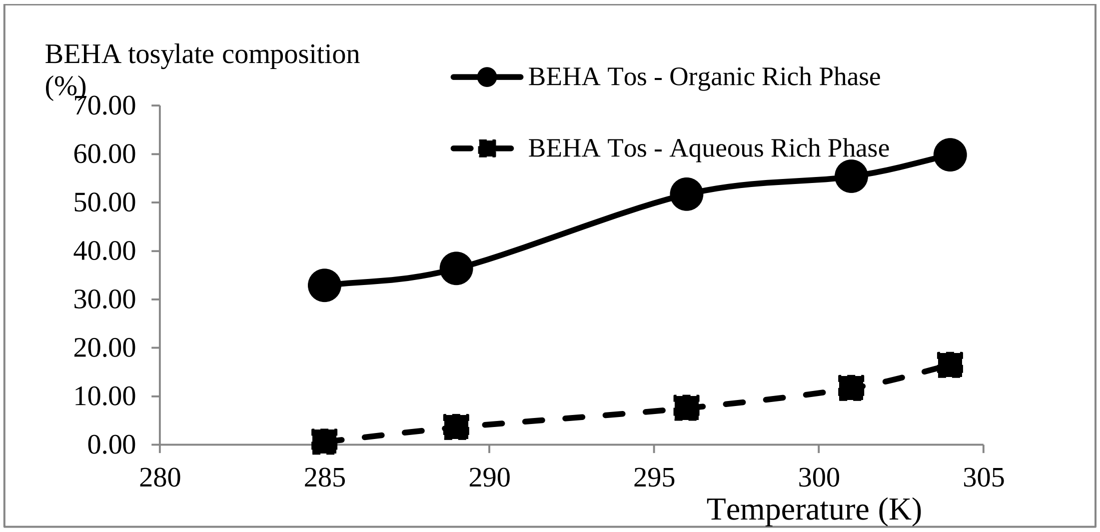


Figure 4.8 (a). Data plot for bis-(2-ethylhexyl)ammonium tosylate composition in both phases in bis-(2-ethylhexyl)ammonium tosylate + water + isopropanol system.

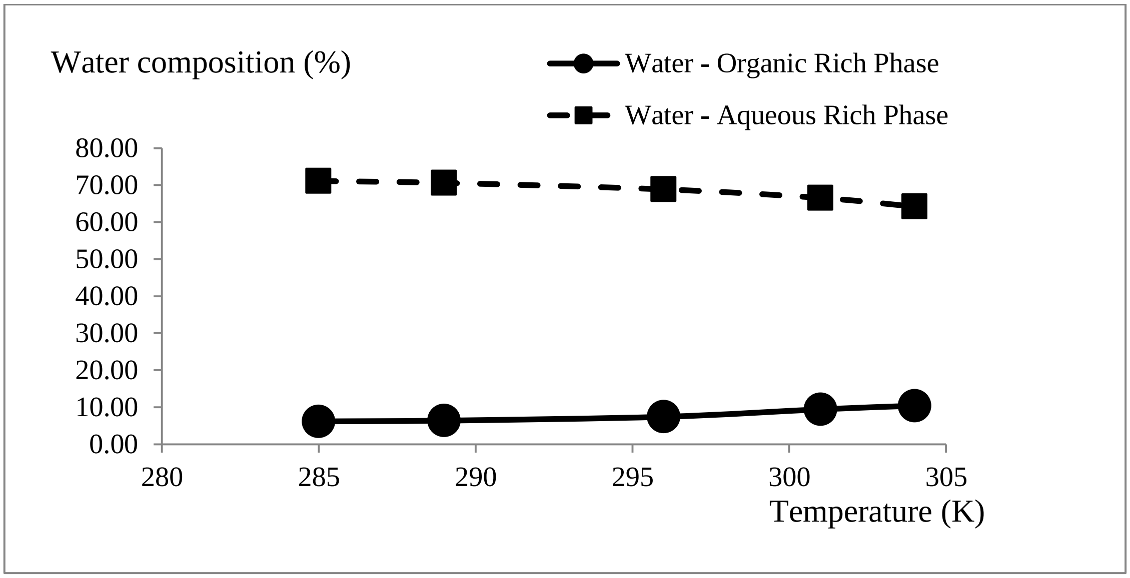


Figure 4.8 (b). Data plot for water composition in both phases in bis-(2-ethylhexyl)ammonium tosylate + water + isopropanol system.

