CHAPTER 2
LITERATURE REVIEW

2.0 Overview

In this chapter, a review on ILs from types of ILs to their interactions and applications especially for extractive desulfurization are discussed in detail. The optimization, ternary diagram and regeneration studies for ILs are also comprehensively discussed.

2.1 Ionic Liquids (ILs)

ILs have been mentioned for the first time in the open literature in 1914 by Walden. ILs are mainly developed by electrochemists in the search of ideal electrolytes for batteries, thus they have been used initially for those and related applications like semiconductors (electroplating and electrosynthesis) and fuel cell. In 1992, the first water stable ILs was reported by Wilkes and Zaworotko, from which many other applications outside the field of electrochemistry were developed. Since then, ILs have been explored for electrochemical applications, catalysis and/or reaction media, lubricant, organic synthesis, separations, biotransformation, enzymatic catalysis, biphasic reaction, chiral induction and many more. Some applications had been tested on pilot plant scale such as homogeneous catalytic, acid scavenging, extractive distillation, compatibilizers in pigment pastes, cooling agent, gas adsorption, storage of gases and more (*Huddleston et al. 2001; Holbrey et al. 2002; Marsh et al. 2004; Nefedieva et al. 2010*).

Recently, ILs technology has reached another milestone where a large scale industrial application involving ILs such as the BASIL process has been commercialized. In the BASIL process, the ILs replaces conventional materials such as catalyst and solvent. The use of ILs has been proven in enhancing catalytic reactions; and simplifying products or catalytic separation; including reducing the risks associated with using conventional organic compounds which are known as being volatile and flammable (*Domanska, 2005; Krossing et al. 2006*).

ILs are made up of at least two components namely cation and anion. The ILs known today are based on a wide variety of organic cations combined with a great variety of organic and inorganic anions. The selection of a particular cation and anion allows the ILs to be designed to possess a particular set of properties to suit a particular application or process (*Domanska, 2005; Heintz et al. 2009; Wong et al. 2009*).

ILs are liquids that contain only ions which include all the molten salts whose melting point is below 100°C or 212°F. Ironically, ILs in their liquid state, due to the delocalised charge and structural hindrance, have an awkward molecules packing, as shown in Figure 2.1.
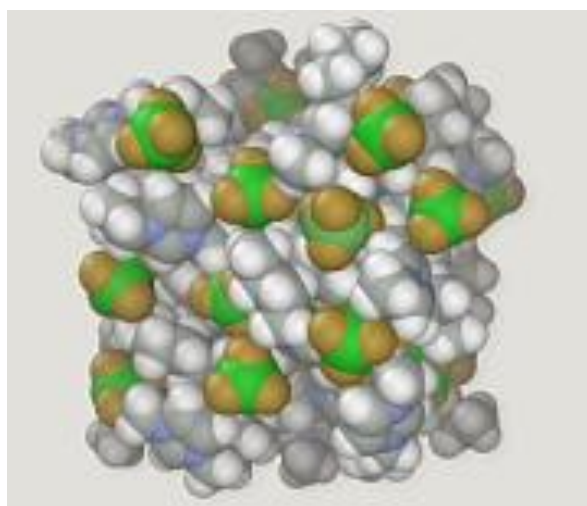

Figure 2.1: Simulated model of ILs showing awkward molecules packing
(*Raabe and Kohler, 2008*)

Most ILs are thermally stable, with some able to withstand up to 400°C. To date, most of the identified ILs are hygroscopic hence they absorb water from the environment. The miscibility of ILs in water are commonly used to classify ILs; those which are completely miscible are named hydrophilic ILs whilst those that form biphasic mixtures in combination with water are named as hydrophobic ILs. However, a few of the classified hydrophobic ILs may become completely miscible in water at elevated temperatures (*Earle and Seddon, 2000; Huddleston et al. 2001; Visser et al. 2001; Holbrey et al. 2002; Heintz, 2005; Domanska, 2005; Arce[a] et al. 2007; Chen et al. 2008*).

Due to their highly stable nature with almost unmeasurable vapour pressure and other unique solvent properties, ILs have been the subject of enormous research effort, but researchers recently have discovered that they do have problems including hydrolytic instability of halogen-containing anions, which can lead to halide waste. With regard to the environmental impact of technical processes which employ this kind of ILs, their presence may cause serious concerns under certain conditions. This would be explicitly the case for relatively hydrolytic labile anions ($AlCl_4$, PF_6; BF_4; Cl), if water is present. For example, ILs based on aluminium chloride ($AlCl_4$) are generally very hygroscopic, therefore studies have to be done in the absence of moisture. On the other hand, ILs based on tetrafluoroborate (BF_4) are generally stable toward moisture, but have a high solubility in water. In this case, significant amount of HCl and HF would be liberated, and due to their high solubility in water, would remain in solution in process water which is eventually released to the environment as wastewater. The contamination of HCl and HF in wastewater requires additional efforts and cost consideration during the treatment process to avoid the release of these toxic and corrosive substances into the environment. The aspect of ILs disposal gets more important since the disposal alternatives such as the treatment of spent ILs in biological waste water treatment is equally affected by the presence of halogen atoms in the ILs (*Visser et al. 2000; Visser et al. 2001; Wasserscheid et al. 2002; Tokuda et al. 2006; Wang[a] et al. 2008; Wang[b] et al. 2008; Wu et al. 2010*).

The term "room-temperature ILs" has been assigned to organic salts that are liquids at or close to ambient conditions. Owing to the multitude of possible

combinations of cations and anions, ILs are susceptible to numerous permutations that allow the various physical and chemical properties to be adjusted almost at will. For example, the change in length of alkyl side-chain from 1 to 9 of imidazolium-based hexafluorophosphate (PF_6) turns the liquid from being highly miscible in water to immiscible. Conversely, by replacing the PF_6^- with BF_4^- anion, increases the solubility of that ILs in water while replacing it with bis(trifluoromethylsulfonyl)imide (NTf_2) anion decreases the solubility in water (*Marsh et al. 2002; Rakita, 2003; Su et al. 2007; Chen et al. 2008*).
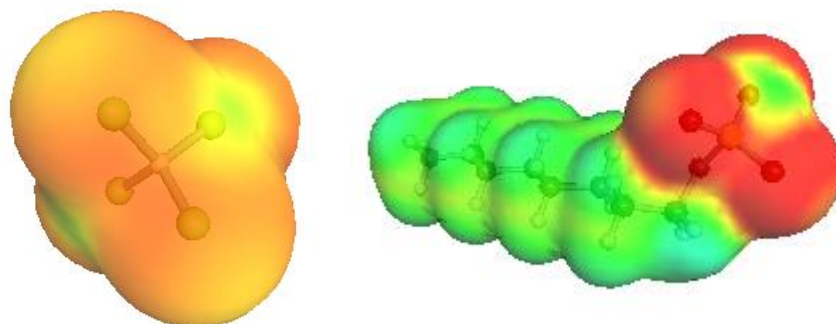
2.1.1 Types of ILs

Compared with traditional solvents, ILs have the advantage of being liquid over a wide range of temperatures in addition of having a non-volatile nature. The latter property has become the reason for recognizing ILs as "green solvent", and for their development as an alternative and environmental-friendly solvent. ILs can be easily produced as they can remain in liquid form at room temperature, and may be inexpensive to manufacture if they are produced in bulk (*Holbrey et al. 2002*).
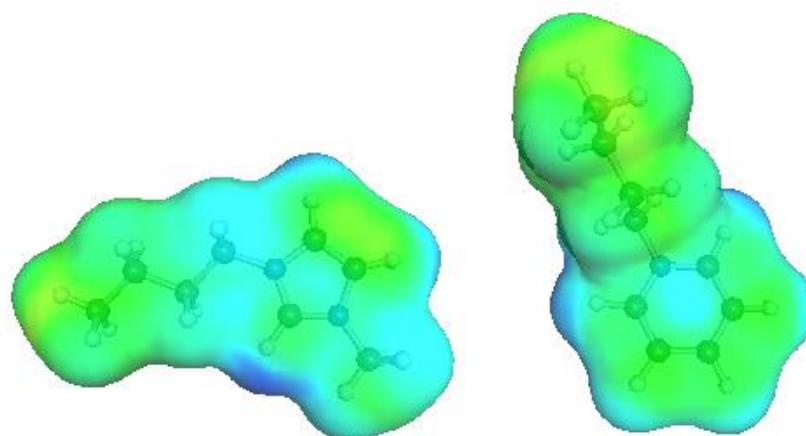
Most of the studies on extracting sulfur containing polyaromatics, such as thiophene, BT, DBT and 4,6-DMDBT have used *n*-dodecane as the model oil system (*Holbrey et al. 2008*). While, the ILs that have been studied were chosen principally for their availability in the market at relatively low cost and low environmental impact. Figure 2.2 shows the most common selection of ILs cations and anions for the application of extractive desulfurization, whether for model oils or real fuels.

There are several routes to synthesize ILs. The first is metathesis of a halide salt with a salt of the desired anion which requires quaternization process prior to the metathesis. A second route is acid-base neutralization reactions and finally direct reaction or combination of halide salt with a salt of the desired metal-based anion. For halide-free ILs, they can be synthesized using alkylating reagents which generally act as the desired anion. Furthermore, ILs can be functionalized to act as acids, bases or ligands which can be achieved by adjusting the length of the alkyl side-chain whether on the cation or anion side. Recent investigations is focusing more on low

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environmental impact ILs that have the desired physical properties (*Visser et al. 2001; Marsh et al. 2002; Rakita, 2003; Laus et al. 2005*).

Anion: tetrafluoroborate and octylsulfate

Cation: 1-butyl-3-methylimidazolium and n-butylpyridinium

Figure 2.2: Typical anions and cations of ILs used in desulfurization

ILs are able to solvate a wide range of species including organic, inorganic and organometallic compounds. Having dual nature, ILs behave similar to a non-polar stationary phase when separating non-polar mixtures and polar fluids that are not proton donors or acceptors. On the other hand, they behave in the opposite manner when used to separate polar molecules that are capable of either donating or accepting proton. As a class of solvents, ILs are non-coordinating and stable towards moisture, polar and non-polar organic liquids, which makes them suitable for various

applications such as gas separation, as heat transfer fluid and as solvent for extraction process. The most commonly used cations in ILs are imidazolium, pyridinium, pyrrolidinium, ammonium and phosphonium whereas the most popular anions are chloride, nitrate, acetate, BF_4, PF_6 and NTf_2, as listed below in Table 2.1. ILs based on imidazoles and pyridines are favourable species for investigation because of their stability towards air and water, ability to stay in liquid form over a wide range of temperature and their relatively favourable density and viscosity. In addition, the alkyl group attached to either the cation or anion site is variable, and may be used to fine tune the properties of the ILs (*Huddleston et al. 1998; Visser et al. 2000; Marsh et al. 2002; Marsh et al. 2004; Domanska, 2005; Shariati et al. 2005*). The appealing features of ILs for extractive desulfurization are their low viscosity and high electrochemical stability, as mentioned in the literatures.

Table 2.1: Summary of cation and anion types along with their general description

Cation	Description
Imidazolium	- the most studied and has the most information; - produces ILs with the lowest viscosity; - strong proton donor.
Pyridinium	- produces low viscosity of ILs; - has the lowest electrochemical stability.
Pyrrolidinium	- produces high viscosity of ILs; - poor proton donor; - has high electrochemical stability.
Ammonium	- poor proton donor; - produces high viscosity of ILs; - has the highest electrochemical stability.
Phosphonium	- poor proton donor; - produces the highest viscosity of ILs; - has high affinity for alkanes and non-polar solvents; - has high electrochemical stability.
Anion	
Chloride	- basic building blocks for making other ILs; - generally solid at room temperature; - water miscible.
Nitrate, Acetate	- have high viscosity; - water miscible; - strong proton acceptor and very polar.
BF_4, PF_6, NTf_2	- have low viscosity; - have the highest electrochemical stability.

2.1.2 Physical and Thermodynamic Properties of ILs

All substances can be characterized by their unique sets of physical properties. Properties that can be determined without changing the composition of a substance are referred to as physical properties. ILs consist of cations and anions which are presumed to be bonded to each other by means of electrostatic attractions. Classified as ionic compounds, ILs are often soluble in water, conduct electricity when in aqueous solution or in molten state, and do not burn in flame. Intermolecular forces are also recognized as electrostatic in nature, but are much weaker than the ionic bonds that hold the ionic compounds together (*Huddleston et al. 2001; Holbrey et al. 2002; Domanska, 2005; Hao et al. 2010*).

The determination and identification of physical properties of ILs are essential since the physical properties determine the ideal condition for extraction of sulfur compounds, as well as to understand the molecular structures of ILs. Few researchers have been actively gathering physical properties data on ILs. A number of compilations as well as an on-line database, which provide easy access, are available now.

In addition, the study on physical properties is important for the design and scale up of process equipment. In order to design any process involving ILs, it is necessary to know the range of physical properties including density (ρ) and refractive index (*RI*) of the ILs. During the measurement of physical properties, purity of ILs is a very important issue; contamination due to water and halides has major influence on some physical properties of ILs (*Marsh et al. 2004; Yunus et al. 2010*).

It would be impossible to measure all properties of the almost 10^{18} or maybe more potential ILs, therefore correlations or predictive tools have been developed. There are numerous physical properties correlations currently being studied by researchers but no correlation against process performance is made. Therefore, it is essential to develop and verify the developed correlations. In this work, only four properties are being focused namely density (ρ), refractive index (*RI*), lattice potential energy (U_{POT}) and entropy at ambient conditions (S_{298}), where both thermodynamic properties; U_{POT} and S_{298} are solely estimated from density and molecular mass (M_W).

2.1.3 Mapping and Correlation using Physical Properties of ILs

Data mapping is a process of developing data component mappings between two distinct components. Normally, data mapping is used as a first step for a wide variety of data integration tasks. These include data distribution and data mediation between data source and a destination, data lineage analysis through identification of data relationships, data discrimination where hidden sensitive data are discovered, consolidation of multiple database into a single database and identification of redundant data for consolidation or elimination (*Yeung and Ruzzo, 2001*). Data mappings can be done in a variety ways but usually via graphical or visual tools. The latest approach in data mapping involves simultaneous evaluation on actual data values using heuristics or statistics, which automatically discovers new or complex mappings between two data sets (*Shams et al. 2006; Shen et al. 2011*). This mapping method can be efficiently applied for ILs to map the physical properties against desulfurization performance.

In the field of desulfurization using ILs, quite a substantial amount of physical properties of ILs have been reported and it has been recognized that there are possible relationships between the physical properties for a series of ILs. Thus, an efficient method that relates the data need to be introduced which would enable the use of ILs data mapping in preliminary screening of ILs for desulfurization purposes (*Cassol et al. 2007; Holbrey et al. 2008*). By manipulating the data, and using a simple statistical approach applicable in MATLAB software, it might be possible to compare and explain the physical properties in terms of their similarities, and hence to group them accordingly. From the plotted data, perhaps it would be possible to predict desulfurization performance for new ILs.

2.2 Interaction of ILs

Within recent years, ILs has gained increasing interest for application to different kinds of processes, amongst those is as separation media for LLE processes. Basically the optimization in LLE process or technique is mostly influenced by the interaction mechanism between the solute and solvent. Therefore, for desulfurization process it is vital to identify the interaction mechanism between sulfur compounds (solute) and ILs

(solvent) since the interaction mechanism will determine the extraction efficiency and recycling capability of the ILs. Since the number of conceivable combinations between cations and anions are almost unlimited, and sole experimental screening is impossible, the use of simulation tools becomes important. Since ILs are a relatively new class of compounds, the use of common activity coefficient model for example group contribution method like UNIFAC is complicated, because it requires the input of interaction parameters, which for ILs have not been fully determined thus far. In order to describe the interaction mechanism and behaviour of ILs, the dielectric continuum model COSMO-RS has been introduced, and it is gaining more interest for ILs prediction for various applications (*Klamt and Eckert, 2000; Diedenhofen et al. 2003*).

2.2.1 Interaction Mechanism in COSMO-RS

COSMO-RS is independent of specific interaction parameters; therefore it is a promising approach for ILs. The name of COSMO-RS is derived from "**Co**nductor-like-**S**creening-**Mo**del" (COSMO) and its extension RS stands for "real solvents". This approach belongs to the class of quantum chemistry of continuum solvation models (CSMs). CSMs are an extension of the basic quantum chemistry where a molecule in solution is described through a quantum chemical calculation of the solute molecule with an approximate representation of the surrounding solvent as a continuum. The solute is treated as if embedded in a dielectric medium via a molecular surface or cavity that is constructed around the molecule (*Eckert and Klamt, 2002*).

COSMO-RS uses only structural information of the molecules for the priori prediction of activity coefficients and other thermophysical data; thus the program is independent of specific interaction parameters. In COSMO-RS, a number of quantum chemical calculations are combined with statistical thermodynamics in order to enable the prediction of thermodynamic properties without any experimental data (*Klamt and Eckert, 2000; Banerjee and Khanna, 2006*).

COSMO-RS is a combination of electrostatic theory of locally interacting molecular surface descriptors, which are computed by quantum chemical method

(QM) with exact statistical thermodynamics methodology. In other words, it integrates concepts from quantum chemistry, dielectric continuum models, electrostatic forces interactions and statistical thermodynamics. It is based upon information evaluated by QM-COSMO calculations, which describe discrete surface around a molecule embedded in a virtual conductor. It treats a liquid as an ensemble of closely packed ideally screened molecules, where the molecular surface is in close contact with one another. Assuming that each molecule is still enclosed by virtual conductor, the interaction energies of the surface pairs are defined in terms of screening charge densities (SCDs), where σ and σ' of the respective surface segments. The SCDs measure electrostatic screening of the solute molecule by its surrounding and the back-polarization of the solute molecule (*Klamt and Eckert, 2000; Eckert and Klamt, 2002*).

Meanwhile, the statistical thermodynamic provides a link between the microscopic surface interaction energy and the macroscopic thermodynamic properties of a liquid. Since in COSMO-RS all molecular interactions are viewed as consisting of local pair-wise interactions of surface segments, the statistical averaging can be done in the ensemble of interacting surface pieces. In order to describe the composition of the surface segment ensemble which depends on σ, it is sufficient to consider histograms of the SCDs, the so-called σ-profiles. Such probability distribution gives the relative amount of surface with polarity σ for a molecule (*Klamt and Eckert, 2000; Palomar et al. 2009*).

The COSMO-RS prediction that starts with QM-COSMO calculation is performed on the density functional theory (DFT) level, utilizing the BP functional with RI (resolution of identity) approximation and a triple-ζ valence polarized (TZVP) basis set. These QM-COSMO calculations are done in a Turbomole program package. The geometries of all molecules involved in these calculations are first fully optimized and the calculations are only performed once for each compound. The result of the COSMO calculation which is the charge distribution on the molecular surface is stored in the so-called COSMO-files, which are collected in the database. COSMO-RS calculations are then performed using COSMOtherm program, which provides an efficient and flexible implementation of the COSMO-RS method. Thus in

combination with a large database of solvents including ILs, COSMO-RS allows fast and efficient large scale solvent screening (*Eckert and Klamt, 2002; Grensemann and Gmehling, 2005; Kumar and Banerjee, 2009*). Figure 2.3 below is shown for an overall COSMO-RS procedure.
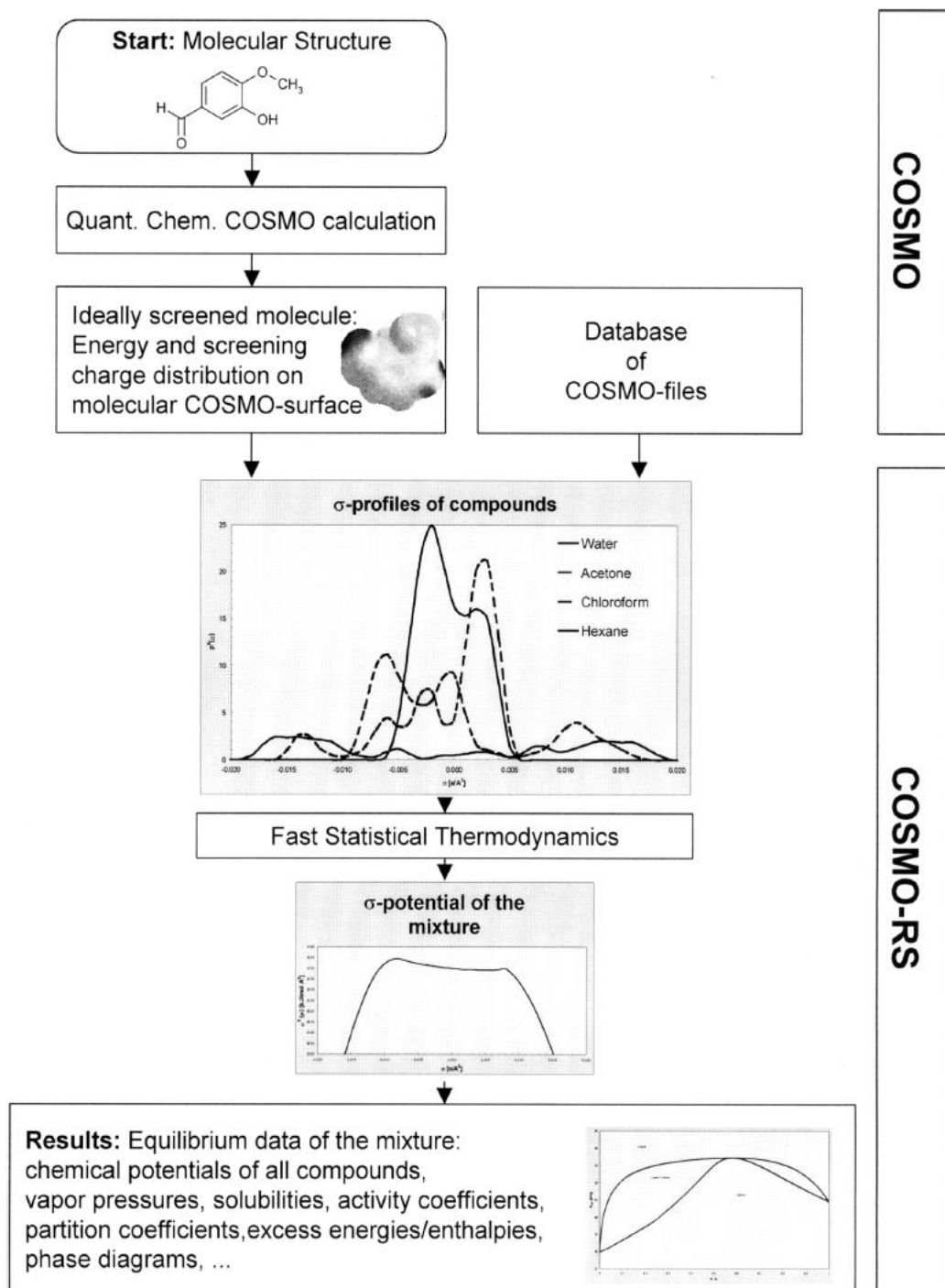

Figure 2.3: COSMO-RS calculation of thermodynamic properties (*Eckert and Klamt, 2002*)

In COSMO-RS, the bulk of a liquid phase is considered to be built of closely packed molecular cavities, and each molecule is divided into discrete segments, where each segment is assigned with a screening charge density, σ_i. Then, the interactions between the molecules are reduced to the interactions of the molecular segments, or rather the interactions of the screening charge densities. In order to describe the entire molecule and molecular properties the screening charge density distribution of a molecule, the so called σ-profile as shown in Figure 2.4 is used (*Grensemann and Gmehling, 2005*).
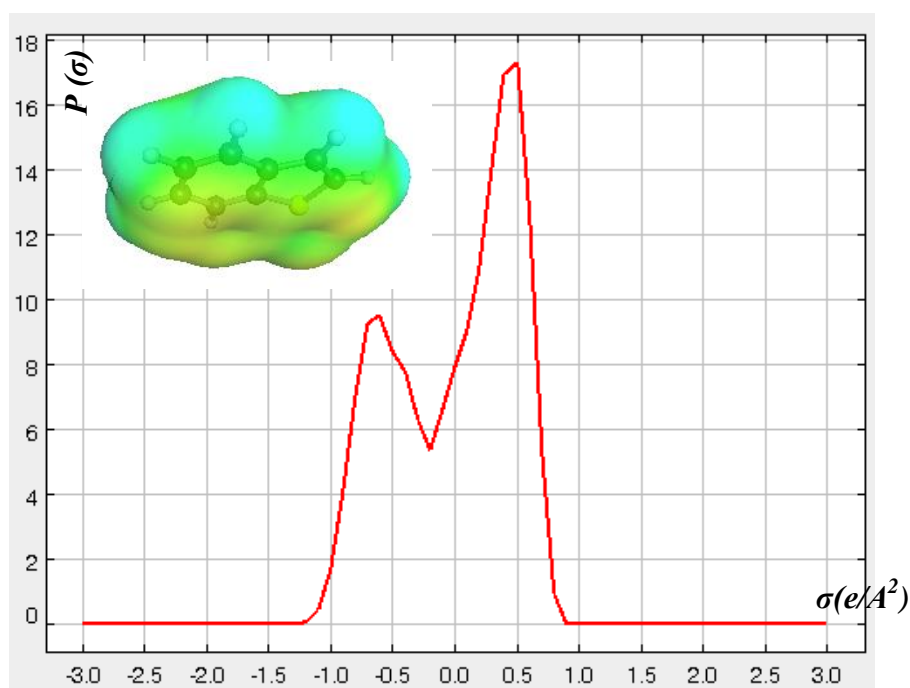

Figure 2.4: Screening charge distribution and σ-profile of BT

Initially, the assumption has been made that a liquid consists of close packed molecules, as a logical consequence, the properties of this liquid can also be described by means of the σ-profiles. Next, based on the σ-profiles, the σ-potential, μ (σ) of a molecule is calculated. The σ-potential is the central equation in COSMO-RS where all other equations for the calculation of thermodynamic data are based on. Additionally, electrostatic interactions (E_{misfit}) and hydrogen bond interactions (E_{HB}) between the molecular surfaces pieces are described in dependence of σ. Therewith,

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the screening charge distribution profile holds all the information which is necessary for COSMO-RS (*Klamt, 1995; Klamt and Eckert, 2000*).

Activity coefficient at infinite dilution, ln (γ_i^{inf}) is an important parameter in order to study the deviation from ideal behaviour in a mixture of ILs + sulfur compound in hydrocarbon. Basically, it provides information regarding non-ideality of the chosen species in a mixture. The value describes the extreme case in which only solute-solvent interaction contributes to non-ideality that has practical implications in chemical and industrial processes. In the case of desulfurization, it provides information about interaction between solvent, where in this case is ILs (solvent) and solute i.e. sulfur compounds. This is a useful tool for solvent selection for extractive desulfurization process. The separation factor of species to be separated at infinite dilution is sufficient for determining the suitability of an IL as solvent for selective extraction. Experimentally, the activity coefficient at infinite dilution of some ILs in hydrocarbons, polar and non-polar solvents is measured using either gas-liquid chromatography or the dilutor technique (*Diedenhofen et al. 2003*).

Several thermodynamic models are available such as NRTL and UNIFAC for predicting activity coefficient at infinite dilution, but the accuracy of the measurement needs to be improved in order to enhance the prediction. Besides that, new experimental data are required to generate quantitative interaction parameter, which hinders the use of these models (*Mohanty et al. 2010*). On the other hand, COSMO-RS is a novel and efficient model for priori prediction of activity coefficient at infinite dilution for a mixture of ILs from thermodynamic aspects as it relies on optimized molecular structure as the only information; no experimental data is needed (*Diedenhofen et al. 2003; Gracia-Chavez et al. 2012*).

The predicted activity coefficient values obtained through COSMO-RS using different or modified parameterization have been done by Banerjee group to predict potential ILs for separation of sulfur compounds (thiophene, BT and DBT), by means of selectivity, capacity and performance index at infinite dilution. In the first study, they selectively screened out 264 suitable ILs (from 24 anions and 11 cations) and found that smaller sized cations have higher selectivity, but lower capacity and vice

versa (*Kumar and Banerjee, 2009*). They identified that for fluorinated anions, the removal of sulfur compound (thiophene) increases with the increase of the van der Waals volume. While a smaller cation with a sterically shielded large anion gave high extraction efficiency. In a second study they screened out 168 suitable ILs based on the permutations of 28 anions and 6 cations, and found that the cation without aromatic ring combined with anions having sterical shielding effect such as thiocyanate, acetate and chloride proved to be the most favourable ILs (*Anantharaj and Banerjee, 2011*). However, their predictions were not consistent with the literatures. This shows that COSMO-RS has a limitation to some extent. For example, COSMO-RS may not be able to represent the π-π interaction effect which has resulted in inconsistent result between prediction and experiment. Therefore, there is a need to introduce new predictive approach for selecting appropriate ILs for desulfurization via interaction mechanism.

2.2.2 Interaction Mechanism in Extractive Desulfurization

ILs consist of complex ions with multiple types of interaction, where each solute molecule will possess somewhat different solute-solvent interactions due to the various acidic, basic, electron donating and electron withdrawing properties. There are several possible contributing mechanism theories in extractive desulfurization as listed in Figure 2.5.
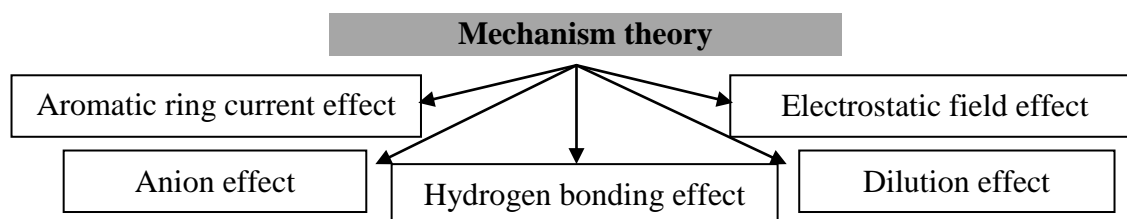

Figure 2.5: Possible contributing theories of interaction mechanism in extractive desulfurization by ILs

- ➢ Aromatic ring current effect (i.e., π-π interaction and CH-π interaction) occurs between aromatic-type-cation of ILs and aromatic sulfur compound.
- ➢ Electrostatic field effect (i.e., Columbic interaction)

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occurs when bonding between the anion and cation of ILs becomes weaker because of their structures (most probably due to the length of substituted alkyl side-chain on the cation), which makes it more easier for insertion or interaction of aromatic sulfur compound in/with ILs.

- ➢ Hydrogen bonding effect
  occurs due to the H-bond donation of cation part of ILs to the sulfur atom of aromatic sulfur.
- ➢ Anion effect.
- ➢ Dilution effect.

The CH-π interaction between the imidazolium cation and aromatic ring of sulfur compound becomes one of the major mechanisms during sulfur extraction as indicated by chemical quantum simulation (*Kumar and Banerjee, 2009*) and NMR observations (Su et *al*. 2004). By using quantum chemical calculation approach (namely ab initio calculations correlated with experimental results), it was suggested that the positively charged atoms of the imidazolium cation can be the most approachable to the negatively charged atoms of the sulfur compounds, producing a maximal Columbic interaction (*Nie et al. 2008; Zhou et al. 2008*). On the other hand, the formation of hydrogen bonding between acidic hydrogen of the imidazolium cation and the sulfur compound is weak due to poor H-bond acceptor by the sulfur compound, but becomes stronger with increasing alkyl side-chain length. The anion and dilution effects (the dilution of ILs by sulfur compound insertion) are not the dominant factors in determining the absorption capacity and selectivity of sulfur compounds in model oil/imidazolium based-ILs systems (*Anderson et al. 2002; Su et al. 2004; Liu et al. 2010*).

Meanwhile, the specific π-π interaction due to aromatic current effects was first predicted between imidazolium cation and sulfur compound (thiophene) using NMR analysis approach (*Su et al. 2004*). The aromatic current effect is largely affected by the size of the cation itself and the length of alkyl side-chain substituted on the cation. Since then, it was predicted by many researchers that the stronger selective extraction of aromatic sulfur compounds resulted from the π-π interaction between the

imidazolium-based ILs and aromatic sulfur ring (*Nie et al. 2006; Nie et al. 2007; Mochizuki and Sugawara, 2008; Chu et al. 2008; Ko et al. 2008; Zhou et al. 2008*).

There was also a suggestion that π-π interaction between the unsaturated bonds of sulfur and the imidazole ring leads to the formation of liquid clathrate. Liquid clathrate is a semi-ordered liquid formed by associative interactions between ILs and aromatic sulfur compounds which separate the cation-anion packing interactions to a sufficient degree resulting in the formation of localized cage-structures; in this case ILs are trapping the aromatic sulfur compounds. With too little interaction, the ILs are simply completely miscible or immiscible with the aromatic sulfur compound, whereas, if the cation-anion interaction of ILs are too great, then crystallization of the ILs occurs (*Crowhurst et al. 2003; Holbrey et al. 2003; Eßer et al. 2004*). Since the aromatic sulfur compounds e.g. DBT, BT, 3-methylthiophene are conjugated structure, the lone pairs on the sulfur atom or the π-electrons on the aromatic sulfur compound ring preferentially insert into the molecular structure of the ILs. The steric effect between the interacting compounds also influences the interaction mechanism involved (*Cassol et al. 2007; Jiang et al. 2008; Zhou et al. 2008*).

According to the above theories, the knowledge on π electron delocalisation is very important to justify the selection of ILs for extractive desulfurization based on interaction mechanism to assist COSMO-RS prediction. Recognizing π-π interaction as a major attribute to interaction mechanism, two variables can be quantified in defining π electron and lone pairs, namely aromaticity index (AI) and double bond equivalent (DBE). The AI is a quantitative descriptor of π electron delocalised for cation part while DBE is a quantitative descriptor of lone pairs or unsaturated bonds for anion part (*Koch and Dittmar, 2006*). Later, these variables used in selecting potential ILs for extractive desulfurization process, where both cation and anion with high calculated value of AI and DBE respectively, are selected.

2.2.3 Aromaticity Index (AI)

The stability of certain molecular structures is attributed to, either a gain or loss of their aromaticity since their similarity to benzene is beyond the scope of simple Hückel theory on which aromaticity was originally based on. Since aromaticity is not

yet observable using quantum chemical basis and not a directly measurable quantity either, several definitions of aromaticity have been put forward. The most accepted definition of aromaticity is referring to the electronic cyclic delocalization which is present in all aromatic species. Earlier on, many different quantities have been derived to express the degree of aromaticity in various types of molecules. Pozharskii (*Katritzky et al. 1995*) for example, introduced aromaticity index as the average of the fluctuations of all ring bonds whereby the total number of differences between each possible pair of bond order in the ring is being manipulated. Meanwhile, Bird aromaticity index takes into account the degree of statistical uniformity of the bond orders of the ring, but uses the differences between the actual bond orders and the arithmetic mean of these bond orders. Bird also has modified his aromaticity index to be applicable to all ring sizes including bicyclics, nitrogen, phosphorus and arsenic compounds (*Kotelevskii and Prezhdo, 2001*). These aromaticity indices may serve as good descriptors of π-electron delocalization for heterocycles organic molecules, some carbocycles and benzo-fused derivatives (*Krygowski and Stepien, 2005; Bultinck et al. 2006*).

Koch and Dittmar in 2006 introduced a new method for estimating aromaticity index (AI) calculated solely from the exact molecular formula, where the exact molecular masses of naturally occurring compounds containing C, H, O, N, S and P have been established and validated through extensive ultra-high resolution mass spectrometry like Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS) AI is a measure for C-C double-bond 'density' which additionally considers the contribution of π-bonds by the heteroatoms. Since all heteroatoms are taken into account as potential contributors, the actual aromaticity in a molecule can be higher and AI must be regarded as a conservative approach. AI has the potential to be expressed for quantitative electron delocalized of ILs; therefore AI can be used as ILs screening tool (for cation part selection). Coupled with double bond equivalent (DBE), it would be possible to screen potential ILs for desulfurization.

2.2.4 Double Bond Equivalent (DBE)

Double Bond Equivalent (DBE), also known as degree of unsaturation of an organic molecule is basically related to π-bonds or rings. It illustrates the number of

hydrogens or halogens that would have to be added to a molecule by 2 in order to convert all π-bonds to single bond, or all rings to acyclic structures. DBE is calculated by simply comparing the number of hydrogens that would be present in the fully saturated or acyclic structure with the number actually present and dividing with 2 to get the number of DBEs.

Recently attempted study found that a linear relationship exists between calculated DBE values and the ratio of carbon to oxygen atoms in oxygenated compounds of dissolved organic matter (*Bae et al. 2011*). In organic non-spectroscopic analysis, the first attempted calculation of DBEs solely involved organic molecules that contain only carbon (C), hydrogen (H) and nitrogen (N) atoms and later expanded to oxygen (O), sulfur (S) and phosphorus (P) -containing molecules. DBE value is being investigated intensively for dissolved or natural organic molecules characterization studies even though DBE calculation is a well-established tool in non-spectroscopic studies based on value validation using mass spectrometry data.

Both AI and DBE values provide information of the potential contribution due to aromaticity, heteroatoms and unsaturated structures (*Matito et al. 2005; Koch and Dittmar, 2006*). The combination of AI and DBE would promote further understanding of ILs selection and interaction mechanism as compared to COSMO-RS approach alone.

2.3 Selection of ILs for Extractive Desulfurization

Preliminary selection and screening of suitable ILs by relying on physical, chemical and thermodynamic properties have been intensively investigated and reported in literatures. However, the reported predictive tools for selecting potential ILs are still not satisfactory, as these tools still lack the capability to identify the correct combination of cations and anions matchup for a particular application; this needs further investigations.

2.3.1 Predictive Approach

Due to the enormous number of possible combinations of cations and anions to produce ILs, an accurate prediction for a particular application is necessary. Predictive approach will reduce cost and time as opposed to trial and error using experimental work. One of the predictive approaches is COSMO-RS which is based on quantum chemistry approach. