

CHAPTER 3

MATERIAL AND METHOD

3.0 Overview

In this chapter the methods used for the synthesis of potential ILs and extractive desulfurization process are discussed in detail. The chemicals and reagents used and their sources are also listed.

3.1 Chemical and Reagent

All the chemicals and reagents used in the present study are classified into two parts namely for synthesis and extraction purposes, which are listed in Table 3.1 and Table 3.2, accordingly. The chemicals were used as received without further purification except for those used for extractive desulfurization.

3.1.1 Chemicals in ILs Synthesis

The exploitation of various precursors along with their reagents used in producing in-house ILs for extractive desulfurization purposes are listed in Table 3.1 below. Several of the synthesized ILs are new and currently are not available in the market.

Table 3.1: List of precursors, chemicals and reagents for synthesizing ILs

	Name of Chemical	Assay	Supplier
ILs	1-butyl-3-methylimidazolium hydrogensulfate	98%	Merck
	1-butyl-3-methylimidazolium bromide	98%	Merck
	1-butyl-3-methylimidazolium chloride	98%	Merck
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	1-butylimidazole	98%	Sigma Aldrich
	1-methylimidazole	99%	Sigma Aldrich
	4-methylpyridine	97%	Sigma Aldrich
	1-methylpyrazole	99%	Sigma Aldrich
	1-methylpyrrolidine	97%	Sigma Aldrich
	1-methylbenzimidazole	99%	Sigma Aldrich
	Barium hydroxide	95%	Sigma Aldrich
	Salicylic acid	99.94%	Fisher Scientific
	Sodium benzoate	99%	Sigma Aldrich
	Sodium chloride	99%	Merck
	Sodium salicylate	99.5%	R&M Chemicals
	Potassium dihydrogenphosphate	98%	HmbG Chemicals
	Dibutyl sulfate	98%	Sigma Aldrich
	Dimethyl sulfate	99%	Merck
	Tributylphosphate	99%	Merck
	Trimethylphosphate	98%	Merck
	Imidazole	99%	Sigma Aldrich
	Pyrazole	98%	Sigma Aldrich
	Acetone	99.8%	Merck
	Diethyl ether	99.7	BDH Chemicals
	Methanol	99.9%	Merck
	Toluene	99.99%	Fisher Scientific
	N ₂ gas	99.999%	MOX Linde
	Deionized water	-	-

3.1.2 Chemicals in Extractive Desulfurization

The chemicals used in the extractive desulfurization process are listed in Table 3.2. Prior to use the ILs for the extraction process, water content in the ILs was removed by subjecting the ILs to vacuum evaporation at 70°C and 10⁻² mbar for 24 hours. High content of water may affect the extraction efficiency. This step was necessary to reduce the water content below 500 ppm as well as other volatile solvent contained in the ILs.

Table 3.2: List of ILs and reagents for extractive desulfurization

	Name of Chemical	Assay	Supplier
	1-butyl-3-methylimidazolium trifluoroacetate	98%	Merck
	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	98%	Merck
Ionic Liquids	1-butyl-3-methylimidazolium trifluoromethanesulfonate	98%	Merck
	1-butyl-3-methylimidazolium octylsulfate	98%	Merck
	1-butyl-3-methylimidazolium tricyanomethane	98%	Merck
	1-butyl-3-methylimidazolium dicyanamide	98%	Merck
	1-butyl-3-methylimidazolium nitrate	98%	Merck
	1-butyl-3-methylimidazolium thiocyanate	98%	Merck
	1-butyl-3-methylimidazolium acetate	98%	Merck
	1-butyl-3-methylimidazolium tosylate	97%	Fluka
	1-butyl-3-methylimidazolium methylsulfate	98%	Merck
	<i>n</i> -dodecane	99%	Merck
	<i>n</i> -heptane	99.3%	Merck
	Benzene	99.7%	Merck
	<i>p</i> -Xylene	99%	Sigma Aldrich
Benzothiophene	97%	Acros	
Dibenzothiophene	99%	Acros	

3.2 Overall Experimental Flowchart

The overall experimental flowchart for this study basically on extractive desulfurization using ILs is given in Figure 3.1. The detail experimental procedure for each part is described further in this chapter, whereby five main parts are contained throughout this study. The main parts are screening process using predictive tools to select potential ILs, synthesis of ILs, ILs characterization, extractive desulfurization performance and lastly regeneration of spent ILs.

In the ILs screening process, the procedures for selecting suitable ILs are described in detail. The selected ILs were then synthesized according to the procedures as described in synthesis part. Before conducting any experiment, all ILs were characterized in order to understand their behaviour during desulfurization. Finally, the spent ILs were regenerated to study the potential ILs for reuse purposes besides to complete the process loop of using ILs in desulfurization process.

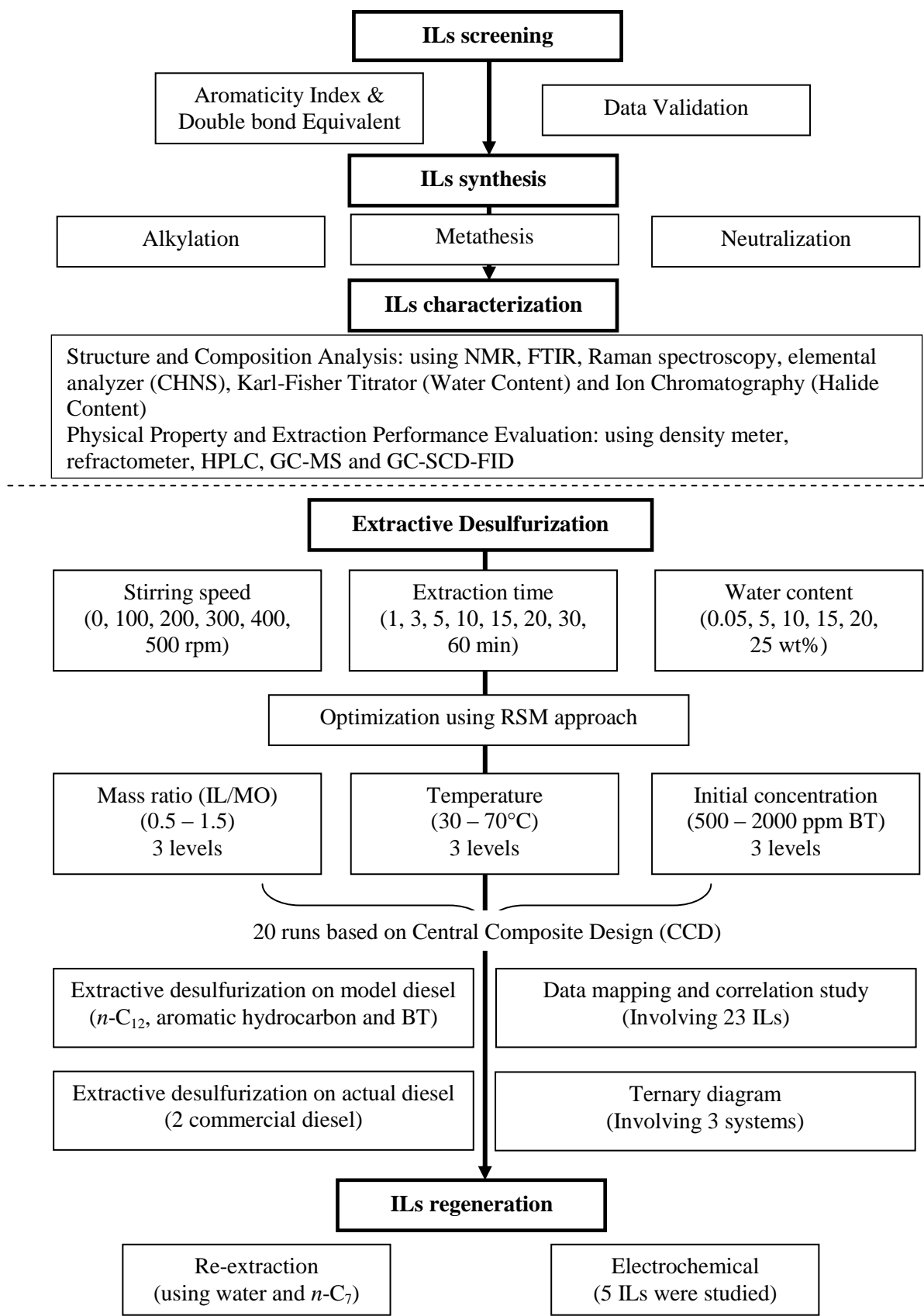


Figure 3.1: Flowchart of overall experimental activities involved in this study

3.3 ILs Screening

Screening of ILs using conventional approach involving entirely experimental works is very costly as it is very time consuming, beside needing high amount of materials for the process. Therefore, in this study the potential ILs was screened using suitable model or software. One of the established methods for ILs screening for liquid-liquid extraction is Conductor like Screening Model for Realistic Solvents (COSMO-RS).

3.3.1 Application of COSMO-RS for ILs Screening

COSMO-RS is known as a powerful method for molecular description and solvents screening based on quantum chemical approach. Successful application of COSMO-RS has been reported recently for selection of ILs for extraction of phenol, aliphatic hydrocarbons, flavonoids and mono ethylene glycol from different streams (*Mohanty et al. 2010; Garcia-Chavez et al. 2012*). The present study utilized the same method to screen potential ILs for sulfur compound extraction from model oil.

COSMOTerm C2.1 is a software package that calculates thermodynamic properties using the COSMO-RS theory. The theory is based on quantum chemical computations and statistical thermodynamics. Evaluation of a possible ILs with COSMO-RS firstly involves quantum chemical calculations to approximate the electron density functions of the solvents (ILs) and solutes (sulfur compounds) by molecular surface σ -electron density profiles. Then, it involves the surface σ -electron profiles in statistical thermodynamics to estimate the activity coefficient (γ) of the solute in the solvent (*Eckert and Klamt, 2002*).

There are two important parameters that determine the extractability of a solvent at infinite dilution namely capacity, C and selectivity, S. Capacity is defined as the maximum amount of sulfur compound that can be dissolved in the ILs and is numerically expressed as in Eq. 3.1. Selectivity is defined as the ratio of sulfur compound in the ILs rich phase and in model oil rich phase. It is given by the Eq. 3.2 below (*Kumar and Banerjee, 2009*).

$$C_{12}^{\infty} = \left(\frac{1}{\gamma_1^{\infty}} \right) \quad (3.1)$$

$$S_{12}^{\infty} = \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}} \right)^{ILs\ Phase} \left(\frac{\gamma_1^{\infty}}{\gamma_2^{\infty}} \right)^{Model\ Oil\ Phase} \approx \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}} \right)^{ILs\ Phase} \quad (3.2)$$

Here ‘1’ and ‘2’ represents the sulfur compounds (i.e. BT and DBT) and *n*-dodecane (as the model oil) respectively. In order to judge the effectiveness of ILs as a solvent, the overall performance of the ILs can be calculated by the performance index (PI) as given by the Eq. 3.3 (Kumar and Banerjee, 2009).

$$PI = C_{12}^{\infty} \cdot S_{12}^{\infty} \quad (3.3)$$

3.3.2 AI assisted COSMO-RS for ILs Screening

Due to inconsistent results predicted by COSMO-RS and interaction mechanism theory, aromaticity index (AI) was introduced to assist or support COSMO-RS prediction. The AI value is solely calculated from the exact molecular mass formula of the only cation part of ILs using Eq. 3.4 which has been simplified by Koch and Dittmar in 2006 for natural organic compounds studies.

$$AI = \frac{1 + C - O - S - 0.5H}{C - O - S - N - P} \quad (3.4)$$

The number of each atom of carbon, C, oxygen, O, sulfur, S, hydrogen, H, nitrogen, N and phosphorus, P in the cation of ILs provide the value of AI.

3.3.3 DBE assisted COSMO-RS for ILs

Besides AI, double bond equivalent (DBE) was also introduced based on the same reasons described for AI where DBE is estimated from the molecular mass formula of the other ILs part which is the anion. Koch and Dittmar, (2006) simplified the relationship in Eq. 3.5 where N_i and V_i are the number of atom and valence of each atom, respectively.

$$DBE = 1 + \frac{\sum_i^{i \max} N_i (V_i - 2)}{2} \quad (3.5)$$

3.4 ILs Synthesis

Using the above screening method of COSMO-RS approach assisted by AI and DBE predictions, 25 ILs were selected for further studies. From the 25 selected ILs, 13 ILs were synthesized in-house according to the procedures reported in the literatures with slight modification, while the rest were purchased largely from Merck chemicals supplier. Three different methods namely metathesis, alkylation and neutralization were employed to synthesize the 13 ILs. A brief description of each method is given below.

3.4.1 Metathesis

Metathesis usually refers to salt transposition which involves exchange of parts between two reacting chemical compounds to create the product with identical bonding affiliations. This is the common method for producing in-house ILs. In this study, four ILs were synthesized via this method.

3.4.1.1 Preparation of [bmim][DHP]

Equimolar of 1-butyl-3-methylimidazolium chloride, [bmim][Cl] (**1**) was added to a solution of potassium dihydrogen phosphate (**2**), KDHP in acetone/water mixture at 7/3 volume ratio. The mixture was stirred at room temperature for at least 24 hours. The mixture was then centrifuged, and the resulting precipitate of potassium chloride, KCl (**4**) was removed by filtration, while the filtrate was rotary evaporated under reduced pressure. The resultant liquid was then washed repeatedly with cooled acetone followed by evaporation under reduced pressure to yield 1-butyl-3-methylimidazolium dihydrogen phosphate (**3**), [bmim][DHP], a colourless liquid.

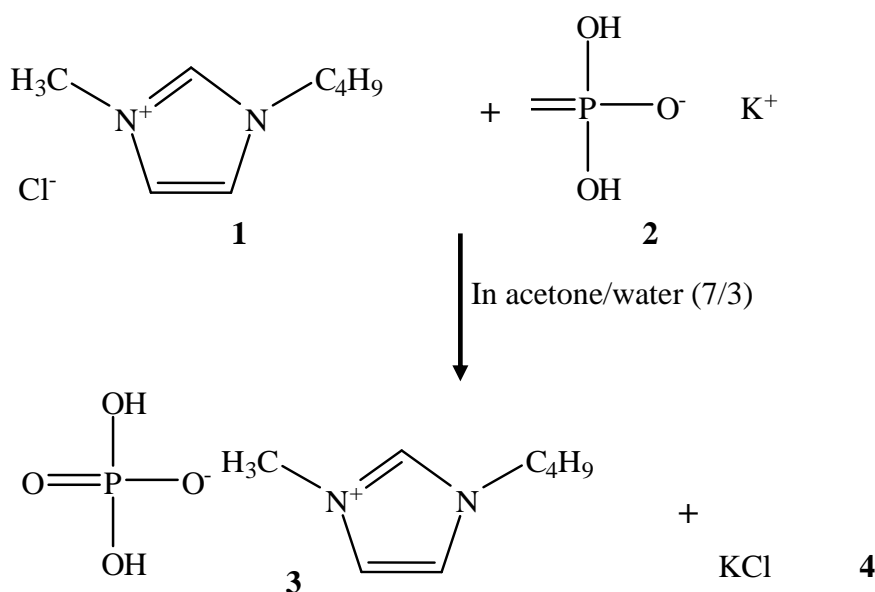


Figure 3.2: Synthesis via metathesis of [bmim][Cl] with KDHP to produce [bmim][DHP] and by-product KCl in acetone/water mixture. The volume ratio of acetone/water (7/3) was used to completely dissolve KDHP in the mixture during stirring process.

3.4.1.2 Preparation of [bmim][Imd] and [bmim][Pyd]

Equimolar of the respective salt, imidazole (1) or pyrazole (2) was added to a solution of sodium hydroxide, NaOH in methanol, and the mixture was stirred at room temperature for at least half an hour. Equimolar of 1-butyl-3-methylimidazolium bromide (3), [bmim][Br] was added and the mixture was stirred for another three hours. After three hours, appropriate amount of diethyl ether was added, and stirring was continued overnight. Three layers were obtained; the bottom layer (third layer), which was sodium bromide, was removed by filtration. The filtrate which contained of two layers was carefully rotary evaporated under reduced pressure. The mixture was then repeatedly cooled with diethyl ether followed by evaporated under reduced pressure to yield 1-butyl-3-methylimidazolium imidazolid (4), [bmim][Imd], the brownish liquid or 1-butyl-3-methylimidazolium pyrazolide (5), [bmim][Pyd], the yellowish liquid, respectively.

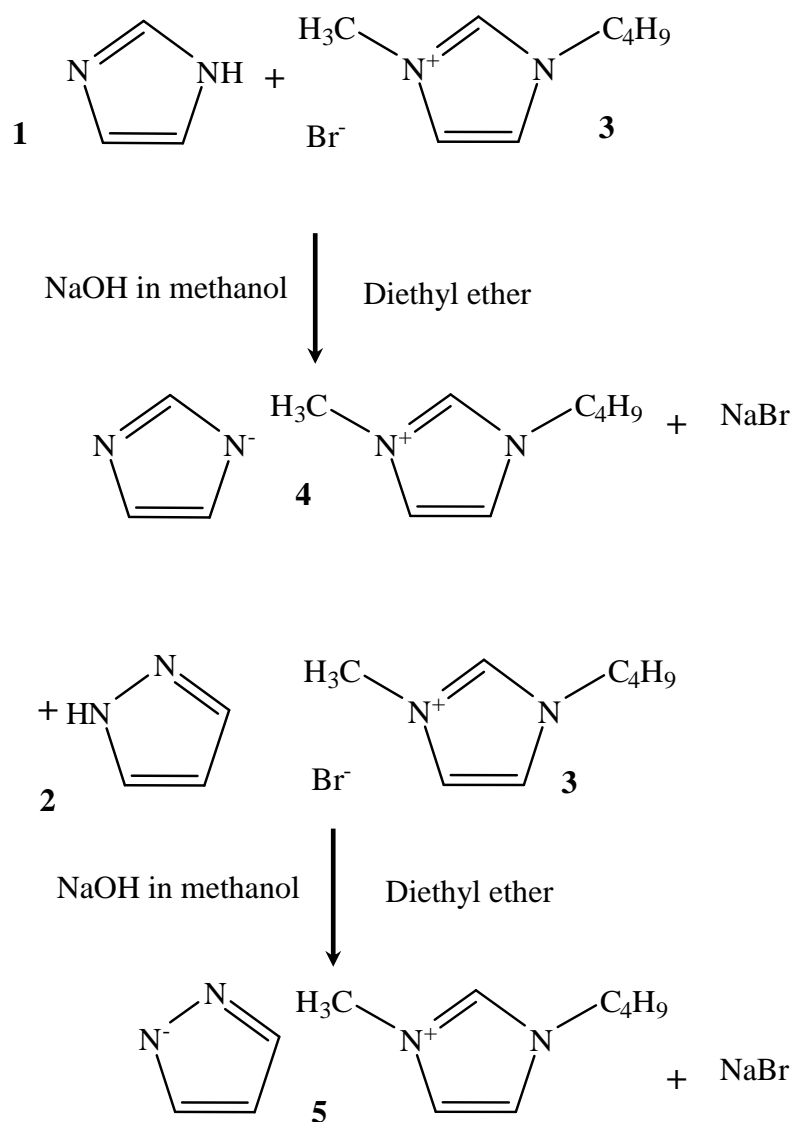


Figure 3.3: Synthesis route of [bimim][Imd] and [bimim][Pyd]

3.4.1.3 Preparation of [bimim][SCL]

Equimolar of [bimim][Cl] (2) was added to a sodium salicylate (1) in an appropriate amount of acetone, and the mixture was stirred at room temperature for at least 24 hours. Then the mixture was centrifuged, and the resulting precipitate of sodium chloride, NaCl was removed by filtration, while the filtrate was evaporated under reduced pressure. Then, the reduced filtrate was washed repeatedly with cooled acetone followed by evaporated under reduced pressure to yield 1-butyl-3-methylimidazolium salicylate (3), [bimim][SCL] a light brown liquid.

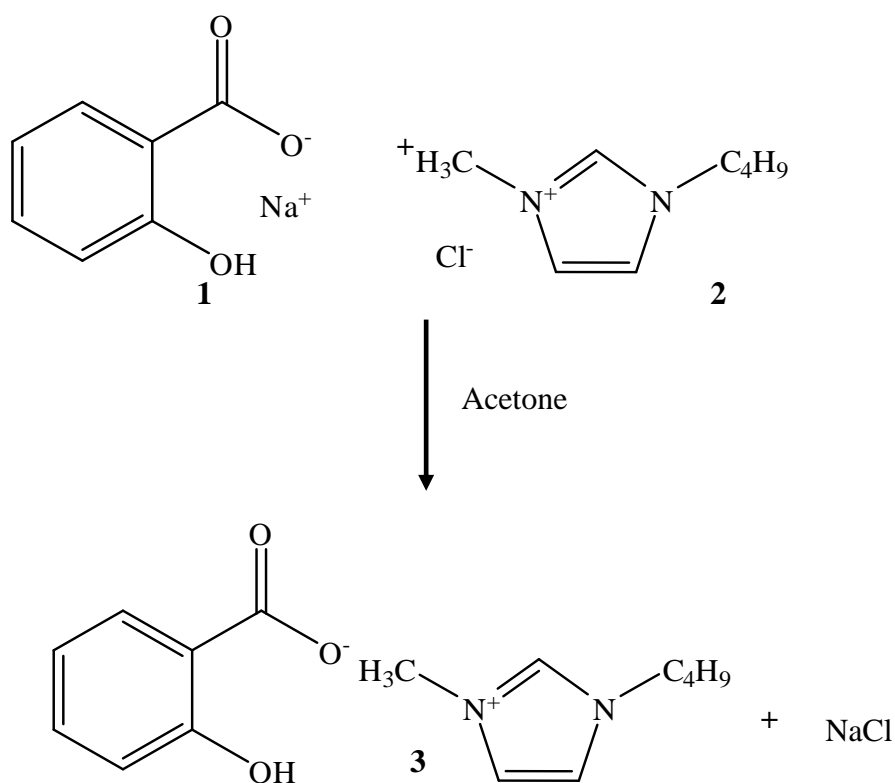


Figure 3.4: Metathesis synthesis of [bmim][SCL]. Here, acetone is preferred as a solvent for easy removal of sodium chloride, NaCl which is insoluble in this solvent.

3.4.2 Alkylation

Producing ILs without traces of halides is a requirement because they may affect the extraction performance. The presence of traces of halides in ILs can be eliminated by alkylation method (*Eber et al. 2004*). In this study, eight ILs that were classified as sulfate-based and phosphate-based ILs were synthesized via this method.

3.4.2.1 Preparation of Sulfate-based ILs

Six alkyl sulfate-based ILs were prepared by alkylation using alkyl salts namely 1-methylbenzimidazole, 1-methylimidazole, 1-methylpyridine, 1-methylpyrazole and lastly 1-methylpyrrolidine with either dimethyl sulfate or dibutyl sulfate in toluene at certain temperature. The reactions were spontaneous and toluene was used to act as diluent and heat-sink to reduce the exothermic reactions that occurred (*Mochizuki and Sugawara, 2008; Holbrey et al. 2002*).

In a round bottom flask fitted with a reflux condenser, dimethyl sulfate (**2**) was added dropwise to an equimolar of 1-methylbenzimidazole (**1**) in toluene (15mL), and the mixture was heated up to 75°C in an oil bath filled with paraffin oil. The reaction was conducted in an inert condition by introducing N₂ into the round bottom flask. The formation of 1,3-dimethylbenzimidazolium methylsulfate (**3**), [mmBzim][MSO₄] was instantaneous with biphasic formation; the top layer was toluene and the opaque layer at the bottom was the resultant IL. After the addition of dimethyl sulphate (2.4mL, 25mmol), the reaction mixture was stirred at 70°C for one hour. The upper, organic phase was decanted and the lower, IL phase was washed several times with toluene, followed by drying at 70°C under reduced pressure to remove the residual reactants and organic solvents. Finally, the reduced liquid was dried in a vacuum oven to yield a white powder salt of [mmBzim][MSO₄] free from residues.

The same procedures were applied for the syntheses of five other ILs, which are briefly described below. Figure 3.5 showed the syntheses route of all five ILs.

Ionic liquid: 1,3-dimethylimidazolium methylsulfate (**6**), [mmim][MSO₄]

Reactants: 1-methylimidazole (**4**) (2.0mL, 24mmol) and equimolar of dimethyl sulfate (**5**) in toluene (15mL) at room temperature.

Ionic liquid: 1-butyl-3-methylimidazolium butylsulfate (**9**), [bmim][BSO₄]

Reactants: 1-methylimidazole (**7**) (2.0mL, 24mmol) and equimolar dibutyl sulfate (**8**) in toluene (15mL) at room temperature

Ionic liquid: 1,4-dimethylpyridinium methylsulfate (**12**), [mmpy][MSO₄]

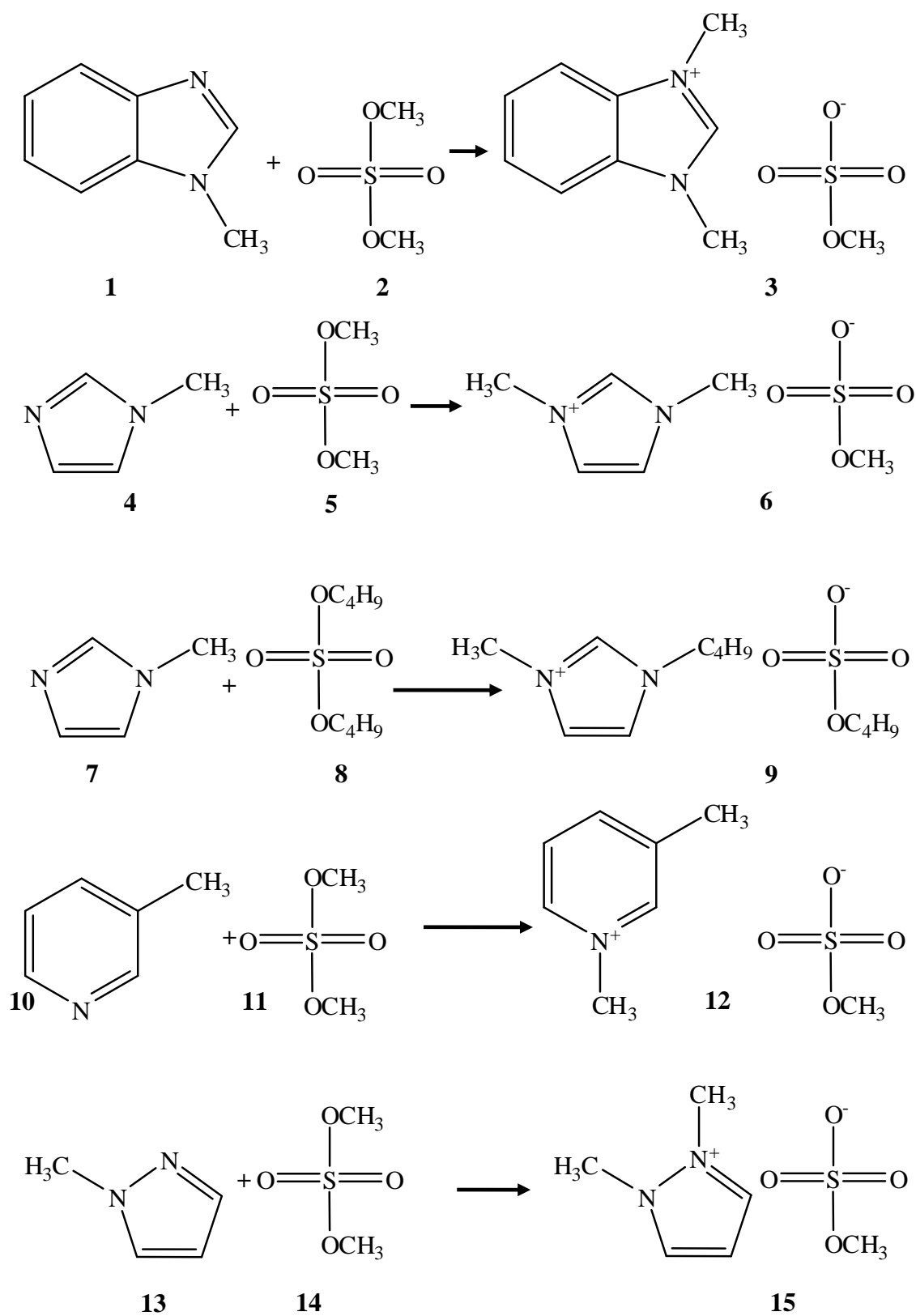
Reactants: 3-methylpyridine (**10**) (2.2mL, 25mmol) and equimolar dimethyl sulfate (**11**) in toluene (15mL) at room temperature

Ionic liquid: 1,2-dimethylpyrazolium methylsulfate (**15**), [mmpyz][MSO₄]

Reactants: 1-methylpyrazole (**13**) (2.0mL, 24mmol) and equimolar dimethyl sulfate (**14**) in toluene (15mL) at room temperature

Ionic liquid: 1,1-dimethylpyrrolidinium methylsulfate (**18**), [mmpyrr][MSO₄]

Reactants: 1-methylpyrrolidine (**16**) (2.0g, 24mmol) and equimolar diethyl sulfate (**17**) in toluene (15mL) at 45°C reaction



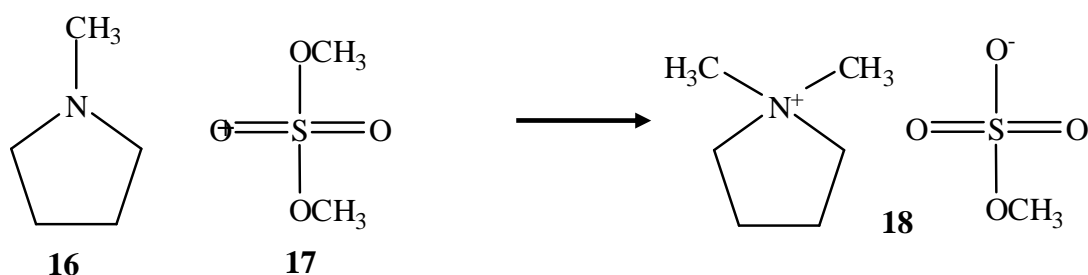


Figure 3.5: Synthesis route of sulfate-based ILs

3.4.2.2 Preparation of Phosphate-based ILs

Two potential ILs namely 1-butyl-3-methylimidazolium dimethyl phosphate, [bmim][DMP] and 1-butyl-3-methylimidazolium dibutyl phosphate, [bmim][DBP] were prepared by adding equimolar quantities of 1-alkylimidazole and the corresponding trialkyl phosphate. Then the mixtures were refluxed at certain temperatures (*Nie et al.2008*). Slow heating was applied to ensure a slow reaction since at least 24 hours are needed to optimize the production of phosphate-based ILs in inert condition.

In this work, [bmim][DMP] (**3**) was synthesized by reacting 1-butylimidazole (**1**) (2.8mL, 24mmol) with equimolar of trimethylphosphate (**2**) at 110°C for 48 hours. A yield of 5.8g (91%) as yellowish liquid was obtained. The resulting liquid was cooled to room temperature, and then washed several times with diethyl ether followed by rotary evaporation at 70°C under reduced pressure for five hours to remove all residues including the remaining reactants and diethyl ether.

To synthesize [bmim][DBP] (**6**), 1-methylimidazole (**4**) (2.0mL, 24mmol) was reacted with equimolar of tributylphosphate (**5**) at 150°C for 48 hours. The yield 7.8g (93%) of pale yellow liquid. The resulting ILs was subjected to vacuum evaporation at 70°C and 10^{-2} mbar for another 24 hours before stored in dessicator. The same procedures for [bmim][DBP] were applied for synthesizing [bmim][DMP]. A schematic diagram of the laboratory set-up used in this alkylation synthesis is shown in Figure 3.7.

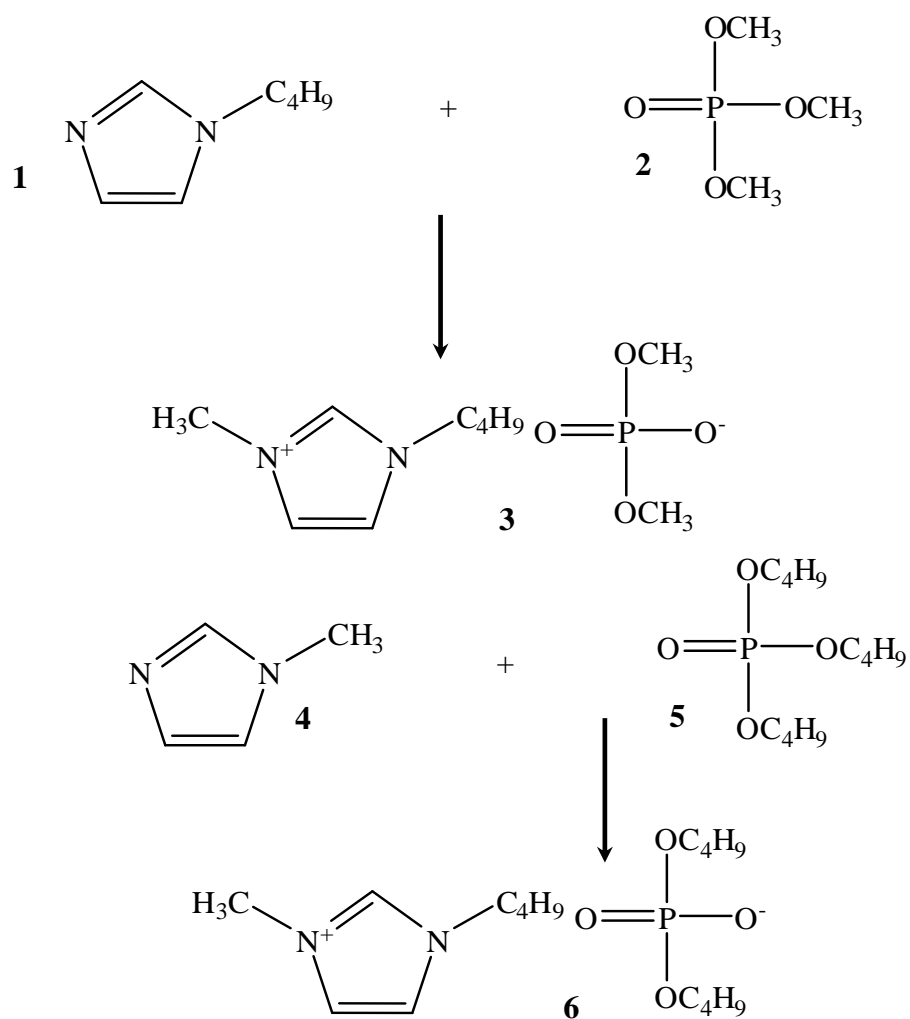


Figure 3.6: Direct alkylation of two types of phosphate-based ILs. Biphasic separation occurred between diethyl ether and phosphate-based ILs, but the IL was miscible with the reactants.

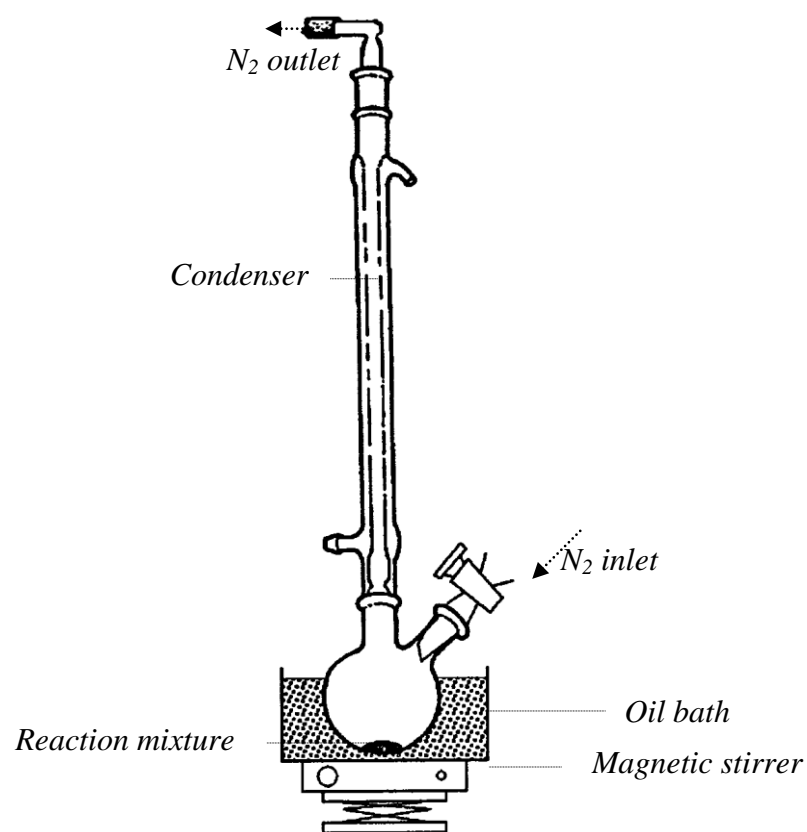


Figure 3.7: Batch experimental set-up reactor used for ILs synthesis

3.4.3 Neutralization

The final procedure for synthesizing ILs is through neutralization. The potential ILs for desulfurization, 1-butyl-3-methylimidazolium benzoate, [bmim][BZT] was synthesized according to the procedures described below.

Deionized water (500mL) was boiled first in order to dissolve the barium hydroxide, $\text{Ba}(\text{OH})_2$ powder (8.6g, 50mmol). After that, an equimolar of 1-butyl-3-methylimidazolium hydrogen sulfate (**1**), [bmim][HSO_4] was added to the solution. The formation of 1-butyl-3-methylimidazolium hydroxide (**2**), [bmim][OH] was immediate and a by-product of barium sulfate, BaSO_4 which is white in colour was then removed through filtration. The filtrate (containing [bmim][OH] which is miscible in water) was subjected to rotary evaporator at 50°C under reduced pressure to reduce the filtrate volume to about one quarter of its original volume to increase

pH of the solution. The process was carefully done due to the vulnerability of [bmim][OH] against temperature. The desired pH for the reduced filtrate is in the range of 12.5 – 13.5. Then an equimolar of benzoate acid (**3**) was added to the mixture, and the solution was stirred vigorously for five minutes followed by evaporation under reduced pressure. The yield obtained was yellowish of liquid [bmim][BZT] (**4**). The resulting yellowish liquid was then subjected to vacuum evaporation at 70°C and 10⁻² mbar in a vacuum oven for 24 hours before storing in the dessicator.

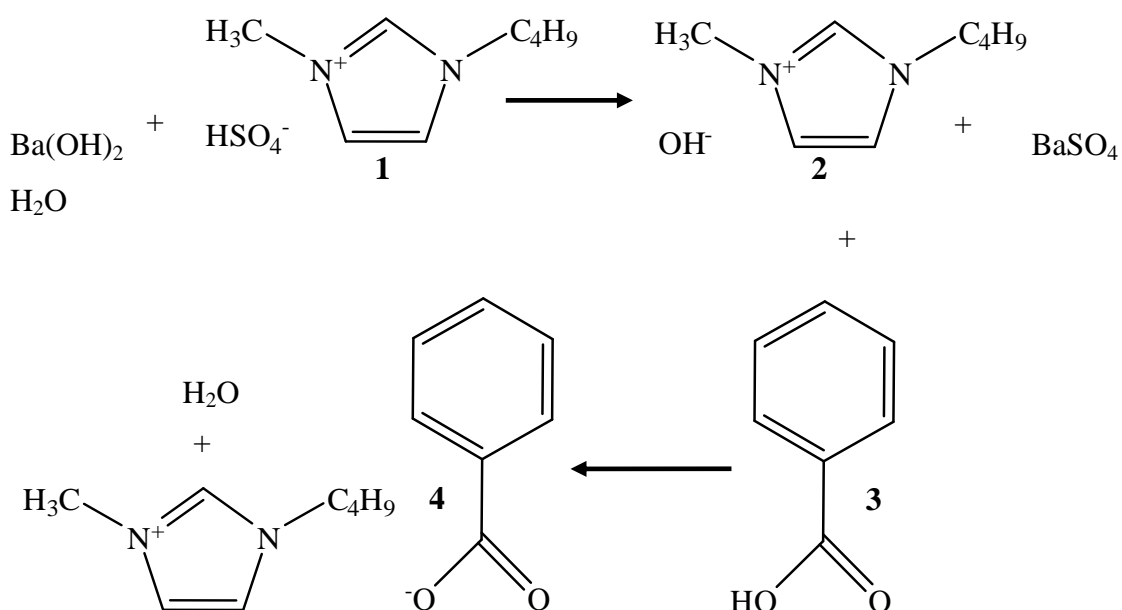


Figure 3.8: Two step reaction which initially produces [bmim][OH], the main reactant in the second step for producing [bmim][BZT], the final product.

Table 3.3: List of synthesized ILs for further characterization and extraction study

ILs	Name	Synthesis route	Physical state at room temperature
[bmim][DHP]	1-butyl-3-methylimidazolium dihydrogenphosphate	Metathesis	Liquid
[bmim][Imd]	1-butyl-3-methylimidazolium imidazolid	Metathesis	Liquid
[bmim][Pyd]	1-butyl-3-methylimidazolium pyrazolid	Metathesis	Liquid
[bmim][SCL]	1-butyl-3-methylimidazolium salicylate	Metathesis	Liquid
[mmBzim][MSO ₄]	1,3-dimethylbenzimidazolium methylsulfate	Alkylation	Solid
[mmim][MSO ₄]	1,3-dimethylimidazolium methylsulfate	Alkylation	Liquid
[bmim][BSO ₄]	1-butyl-3-methylimidazolium butylsulfate	Alkylation	Liquid
[mmpy][MSO ₄]	1,4-dimethylpyridinium methylsulfate	Alkylation	Liquid
[mmpyz][MSO ₄]	1,2-dimethylpyrazolium methylsulfate	Alkylation	Liquid
[mmpyrr][MSO ₄]	1,1-dimethylpyrrolidinium methylsulfate	Alkylation	Liquid
[bmim][DMP]	1-butyl-3-methylimidazolium dimethylphosphate	Alkylation	Liquid
[bmim][DBP]	1-butyl-3-methylimidazolium dibutylphosphate	Alkylation	Liquid
[bmim][BZT]	1-butyl-3-methylimidazolium benzoate	Neutralization	Liquid

3.5 ILs Characterization

All 13 of the synthesized ILs were characterized using NMR, elemental analyser (CHNS), Raman spectroscopy, FTIR spectroscopy, Karl-Fisher Titrator and Ion Chromatography (IC). From NMR spectroscopy analysis, which is based on theoretical estimation, the structures of the synthesized ILs were confirmed and identified, whereas Raman and FTIR spectroscopy were used to justify the interaction mechanism and to approve the BT structure. Then, further studies using elemental analyser were conducted to ascertain other elements contained in these ILs. Water and halide content were also measured. The density and refractive index were studied

against temperature using density meter and refractometer, respectively. The characterization techniques are detailed out below.

3.5.1 Structure Characterization

3.5.1.1 NMR Spectroscopy

In this work, Nuclear Magnetic Resonance (NMR Bruker Avance, 500MHz, Germany) spectrometer was used to confirm the structure of synthesized ILs. The structure of the synthesized ILs were analysed with one dimensional proton (^1H) and carbon 13 (^{13}C). The samples were prepared by dissolving about 20 to 50mg of ILs samples in 0.7mL deuterated water in a 5mm thin-wall glass tube (NMR tube). The ILs samples must be fully dissolved before measurements were taken. NMR data were collected and interpreted using Topspin 3.0 software.

3.5.1.2 Interaction Study using Raman Spectroscopy

Raman spectroscopy (DXR Smart Raman, Thermo Scientific, US, with 780nm high performance laser) was used to study the interaction mechanism between sulfur compound and ILs. The sample preparation for Raman spectroscopy required less time compared to other Fourier Transform techniques. Generally, Raman spectroscopy is a vibrational molecular spectroscopy, which derives from an inelastic light scattering process, whereby a laser photon is scattered by a sample molecule and losses or gains energy during the process. The amount of energy lost is seen as a change in energy (wavelength) of the irradiating photon. This energy loss is characteristics for a particular bond in the molecule.

For the measurement, the BT/[bmim][OSO₄] mixture sample was put in a vial and was placed on top of the laser spot. For the purpose of identifying the interaction mechanism between BT molecules and [bmim][OSO₄], a series of BT/[bmim][OSO₄] binary system was prepared. The binary mixture was prepared according to the formula $\{x \text{ BT} + (1-x) [\text{bmim}][\text{OSO}_4]\}$ where x is the mole fraction of BT with the values of 0.22, 0.53 and 0.72. The spectrum of each mixture was collected and identified using OMNIC Spectra software.

3.5.1.3 BT Identification using FTIR

Fourier Transform Infrared (FTIR 8400S Spectrophotometer, Shimadzu, Japan), spectroscopy was used to identify and ratify BT structure. Basically, FTIR is a technique that utilizes infrared radiation which is passed through a sample, where some is absorbed while some is transmitted by the sample, hence a spectrum is obtained. This analysis provides information about the chemical bonding or molecular structure of ILs based on IR absorption plot consisting of reverse peaks. In this study, the sample that deposited on the glassy carbon electrode during electrochemical process was analyzed using this technique. The deposited sample was washed with *n*-heptane first, and dried in the oven at 50°C for half an hour before preparing the sample pellet with KBr. Pure BT was also prepared with KBr for a comparison study.

3.5.2 Elemental Analysis

A CHN-900/CHNS-932 (LECO VTF-900, US) was used to determine the amount of elemental carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) in the synthesized ILs, and hence the empirical formulation of these ILs was calculated. The samples were prepared by putting 2 mg of synthesized ILs on sorbit which was then placed in the tin capsule. The prepared samples were then burned in the combustion chamber. The elemental percentage was calculated based on the combustion products of CO₂, H₂O, N₂ and SO_x. Each of the synthesized ILs was evaluated in triplicate analysis and the average value was reported.

Table 3.4: Instrument settings for LECO CHNS-932

	Description
Furnace temperature	1000°C
Oxygen dose	20 cm ³
Sample weight	1-2 mg
Analysis time	3 min

3.5.3 Water Content Evaluation

Water content is an important characteristic for all ILs. It was measured using a Karl Fisher titration for liquid ILs, and Stromboli method for solid ILs in KF coulometer (DL 39, Mettler Toledo, US). The water content was measure each time before any measurements or extraction process was conducted; this was done for all

ILs for every studied process variable. Triplicate measurement was carried out on each sample and the average value is reported. The accepted limit of water content in ILs is below 500ppm (0.05%) due to their effect on extraction performance (*Eber et al. 2004*). If the measured water content was above this limit, the ILs were subjected to further evaporation in the vacuum oven before proceeding with extraction.

3.5.4 Halide Content Evaluation

Halide (chloride/bromide) content is another important characteristic for ILs especially in synthesized ILs. The halide content was measured using ion-exchange chromatography (850 Professional IC, Metrohm, Switzerland), and the results were collected using MagIC Net 2.1 software. The halide content was calculated from the observed conductivity of the sample. The measurement was conducted in triplicate, and the average value is reported. For commercial ILs, the stated halide content is usually around 200ppm (0.02%). The measured ILs should have low halide content around 500ppm since halides also affects the extraction performance.

3.5.5 Density Measurement

The purpose of density measurement of ILs is to evaluate and observe the density of each ILs against temperature. The density of the ILs was measured at temperatures from 298.15 to 348.15K using a rotational automated density meter Anton Paar DMA 5000M. This measurement was conducted only for ILs that are in liquid form at 25.5°C. The reproducibility of the density measurements is $\pm 1 \cdot 10^{-4} \text{g.cm}^{-3}$ while the uncertainty of the temperature measurement is $\pm 0.01 \text{K}$. All measurements were done in triplicate and the average value was used to derive three thermodynamic properties in order to understand the behavior of the ILs using simplified relationships by Glasser (2004).

The first property i.e. molecular volume, V_m ($\text{nm}^3 \cdot \text{molecule}^{-1}$) was estimated based on the average density, ρ (g.cm^{-3}) and molecular weight, M_w (g.mol^{-1}), using Eq. 3.6 below,

$$V_m = 1.66 \times 10^{-3} \left(\frac{M_w}{\rho} \right) \quad (3.6)$$

The second and third properties namely lattice energy, U_{POT} and absolute entropy, S_{298} at ambient conditions were calculated using the following respective equation,

$$U_{POT} = \gamma \left(\frac{\rho}{M_w} \right)^{1/3} + \delta \quad (3.7)$$

$$S_{298} = 1246.5 V_m + 29.5 \quad (3.8)$$

where the constants $\gamma = 1981.2 \text{ kJ}\cdot\text{mol}^{-1}$ and $\delta = 103.8 \text{ kJ}\cdot\text{mol}^{-1}$ (Glasser, 2004).

3.5.6 Refractive Index Measurement

The values of refractive index were determined using ATAGO RX-5000 Alpha digital refractometer with a measuring uncertainty of $4 \cdot 10^{-5}$. The apparatus was calibrated by measuring the refractive index of Millipore quality water and several solvents, including imidazolium-based ILs with known refractive indices. Triplicate measurements were obtained and the average value was calculated. This study was conducted to investigate the possibility of relating refractive index to molecule packing in ILs i.e. whether higher refractive index indicates a more tightly packed compound, and vice-versa (Deetlefs *et al.* 2006). The relationship between refractive index and molecule packing can be used to estimate the compactness of ILs which is important for interaction mechanism evaluation.

3.6 Data Mapping and Correlation

The physical properties data generated in this study, were used to generate a simple prediction method for preliminary selection of ILs for desulfurization purposes. Using data mapping, a simple relationship between two physical properties (molecular weight and density) was developed for a series of ILs; the physical properties used were molecular weight, density and refractive index. Three correlations were developed with respect to desulfurization performance. To correlate the data, statistical analysis was performed by utilizing MATLAB software package. The original data were analysed by auto-scaling, particularly i.e. by subtracting the column averages and dividing them by the column standard deviations to normalize the data

(Shams *et al.* 2006). By this, each of the variables (namely molecular weight, density and refractive index) was given an identical load for identification of linear correlation using statistical approach.