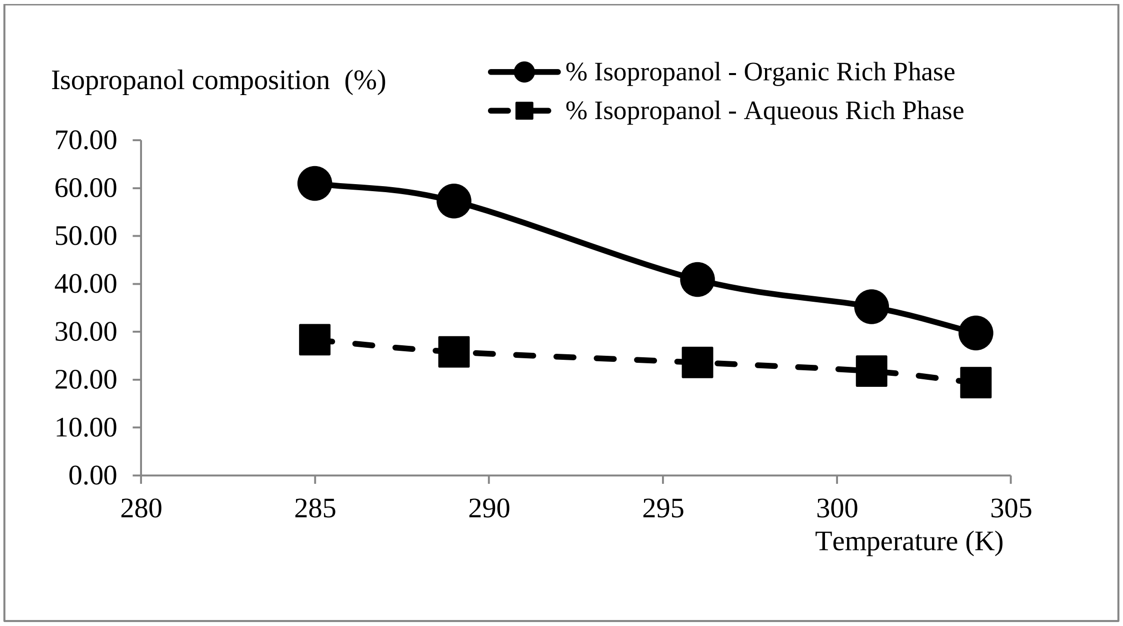


Figure 4.8 (c). Data plot for isopropanol composition in both phases in bis-(2-ethylhexyl)ammonium tosylate + water + isopropanol system.

4.6.2 Tris (2-ethylhexyl) ammonium tosylate / water / isopropanol system

Similar to BEHA tosylate, this particular protic ionic liquid is partially miscible with water. However, due to the extra 2–ethylhexyl chain, TEHA tosylate are more hydrophobic compared to bis-(2-ethylhexyl)ammonium tosylate. This matched up with Freire *et. al.* findings [92] where they have mentioned in their work that ionic liquid's cation with longer and bulky alkyl chain is more unlikely water compliance. As an addition, they have also mentioned, the number of hydrogen substitution in the ionic liquid cation will also affect the mutual solubilities between water and ionic liquid. Upon addition of isopropanol into water – TEHA tosylate mixture, similar to BEHA tosylate / water / isopropanol system, the solubilities improved and after a certain time the mixture turned cloudy and separated into two layers at room temperature (≈ 293K). Table 4.8 shows compositions of each components of each phase at all observed temperatures where the solution formed a biphasic mixture.

Table 4.8. Compositions of the phases in TEHA tosylate + water + isopropanol system.

Organic rich phase

Temperature (K)	TEHA tosylate content (wt %)	Water content (wt %)	Isopropanol content (wt %)
293	39.81	12.27	47.92
298	44.24	13.12	42.64
303	45.78	15.08	39.14
308	50.45	19.21	30.35
313	51.89	21.34	26.77

Aqueous rich phase

Temperature (K)	TEHA tosylate content (wt %)	Water content (wt %)	Isopropanol content (wt %)
293	0.21	76.68	23.01
298	4.26	73.68	22.06
303	8.97	70.91	20.12
308	14.25	66.09	19.66
313	23.15	62.86	13.99

The composition data for each component were plotted into two axis graphs. All three graphs are depicted in Figure 4.9 (a) – (c). From the results, 47.92 % of isopropanol was extracted out from water by 39.81 % of TEHA tosylate at temperature 293 K. The separation behaviour for this system was alike to BEHA tosylate/ water/ isopropanol system where at any temperature, isopropanol is surrounded by TEHA tosylate compared to water. Meanwhile, the upper layer became isopropanol rich phase at 293 K and at other temperatures it switched to TEHA tosylate rich phase.

