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To cite this article: M. A. M. Abdullah *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **736** 042027

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Synthesis and characterization of thermo-responsive ionic liquids (TRILs)

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Abstract. Normally, an ionic liquids (ILs) is classified as hydrophilic or hydrophobic depending on its composition, whether it is miscible or immiscible with water. Nevertheless, this classification is ambiguous, since the miscibility of some ILs with water is strongly depending on temperature change. There are two classifications of thermo-responsive ionic liquids (TRILs) which are lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behavior types. The aim of this study is to synthesis and characterize tetrafluoroborate-based (BF_4^-) anion with different alkyl chain of imidazolium-based cations ([Emim], [Bmim], [Hmim], [Omim]) and trifluoroacetate (CFOO^-) anion with different cations (ammonium, anilinium, pyridinium and phosphonium). The prepared ILs were mixed with water (30:70 wt %) and the resulting solutions were stirred vigorously for certain period of time. These solutions were cooled to 0 °C and then gradually heated to 70 °C. When the solution was found to be phase-separated upon heating, this mixture undergoes the LCST-type phase transition but its contrary with UCST behavioral. The TRILs were characterized using Fourier Transform Infrared (FTIR) to identify the functional group and Nuclear Magnetic Resonance (NMR) in confirming the structure. Due to the special property of TRILs that became phase separation by changing the temperature, it can be recovered easily and reused for many recycles in wide range of application.

1. Introduction

Traditionally ILs are known as molten salts that typically liquid at temperature below 100 °C in atmospheric pressure. The progress of new research areas on ILs is due to their unique properties such as chemical and thermal stability, negligible vapor pressure (non-volatile), high ionic conductivity, high solubility and non-flammability [1–6]. Many unsafe volatile organic compounds as solvent can be replace with ILs because of negligible vapor pressure thus could be considered as “green solvent”. [7–9]. Furthermore, up to trillion possibilities of cation and anion combination can be synthesized by tuning the alkyl chain and an ionic precursor is the major advantage that made ILs widely used for others applications such as catalysis [10–12], electrochemistry [13], extraction [14,15], membrane technology [16–18] and many others by screening and selecting the suitable cations and anions.

Usually, ILs are not miscible in non-polar solvents, but miscible in polar solvent. The main effect that contribute on solubility of ILs in water is typically the anion instead of the cation. Nevertheless some modification of cation can be made by increasing the alkyl chains length that can reduce polarity of ILs in water or others polar solvent [19]. Water solubility is an important parameter, and it also



depending on the anion. Hexafluorophosphate (PF_6) and bis(trifluoromethylsulfonyl)imide (NTf_2) based ILs are hydrophobic. Besides that, halides (Cl, Br, F), tetrafluoroborate (BF_4) and triflate (CF_3) based ILs commonly are hydrophilic [20]. Recently, thermo-responsive ionic liquids (TRILs) behaviour in water have been widely discovered especially as draw solution in forward osmosis process [21–25] and can be considered as ‘smart solvent’ due to temperature depending on miscibility in water. There are two classifications of TRILs which are lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behavior.

In the LCST-type phase transition, the ILs become homogeneous mixture upon cooling and undergo phase separation upon heating. Interestingly, out of millions even many more different cation–anion combinations, most of the LCST-type ILs reported are based on derivations of phosphonium cations, such as tributyloctyl or tetrabutyl phosphonium cations ($[\text{P}_{4448}]$ or $[\text{P}_{4444}]$) and tetrabutylammonium $[\text{N}_{4444}]$. Trifluoroacetate $[\text{CF}_3\text{COO}]$ and derivatives of benzenesulfonate $[\text{C}_6\text{H}_5\text{O}_3\text{S}]$ are the most common anions employed to make LCST-type ILs [26]. Contrary to the LCST-type IL, the UCST-type IL become homogeneous mixture during heating and undergo phase separation upon cooling. The physico-chemical properties of most ILs are strongly dependent on the type of cation and anion, while very small changes in the structure of IL can drastically affect the mutual miscibility with other solvents including ILs [27]. In many mixtures, the observations of UCST were limited by the boiling temperature of the solvent.