3.7 Ternary Study

Table 3.5: Mole fraction of each component in the ternary sample mixture

Sample no.	Mass (<i>n</i> -C ₁₂)	Mass BT	Mass [bmim][TCM]
1	0.465	0.047	0.488
2	0.612	0.060	0.328
3	0.657	0.065	0.278
4	0.711	0.073	0.216
5	0.760	0.083	0.157
Mass (<i>n</i>-C₆)			
1	0.338	0.035	0.627
2	0.431	0.062	0.507
3	0.468	0.091	0.441
4	0.511	0.108	0.381
5	0.590	0.128	0.282
Mass (<i>p</i>-xylene)			
1	0.345	0.028	0.627
2	0.419	0.045	0.536
3	0.524	0.070	0.406
4	0.580	0.092	0.328
5	0.653	0.107	0.240

Three ternary systems containing *n*-dodecane (*n*-C₁₂) + BT + [bmim][TCM]; *n*-hexane (*n*-C₆) + BT + [bmim][TCM] and *p*-xylene + BT + [bmim][TCM] were selected for experimental measurement. Five different compositions of each ternary system were prepared; the mole fraction of each component is tabulated in Table 3.5. The ternary systems were used for liquid-liquid equilibrium study.

All 15 samples were vigorously stirred at 25.5°C for approximately one hour then were left in a glove box (MBraun, Unilab, US) for another one hour to reach equilibrium. A small portion of the upper phase of the mixture (oil phase) was taken and analysed using GC-SCD-FID (7890A GC, Agilent Technologies, US) while the lower phase (ILs phase) was placed in the rotary evaporator for seven hours at 100°C

under reduced pressure for gravimetric analysis. Mass balances of both phases were performed for composition quantification. The upper phase i.e. oil phase basically is constituted of BT and hydrocarbons ($n\text{-C}_{12}$, $n\text{-C}_6$ and $p\text{-xylene}$), where the lower phase is [bmim][TCM]. All the experiments were done in duplicate, and the average value was used for ternary system plot.

3.8 Extractive Desulfurization on Model Oil

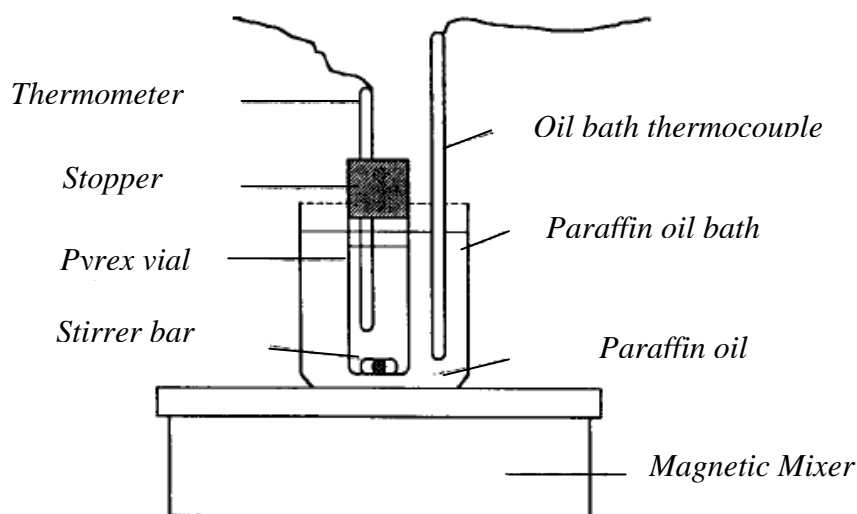


Figure 3.9: Batch experiment set-up used for extraction process

In this study, all extraction experiments were conducted using batch system in atmospheric environmental. A schematic diagram of the laboratory-scale batch extractor rig set-up used in this study is shown in Figure 3.9. The 25mL extractor was filled with known amounts of BT (sulfur compound) in $n\text{-C}_{12}$ (major component in fuels especially diesel) as the model oil. The extractor's cap was fabricated to install the thermometer in order to measure temperature during the extraction process. Due to the hygroscopic nature of ILs, the water content of all ILs were checked before using in the extraction process. If the measured water content of ILs is higher than 500ppm, the ILs was dried in a vacuum oven and its water content re-determined before proceeding for extraction.

3.8.1 Composition Analysis

During the extractive desulfurization process, the mixture of ILs and model oil was stirred at a desired speed and time to attain equilibrium at atmospheric conditions. Two layers were observed. The ILs, which normally have higher density than the model oil, form the lower phase. Thus, the upper phase, which is model oil, could be easily withdrawn for quantitative assay analysis of BT in model oil phase using high performance liquid chromatography (HPLC). The HPLC (HP1100, Agilent, US) was equipped with an auto-sampler, a reverse-phase Zorbax SB-C18 column (4.6 mm X 150 mm; 5 μ m) and a diode array detector (DAD). Detail of the HPLC analysis conditions is shown in Table 3.6. The external standard method at 280nm was used to quantify BT composition the oil phase. Agilent 1200 Series LC software was used for system programming and data retrieval. Appendix B (Figure B1) shows the standard curve of BT, while the peak and retention time of BT are shown in Appendix D (Figure 14). Based on the measured values, the material balance of BT in model ILs phase was made.

Table 3.6: Analytical conditions for HPLC analysis

	Description
Flow rate	0.7 ml/min
Mobile phase	90% methanol in water (v/v %)
Oven temperature	40°C
Injection volume	10 μ L

The composition of BT (sulfur compound) in model oil determined by HPLC analysis was then used to calculate the partition coefficient, K_d which defines the extent of the mobility of BT into ILs phase and the percentage of sulfur removal, % S using the following relationships:

$$K_d = \frac{[C]_{s,IL}}{[C]_{s,MO}} \quad (3.9)$$

$$\% S = \frac{[C]_{s,IL}V_{IL}}{[C]_{s,IL}V_{IL} - [C]_{s,MO}V_{MO}} \quad (3.10)$$

where, $[C]_{s,IL}$ is the concentration of BT in the ILs phase after extraction (ppm), $[C]_{s,MO}$ is the concentration of BT in the model oil phase after extraction (ppm), V_{IL} is the volume of ILs phase and V_{MO} is the volume of model oil phase.

The effect of three process variables namely stirring speed, extraction time and water content was studied using the method of one-factor-at-a-time. The optimum value of each variable was then used in the next study.

3.8.2 Stirring Speed Effect

The 25mL extractor was fed with fixed mass ratio of ILs to model oil. The mixture was stirred at various speed range from 100 to 500rpm. The allowable speed for the 25mL extractor vial is 500rpm using 3.0cm length of magnetic stirrer. Other process variables such as extraction time, initial concentration and temperature were kept constant in this effect study. A comparison using unstirred mixture was also performed.

3.8.3 Extraction Time Effect

The efficiency of BT extraction into the ILs phase was determined by varying the extraction time at a fixed stirring speed of 500rpm. The extraction time was varied from 1, 3, 5, 10, 15, 20, 30 and 60 min respectively. The value of other variables used in this study was fixed as shown in Table 3.7.

Table 3.7: Values of other variables

Variable	Fixed Value
Mass ratio (model oil/ILs)	1:1
Room Temperature	25.5°C
Stirring Speed	500rpm
Settling Time	20min
BT Initial Concentration	2000ppm

3.8.4 Water Content Effect

The effect of water content (estimated in weight percentage) on extractive desulfurization was studied by preparing ILs solution with different water content percentage (0.05, 5, 10, 15, 20 and 25wt %). Other variables in this study were fixed (1:1 model oil to IL mass ratio, 30 min extraction time, 25.5°C temperature, 500rpm

stirring speed, 20 min settling time and 2000 ppm of BT as the initial concentration in model oil). Besides that, loading factor, R was also estimated as the one of the process responses using the following relationships:

$$R = \frac{[C]_{s,IL}}{[C]_{IL}} \quad (3.11)$$

where $[C]_{s,IL}$ is concentration of BT after extraction in the ILs phase and $[C]_{IL}$ is the ILs concentration in the water.

3.8.5 Optimization Study on Extractive Desulfurization of Model Oil

The effects of three important process variables (mass ratio of model oil to ILs, initial concentration and temperature) on extractive desulfurization were investigated. The experiments were designed according to Central Composite Design (CCD) with the variables using Design Expert software (Stat-Ease Inc., version 6.0.6).

The experimental range of the three process variables are identified based on literatures and preliminary study. The range and levels of the variables are presented in Table 3.8, and the experimental conditions are presented in Table 3.9.

Table 3.8: Experimental range and levels of the process variables

Variable	Range and levels		
	-1	0	+1
A - Mass ratio (model oil/ILs)	0.5	1.0	1.5
B - Initial Concentration (ppm)	500	1250	2000
C - Temperature (°C)	30	50	70

Table 3.9: Experimental conditions of CCD applied in this study

Run	Designed values of process variables by DoE		
	Mass ratio (model oil/ILs)	Initial Conc. (ppm)	Temperature (°C)
1	1.5 (+1)	500 (-1)	70 (+1)
2	1.5 (+1)	2000 (+1)	70 (+1)
3	0.5 (-1)	500 (-1)	30 (-1)
4	1.0 (0)	1250 (0)	50 (0)
5	0.5 (-1)	500 (-1)	70 (+1)
6	1.5 (+1)	2000 (+1)	30 (-1)
7	1.0 (0)	500 (-1)	50 (0)
8	1.0 (0)	1250 (0)	30 (-1)
9	0.5 (-1)	1250 (0)	50 (0)
10	1.0 (0)	1250 (0)	50 (0)
11	1.0 (0)	1250 (0)	50 (0)
12	1.0 (0)	1250 (0)	50 (0)
13	1.5 (+1)	1250 (0)	50 (0)
14	0.5 (-1)	2000 (+1)	30 (-1)
15	1.0 (0)	1250 (0)	50 (0)
16	1.5 (+1)	500 (-1)	30 (-1)
17	0.5 (-1)	2000 (+1)	70 (+1)
18	1.0 (0)	1250 (0)	50 (0)
19	1.0 (0)	2000 (+1)	50 (0)
20	1.0 (0)	1250 (0)	70 (+1)

The extractive desulfurization experiments were conducted by fixing the optimum process variables (stirring speed, extraction time) which have been determined previously. The BT composition was obtained from HPLC analysis, and the material balance was made for BT percentage removal (% removal) calculation. The results of % removal as the response were used to analyze the extraction process using Analysis of Variance (ANOVA), which was automatically performed by Design Expert software. A three dimensional plot and their respective contour plots were obtained at every level of the process variables. At the end of the experiment, the optimum conditions for extractive desulfurization were determined; these conditions will be applied to model fuel and actual diesel.

3.9 Extractive Desulfurization on Model Fuel

A model diesel was prepared by dissolving a known amount of aromatic hydrocarbons (benzene and *p*-xylene) with a known amount of sulfur compounds (BT and DBT) in *n*-C₁₂. Five model diesels were studied namely benzene/BT, *p*-xylene/BT, benzene/DBT, *p*-xylene/DBT and BT/DBT, where each was completely dissolved in *n*-C₁₂. The composition of model fuels which contained aromatic hydrocarbons followed the mixture ratio of *n*-C₁₂ to benzene or *p*-xylene (8/2 v/v) as mentioned in section 3.8, while sulfur compounds were dissolved to obtain 2000ppm.

The extractive desulfurization of these model fuel samples was performed at the optimum conditions determined from the optimization study, which are stirring speed: 500rpm, extraction time: 30 minutes, mass ratio of model diesel and ILs: 1:1, temperature: 25.5°C. In this study, the effect of benzene or *p*-xylene in the system toward desulfurization performance was studied. In addition, the effect of *p*-xylene composition was also studied where the volume ratio of *p*-xylene to *n*-C₁₂ was adjusted from 8/2, 7/3, 6/4 and 5/5. Five of ILs which showed high performance in screening part are selected to proceed for this study. In this study, benzene was omitted due to the limitation of HPLC detection capability.

Composition analysis was performed using HPLC (HP1100, Zorbax SB-C18 column, diode array detector), and gas chromatography (7890A GC, Agilent Technologies, DB1 column 30m X 320µm: 1µm) equipped with an auto-sampler and two type of detectors (Sulfur Chemiluminescence Detector – SCD, Flame Ionization Detector – FID). The upper phase of the model fuel after extraction was withdrawn and analysed by injecting 2µL into the GC column. The oven temperature was from 30 to 280°C, helium was the carrier gas with a fixed flow rate at 2mL/min. External standard methods for both HPLC and GC-SCD-FID were used to quantify benzene, *p*-xylene, BT and DBT composition in the model fuel phase. Through material balance of each component, the performance of extractive desulfurization process was evaluated.

3.10 Extractive Desulfurization on Actual Diesel

To evaluate the performance of the selected ILs on actual diesel, two commercial diesel was used in this study. Both were subjected to GC-MS (Agilent Technologies, US) analysis and by applying additional standard method the initial concentration of *n*-C₆, *n*-C₁₂, benzene, toluene, *p*-xylene, BT and DBT was determined. The extractive desulfurization of diesel was conducted at the optimum experimental conditions whereby the mass ratio of diesel to ILs was maintained at 1:1. The mixture was left for 20 minutes to settle and the upper phase (diesel) was then decanted and analysed using GC-MS, where the composition of *n*-C₆, *n*-C₁₂, benzene, toluene, *p*-xylene, BT and DBT was evaluated. For this part of the extractive desulfurization study, only three selected ILs were evaluated.

In order to study the extraction cycle against desulfurization performance, Total Sulfur Analyser, TSA (Rapid CS Cube, Elementar, Germany) was used to determine the percentage of total sulfur in both diesel phase and ILs phase. By combusting the sample with O₂ at high temperature (1000°C), the sulfur compound was converted to SO_x, which is detectable by infrared detector. Coal was used as the standard for calculating total sulfur percentage in the sample. An average percentage of total sulfur from triplicate measurements was obtained.

The cross-miscibility of ILs and diesel was analysed by determining the density of spent ILs at room temperature.

3.11 Regeneration of ILs

A variety of regeneration methods for spent ILs has been reported in the literature, for instance chemical regeneration and thermal regeneration. The chemical regeneration methods are widely used with high efficiency, but they are also characterized by 5-10% ILs loss due to miscibility gap of the solvent used. On the other hand, thermal regeneration is relatively difficult to perform and the regeneration efficiency is only up to 70% due to high boiling point of the solute (*Nefedieva et al. 2010; Schucker and Baird, 2001*). Re-extraction process using water/*n*-heptane and

electrochemical are proposed, due to their reliability, simplicity and costly effective in bench-scale study.

3.11.1 Re-extraction Technique using Water/*n*-heptane

In order to study the regeneration of ILs, BT was loaded first into [bmim][TCM]; mass ratio of [bmim][TCM] to BT was 9/1. The mixture was stirred for about one hour for BT to fully dissolved in [bmim][TCM]. Next, the stirred mixture containing 10% BT (spent IL) was mixed with deionized water, and stirred for 10 minutes. Then, the mixture was filtered to remove precipitate of BT. Finally, *n*-heptane was added to the filtrate and the mixture was stirred for another 10 minutes. The mass ratio of spent IL to *n*-heptane to deionized water was 1:1:1. After obtaining the gravitational separation, the upper and lower phases were collected for further analysis. The lower phase were subjected to rotary evaporator at 100°C under reduced pressure for three hours to remove deionized water from [bmim][TCM]. Both pure and purified [bmim][TCM], and the upper phase were analysed using TSA (Elementar Rapid CS, Interscience, Germany) for BT quantification.

3.11.2 Electrochemical Technique

The regeneration by electrochemical technique can be conveniently operated in-situ and it is possible to perform at bench-scale. First, the electrochemical stabilities of five ILs were analyzed using cyclic voltammetry. Cyclic voltammetry studies were carried out at room temperature (25.5°C) in a glove box (MBraun, Unilab, US) using an electrochemical workstation (Electrochemical Impedance Spectroscopy, WEIS510, Won A Tech, Korea) with unseparated cathodic and anodic areas. The volume of each pure ILs (as electrolyte) around 1 to 2mL was used. The working electrode was a glassy carbon electrode, the counter electrode was a Pt wire and a Ag/AgCl electrode was the quasi-reference electrode. The scan rate of the potential was fixed at 1mV s⁻¹. From the scanning results of five pure ILs, the appropriate IL was identified and loaded with BT according to 9/1 mass ratio (IL/BT). This mixture was later identified as spent IL. A similar cyclic voltammetry was conducted whereby this time pure IL was replaced by spent IL, as the electrolyte.