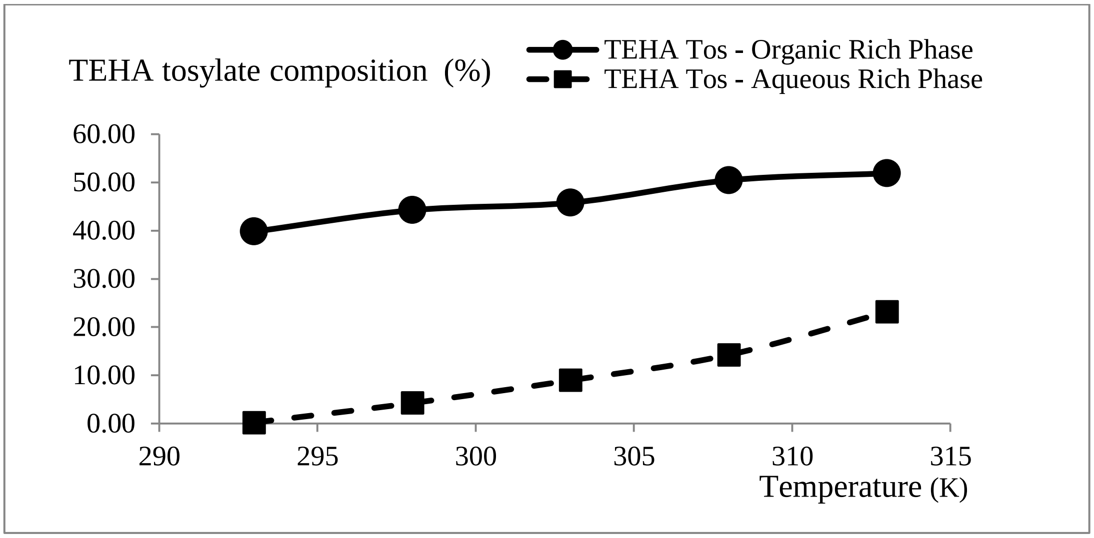


Figure 4.9 (a). Data plot for tris-(2-ethylhexyl) ammonium tosylate composition in both phases in tris (2-ethylhexyl) ammonium tosylate + water + isopropanol system.

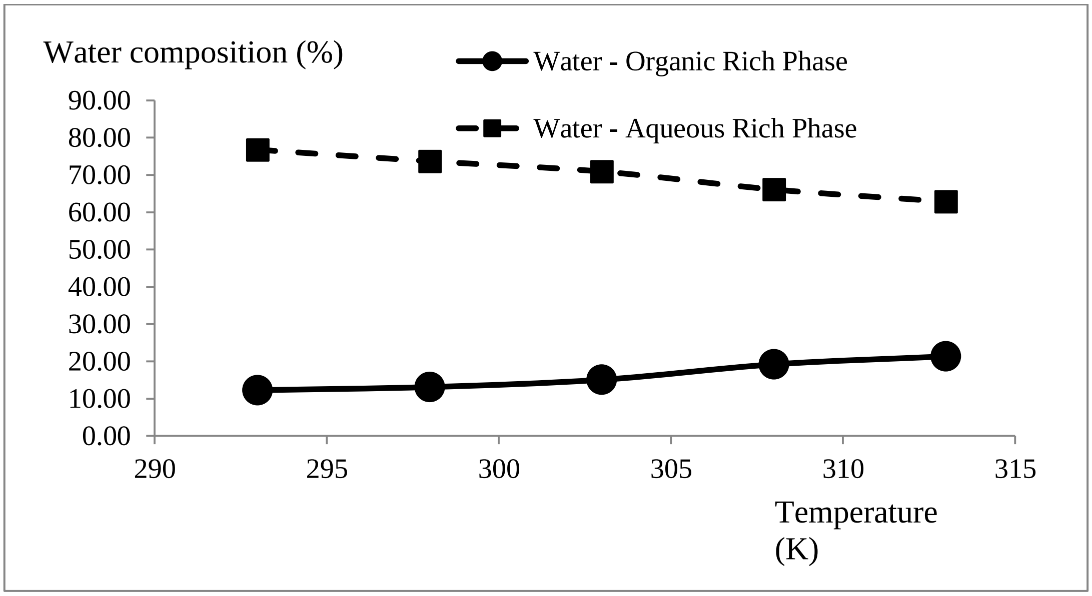


Figure 4.9 (b). Data plot for water composition in both phases in tris-(2-ethylhexyl)ammonium tosylate + water + isopropanol system.

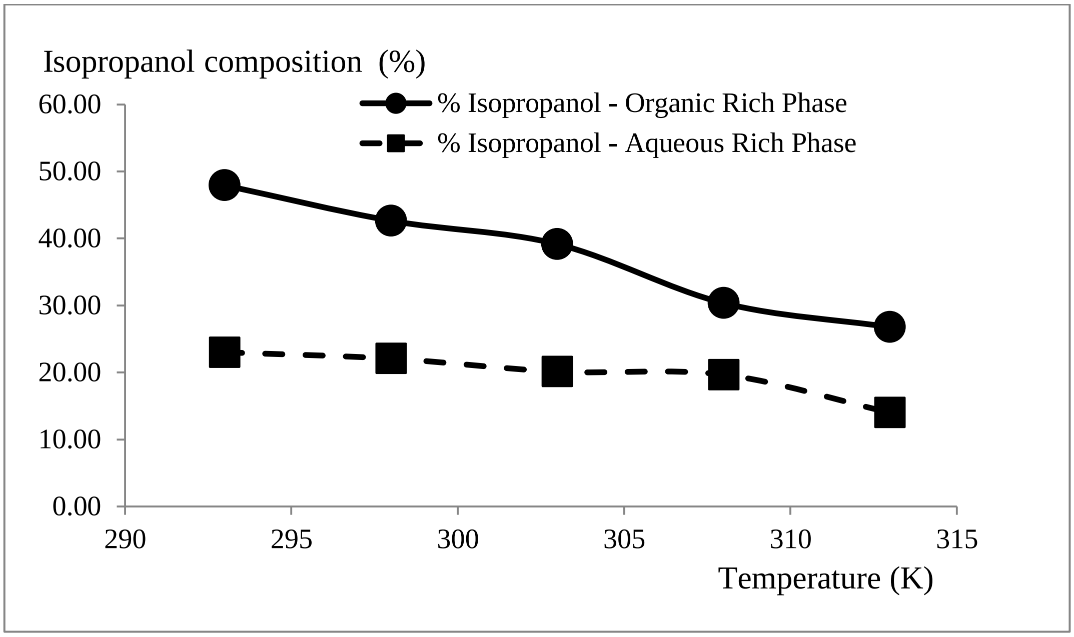


Figure 4.9 (c). Data plot for isopropanol composition in both phases in tris-(2-ethylhexyl)ammonium tosylate + water + isopropanol system.

4.6.3 Comparison between two studied systems based on the composition data.

Based on the composition data for both systems, there were slight differences on the efficiency of selected protic ionic liquids on extracting isopropanol from water. It shows that BEHA tosylate was more capable to do so compared to TEHA tosylate. It is justified from the collection of our data that 60.97 % of isopropanol was extracted out from water consuming only 32.85% of BEHA tosylate, where else, 39.81% of TEHA tosylate was needed to extract only 47.92% of isopropanol at 285 K and 293 K respectively. However, at 296 K which is the closest temperature to 293 K *i.e.* the temperature at which the maximum amount of isopropanol extracted using TEHA tosylate, 51.70% of BEHA tosylate was needed to extract 40.88 % of isopropanol. Again, this observation rationalizes that BEHA tosylate was the better extractant compared to TEHA tosylate. Despite all that, both protic ionic liquids were unable to extract 100 % of isopropanol from water. This might be due to the hydrophobic nature of both protic ionic liquids. In similar work studied by Chowdhury *et. al.* [31], two protic ionic liquids with the same organic cation, *i.e.*trihexyl(tetradecyl)phosphonium ($[P_{6,6,6,14}]+$), and different anions *i.e.* dicyanamide ($[DCA]^-$) and bis-(2,4,4-trimethylpentyl)phosphinate ($[((CH_3)_3(C_5H_8)_2PO_2]^-$) have been studied. The purpose of their study is to determine solubility lines in the $[P_{6,6,6,14}][DCA]$ + water + ethanol (first system), $[P_{6,6,6,14}][DCA]$ + water + acetonitrile (second system), $[P_{6,6,6,14}]$ $[((CH_3)_3(C_5H_8)_2PO_2]$ + water + ethanol (third system) and 1-ethyl-3-methylimidazolium ethylsulfate, [emim] $[C_2H_5SO_4]$ + water + toluene (fourth system). In the first system reported by them, 40 % of acetonitrile managed to be extracted from water by consuming only 8 % of ionic liquid. However, in the second system, 44 % of ethanol was extracted from water with only 9.5 % of $[P_{6,6,6,14}][DCA]$. For the third system, 12.5% of ionic liquid managed to extract 48.5 % of ethanol from water and finally in the fourth system, only 1 % of [emim]$[C_2H_5]$ was used to extract toluene from water. Despite of their outstanding results, much more improvements and studies will be needed as the time evolve before replacing volatile organic solvent to ionic liquid in extracting solvent process.