For this study, imidazolium salt was used eight combination of ILs which are $[\text{Hmim}][\text{BF}_4]$, $[\text{Omim}][\text{BF}_4]$, $[\text{P}_{4444}][\text{TFA}]$, $[\text{TEPy}][\text{TFA}]$, $[\text{Anilinium}][\text{TFA}]$ and $[\text{TEA}][\text{TFA}]$ as show in figure 1 below were synthesized except $[\text{Emim}][\text{BF}_4]$ and $[\text{Bmim}][\text{BF}_4]$ were directly purchased. All prepared ILs were screened to identify the type of phase separation toward water. The TRILs that have been undergo LCST or UCST were accordingly obtained and discussed.

2. Experimental

2.1. Materials

1-ethyl-3-methylimidazolium tetrafluoroborate (97.0%), 1-butyl-3-methylimidazolium tetrafluoroborate (98%), 1-hexyl-3-methylimidazolium chloride (97.0%), 1-octyl-3-methylimidazolium chloride (97.0%), triethylamine (99.5%), 2,3,5-trimethylpyridine (99%), aniline (99%), sodium tetrafluoroborate (98%), tetrabutylphosphonium hydroxide (40 wt. %), trifluoroacetic acid for synthesis was purchased from Sigma Aldrich. Acetone and dichloromethane analytical reagent (AR) grade were purchased from R&M Chemicals. All chemicals were used without any further purification.

2.2. Synthesis of ionic liquids

There are several routes to synthesis ILs and two main techniques of preparing ILs are acid base neutralization and metathesis [28]. The acid-based neutralization technique is quite simple by mixing equimolar of selected acid and based needed to prepare ILs. The advantages using this technique is possible to obtain the salts without the formation of by-products and can avoid contamination [29]. There are several alkyl-imidazolium halides commercially available and they can be used directly in metathesis reactions. However, this technique has some drawbacks because low product yield achieved resulting from by product formation [30].

2.2.1. Acid base neutralization. Equal molar amounts of trifluoroacetic acid and selected cation (triethylamine, 2,3,5-trimethylpyridine, aniline & tetrabutylphosphonium hydroxide) were mixed in a three-necked round bottom flask equipped with reflux condenser and a magnetic hot plate stirrer. The reaction mixture was reacted under N_2 atmosphere at room temperature with stirring for 3 hours in inert condition. After 3 hours, the reaction mixture was heated under N_2 at mild condition about 50°C with stirring for 24 hours to remove the water form during reaction process. Finally, the appearance of

the reaction mixture changed to viscous liquid. Finally, the IL was dried in a rotary evaporator and then under vacuum for 12 h at 65–70 °C.

2.2.2. *Metathesis*. Equal molar of alkyylimidazolium chloride was mixed with sodium tetrafluoroborate in ethanol and stirred vigorously for 24 h. After that, the precipitated was then filtered off and washed with acetone to remove the excess of halide salt. Lastly, the IL was dried in a rotary evaporator as mentioned at neutralization method above. After synthesis of ILs was completed, the mass of ILs was measured and the yield % was calculated by using eq. 1.

$$\text{Yield \%} = \frac{\text{mass}_{\text{actual}}}{\text{mass}_{\text{theoretical}}} \times 100 \quad (1)$$