Zhang *et. al.* [91] indicated in their study smaller imidazolium ionic liquid *i.e.* 1-ethyl-3-methylimidazolium acetate has a significant effect on enhancing relative volatility compared to the bigger ionic liquid *i.e.* 1-butyl-3-methylimidazolium acetate. The advantage of this, it has lower freezing point and viscosity. Thus, 1-ethyl-3-methylimidazolium acetate has a better tendency extracting 2-propanol from water than 1-butyl-3-methylimidazolium acetate. Hence, this partially explains why in this study BEHA tosylate is a better extractor than TEHA tosylate.

As reported in Table 4.1, the density for BEHA tosylate is higher than TEHA tosylate. However, these values do not contribute in the efficiency of separation. Density plays bigger role in determining which layer does an organic or aqueous rich phase sits. In this case, both protic ionic liquids' density values were lower than the density of water ($\rho_{\text{water}} = 1.000$ kg/m^3). Therefore, the upper layer will always be rich with ionic liquid and the bottom layer is rich with water. Nevertheless, it is not possible for any UCST or LCST mixture to have such occurrence where the ionic liquid rich phase and aqueous rich phase exchange places at certain temperature. This has been proven by Kohno and Ohno [81] where they have witnessed the incident in ternary solution of protein cytochrome c, water and amino acid ionic liquid.

Reportedly, viscosity value for BEHA tosylate is much lower than TEHA tosylate, almost half the value. In this case, unlike density, viscosity affecting much more on the chemical behaviour of both mixtures rather than physical observation. It is obvious that separation using TEHA tosylate as an extractant was much more demanding compared to BEHA tosylate. Since TEHA tosylate is much thicker than BEHA tosylate, it is difficult for isopropanol to diffuse into the organic rich phase.

This has been proven from the composition values which have been explained in sections 4.4.1 and 4.4.2. Hence, protic ionic liquid with lower viscosity value *i.e.* BEHA tosylate is the better extractant than protic ionic liquid with higher viscosity value *i.e.* TEHA tosylate.

As an addition to points above, theoretically, as we have always understood, “like dissolves like”, in this case, since water is a very polar molecule, non-polar ionic liquids, BEHA tosylate and TEHA tosylate, as a solute eagerly dissolves and extracts out a semi-polar solvent which is isopropanol in water-isopropanol mixture. Therefore, this explained why isopropanol would dissolve in protic ionic liquid compared to water even though water and isopropanol is very miscible to each other. On the other hand, the nature of isopropanol structure assists protic ionic liquid to select which of the two solvents to be extracted *i.e.* between isopropanol and water. Since both protic ionic liquids used are both bulky and hindered by 2-ethylhexyl groups, it makes water harder to interact with hydrogen attached to nitrogen of ionic liquids.

4.7 Conclusion

The separation process took place essentially at lower temperature for both systems. It was observed that these two ternary systems exhibited upper critical solution temperature (UCST) type phase changes, at when the temperature was at 313 K and 333 K, whereby a clear single mixture for BEHA tosylate/ water/ isopropanol and TEHA tosylate/ water/ isopropanol system is formed respectively.

Since BEHA tosylate's structure is less hindered by (2-ethylhexyl) group compared to TEHA tosylate's structure, it was found that BEHA tosylate/ water/ isopropanol system shows rapid deprotonation during phase separation. However, it is proved that deprotonation was driving phase separation for both systems. It was also verified that the separation process occurred was not just because of physical changes but it was also related to chemical activities between N-H proton and –OH group from isopropanol or water.

As expected from stated observations, it was verified that BEHA tosylate has a better ability to extract isopropanol from water compared to TEHA tosylate. However, both protic ionic liquids failed to extract 100 % composition of isopropanol from water. On the other hand, despite of less than 100% percentage of isopropanol extracted, these studies shows that both protic ionic liquids have the potential to be used in aqueous isopropanol extraction. From the data collected, BEHA tosylate extracted out 60.97 % of isopropanol and TEHA tosylate extracted 47.92 % of isopropanol. Less hydrophobic ionic liquid can be used in future studies in order to get a better extraction. However, it is still not confirmed whether the "less hydrophobic ionic liquid/ water/ isopropanol" will exhibits UCST or LCST type phase behaviour.