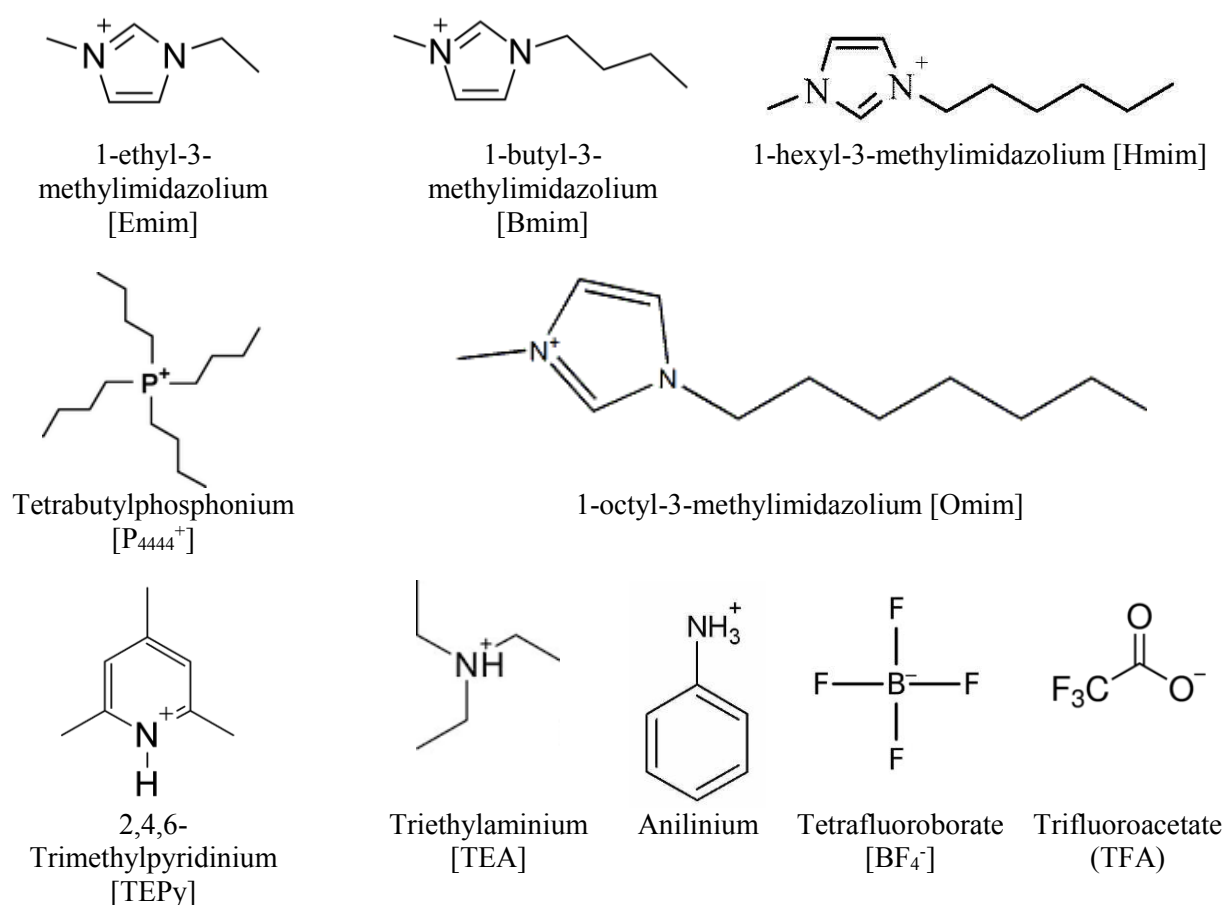


Figure 1. Cation and anion structure of ILs in this study

2.3. Characterization

2.3.1. *FTIR*. FTIR-ATR Spectroscopy analysis was performed on the ILs samples using a Thermo Fisher Nicolet iS5 FT-IR spectrometer with an ID7 ATR. The spectra were recorded in absorbance mode with a resolution of 4 cm⁻¹ in the range of 600–4000 cm⁻¹. Samples are placed on a germanium ATR crystal, which has a 45° angle of incidence, and spectra are recorded with 1 cm⁻¹ resolution under a dry air purge.

2.3.2. *NMR*. ^1H and ^{13}C NMR spectroscopic studies were carried on a Bruker Ultra Shield Plus 500 MHz (^1H —300.53 MHz and ^{13}C — 75.43 MHz). ^1H NMR spectra were referenced to external trimethyl silane (TMS). The sample was placed in a 5 mm NMR tube, degassed by three freeze–pump–thaw cycles and sealed under vacuum. Dimethyl sulfoxide- d_6 (DMSO- d_6) was used as external lock solvent contained in a capillary.

2.4. Phase separation

The 30 wt% of prepared ILs were mixed with 70 wt% of water and the resulting solutions were stirred vigorously. These solutions were cooled to 0 °C and then gradually heated to 70 °C with the heating rate 5 °C per 10 minutes by using water bath. When a solution was found to be phase-separated upon heating, this mixture underwent the LCST-type phase transition and contrary with UCST. The time taken used to complete the phase separation process was determined and recorded.

3. Result and discussion

3.1. Synthesis

This neutralization method results very well with tertiary amines with acetate acids because the [TEA][TFA] achieved highest yield which is 94.27%. In contrast to metathesis of alkyl-imidazolium chloride with sodium BF_4 , the lowest yield achieved which is 50.31% yield of [Omim][BF_4]. The rest of synthesized ILs yield achieved were showed at table 1. Even tough metathesis reaction is quite simple and easy to prepare but its reaction may occur contamination with a small amount of halide ions, which may react with solute materials and the presence of water. On the other hand, the uses of organic solvent like acetone to wash the product to remove halide salt leads to the formation of undesired compound [31].

Table 1. Yield % for synthesized ILs and colour

IL Combination	Yield %	Colour
[Hmim][BF_4]	52.01	Yellowish
[Omim BF_4]	50.31	Yellowish
[P ₄₄₄₄][TFA]	73.22	Colourless
[TEPy][TFA]	83.06	Light pink
[Anilinium][TFA]	79.23	Light blue
[TEA][TFA]	94.27	Yellowish

3.2. Characterization

3.2.1. *FTIR*. The major absorption peaks obtained from FTIR spectrum are listed below and these are identified with the functional groups that are responsible for the different modes of vibrations. The FTIR spectra of synthesized ILs are shown in figure 2.

[Hmim][BF_4]. FTIR spectrum: 1635.95 cm^{-1} (Ring anti-symmetric $\text{N}(\text{CH}_2)$), 1572.11 cm^{-1} (Ethyl HCH anti-symmetric bend), 1465.86 cm^{-1} (CN stretching), 1379.86, 1338.28, 1285.51 cm^{-1} (Aromatic Amine & C=C stretching), 1052.85 (BF_4 anti-symmetric stretching).

[Omim][BF_4]. FTIR spectrum: 1635.95 cm^{-1} (Ring anti-symmetric $\text{N}(\text{CH}_2)$), 1572.11 cm^{-1} (Ethyl HCH anti-symmetric bend), 1465.86 cm^{-1} (CN stretching), 1379.86, 1338.28, 1285.51 cm^{-1} (Aromatic & C=C stretching), 1052.85 (BF_4 anti-symmetric stretching).

[P₄₄₄₄][TFA]. FTIR spectrum: 2937.98 cm⁻¹ (C-H stretching for alkyl), 1735.07 cm⁻¹ (conjugated acid C=O), 1138.81 cm⁻¹ (C-F compound).

[TEPy][TFA]. FTIR spectrum: 2734.89 cm⁻¹ (C-H stretching for alkyl), 1776.29 cm⁻¹ (conjugated acid C=O), 1637.81 cm⁻¹ (conjugated acid C=O), 1430.92 78 cm⁻¹ (Aromatic amine C-N stretching), 1137.27 cm⁻¹ (C-F compound).

[Anilinium][TFA]. FTIR spectrum: 1636.01 cm⁻¹ (conjugated acid C=O), 1498.78 cm⁻¹ (Aromatic amine C-N stretching), 1194.34 cm⁻¹ (C-F compound).

[TEA][TFA]. FTIR spectrum: 2991.72 cm⁻¹ (C-H stretching for alkyl), 1669.87 cm⁻¹ (conjugated acid C=O), 1123.54 cm⁻¹ (C-F compound), 1035.15 cm⁻¹ (C-N stretching for amine).

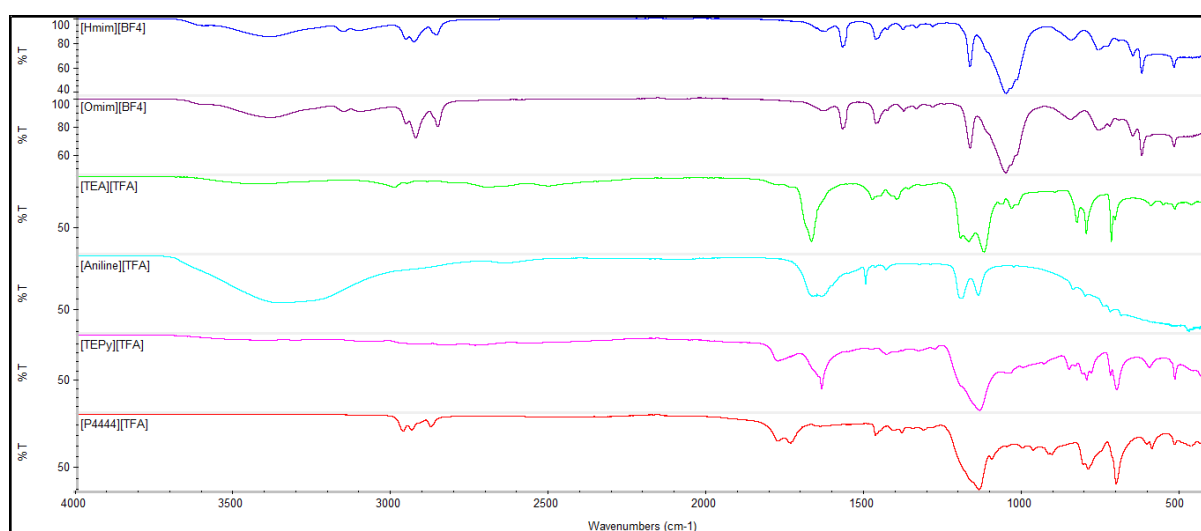


Figure 2. FTIR spectra of synthesized ILs

3.2.2. *NMR*. The chemical shifts of residual H in DMSO is 2.5 ppm relative to TMS. Negative chemical shifts and positive chemical shifts indicate upfield and downfield from the reference correspondingly. The splitting patterns of resonance were described by the following: singlet (s), doublet (d), triplet (t), quartet, (q) and multiplet (m)

[Hmim][BF₄]. ¹H NMR: 0.82 ppm (3H, s, CH₃-), 1.24 ppm (6H, s, -CH₂-CH₂-CH₂-), 1.76 ppm (2H, d, J = 6.3 Hz, -CH₂-), 3.5 ppm (2H, s, -CH₂-), 3.8 ppm (3H, s, CH₃-), 4.19 ppm (2H, m, J = 7.18 Hz, -CH₂-), 7.78 ppm (1H, d, J = 4.15 Hz, -H), 7.86 ppm (1H, d, J = 5.35 Hz -H), 9.42 ppm (1H, d, J = 8.85 Hz, -H). ¹³C NMR: 13.72 ppm (CH₃-), 21.82, 25.08, 29.35, 30.50, 35.60 ppm (-CH₂-), 39.22 ppm (CH₃-N), 48.64 ppm (CH₂-N), 122.17, 123.47, 136.56 ppm (C-Aromatic).

[Omim] [BF₄]. ¹H NMR: 0.57 ppm (3H, s, CH₃-), 0.97 ppm (8H, s, -CH₂-CH₂-CH₂-), 1.56 ppm (2H, d, J = 13.8 Hz, -CH₂-), 3.29 ppm (2H, s, -CH₂-), 3.63 ppm (3H, s, CH₃-), 3.95 ppm (2H, m, J = 7.20 Hz, -CH₂-), 7.55 ppm (1H, d, J = 4.15 Hz, -H), 7.63 ppm (1H, d, J = 5.25 Hz -H), 9.24 ppm (1H, d, J = 8.73 Hz, -H). ¹³C NMR: 14.28 ppm (CH₃-), 22.48, 25.95, 28.81, 28.93, 29.91, 31.61, 36.10 ppm (-CH₂-), 39.96 ppm (CH₃-N), 49.15 ppm (CH₂-N), 122.69, 123.96, 137.12 ppm (C-Aromatic).

[P₄₄₄₄][TFA]. ¹H NMR: 0.916 ppm (12H, t, J = 7.15 Hz, CH₃-), 1.41 ppm (8H, m, J=14.70 Hz, -CH₂-), 1.47 ppm (8H, m, J = 6.05 Hz, -CH₂-), 2.18 ppm (8H, t, J = 2.60 Hz, -CH₂-). ¹³C NMR: 13.53,

17.58, 17.96, 23.05 ppm (CH₃-), 23.08, 23.71, 23.83, 39.38, 39.55, 39.71, 39.88, 40.05, 40.21 ppm (-CH₂-), 40.38 ppm (C-F), 112.73, 115.06, 117.38, 119.70 ppm (C-P), 159.04 ppm (C=O).

[TEPy][TFA]. ¹H NMR: 2.44 ppm (1H, s, N-H), 2.60 ppm (9H, s, (CH₃-), 7.48 ppm (2H, d, J = 2.95 Hz, H-Aromatic). ¹³C NMR: 18.70, 18.74, 21.26 ppm (CH₃-), 39.29 ppm (C-F₃), 112.50, 114.81, 117.12, 119.42, 125.37 ppm (C-Aromatic), 159.11 ppm (C=O).

[Anilinium][TFA]. ¹H NMR: 4.76 ppm (4H, s, -NH₄), 7.37 ppm (5H, m, J = 7.80 Hz, Aromatic-H). ¹³C NMR: 38.77 ppm (C-F₃), 115.78, 118.13, 122.95, 128.52, 130.30, 132.03 ppm (C-Aromatic), 160.65 ppm (C=O).

[TEA][TFA]. ¹H NMR: 1.18 ppm (9H, t, J = 7.32 Hz, (CH₃-), 3.10 ppm (6H, m, J = 7.52 Hz, (-CH₂-). ¹³C NMR: 8.56, 24.45, 29.54 ppm (CH₃-), 33.82, 39.61, 42.83 ppm (-CH₂-), 45.97 ppm (C-F₃), 113.48, 115.83, 118.18 ppm (C-N), 159.71 ppm (C=O).

3.3. Phase separation

The miscibility of ILs at room temperature were observed and we find out all of prepared ILs were miscible in water except [Hmim][BF₄] and [Omim][BF₄]. After IL/water mixture were separated by thermally stimulate, only four combination of ILs undergo phase separation upon cooling or heating as stated in table 1. [P₄₄₄₄][CF₃COO] was undergo LCST phase separation while [Bmim][BF₄], [Hmim][BF₄] and [Omim][BF₄] undergo UCST phase separation.

Table 2. IL/water mixture phase separation behavior with ratio 30:70

IL Combination	Type of separation	CST value (°C)	Cond. at room temperature	Time taken (min)
[Emim][BF ₄]	-	-	Miscible	-
[Bmim][BF ₄]	UCST	5	Miscible	30
[Hmim][BF ₄]	UCST	55	Immiscible	25
[Omim][BF ₄]	UCST	65	Immiscible	10
[P ₄₄₄₄][TFA]	LCST	50	Miscible	60
[TEPy][TFA]	-	-	Miscible	-
[Anilinium][TFA]	-	-	Miscible	-
[TEA][TFA]	-	-	Miscible	-

Based on literature, the LCST of [P₄₄₄₄][TFA] was about 29°C [29]. This temperature stimulated phase change process is reversible and fast. [P₄₄₄₄][TFA] formed homogenous mixtures with water at low temperature. When mild heating was applied about 45 °C, it was observed that the clear solution turned to turbid and phase separation started. When it was heated above LCST, a clear liquid-liquid phase separation appeared which formed H₂O-rich sediment phase and ILs-rich supernatant phase as shown in figure 3.

Differing with LCST type-IL, [Bmim][BF₄] phase separation occurs during cooling in the ice bath. The time taken for phase separation [Bmim][BF₄] about 30 minutes at temperature 5 °C compare to [P₄₄₄₄][CF₃COO] take about 1 hour at temperature 50 °C. In contrast, [Hmim][BF₄] and [Omim][BF₄] was homogenous with water at temperature 70 °C. The phase separation occur when the IL/water mixture was cooling down at temperature 55 °C (25 min) and 65 °C (10 min) respectively.

According to Ohno and Kohno (2012), the phase separation temperature of the IL/water mixtures are strongly depended on the hydrophobicity of the component ions as well as mixing ratio [26]. Obviously in this study, the longer alkyl chain length in alkyl-imidazolium cation would decrease the immiscibility in water cause by stronger hydrophobicity. While for LCST behaviour, it was reported that by increasing the temperature of solution making hydrogen bonding interaction between the

anions of trifluoroacetate acid increased. This means the anion–H₂O electrostatic interaction is weakened and directly causes separation of ILs from water showing LCST behaviour [32]. Thermoregulated property of ILs principally attributed to hydrogen bonding or other possible interactions between IL and certain solvent. Therefore, it can be understood as temperature-dependent solubility property[33].

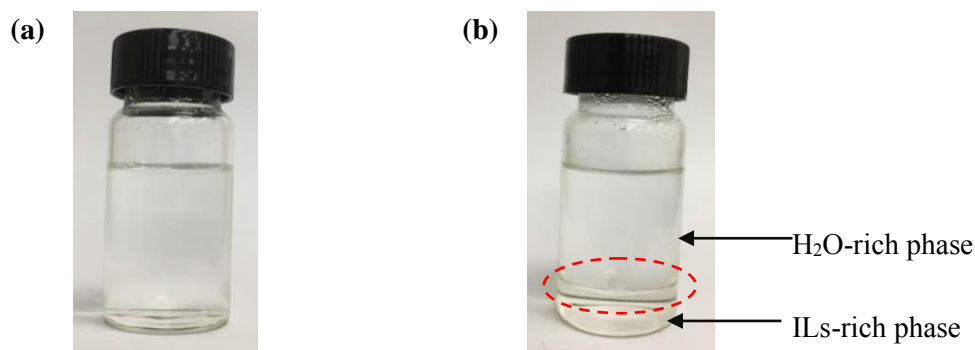


Figure 3. Thermally stimulated phase separation process of LCST-type IL
(a) before heating (b) after heating

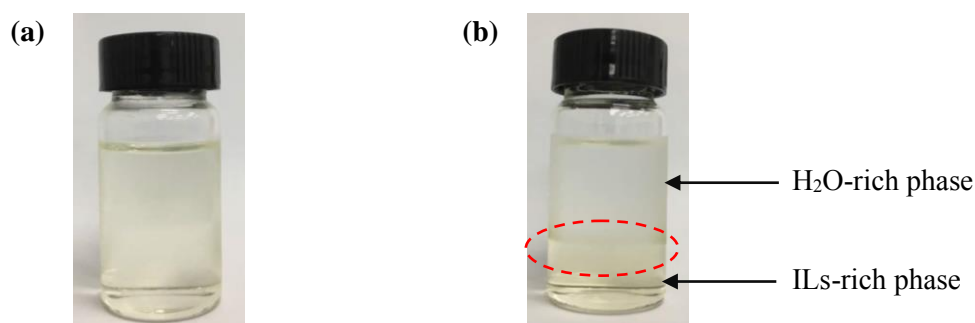


Figure 4. Thermally stimulated phase separation process of UCST-type IL
(a) before cooling (b) after cooling.

4. Conclusion

In this work, six combination of ILs were successfully synthesized by using metathesis method ([Hmim][BF₄] & [Omim][BF₄]) and acid base neutralization ([P₄₄₄₄][TFA], [TEPy][TFA], [Anilinium][TFA] and [TEA][TFA]). Their chemical structures were characterized using ¹H NMR, ¹³C NMR and FTIR. The [P₄₄₄₄][TFA] go through LCST phase separation at temperature 50 °C and alkyl-imidazolium BF₄ except [Emim][BF₄] were go through UCST phase separation at temperature 5 °C ([Bmim][BF₄]), 55 °C ([Hmim][BF₄]) and 65 °C ([Omim][BF₄]). This thermally stimulated phase separation permitted the ILs to be efficiently reused and regenerated for various applications and can be considered as environmental friendly solvent.

Acknowledgments

This research received funding under the Fundamental Research Grant Scheme (FRGS - RDU160128) by the Ministry of Higher Education Malaysia.

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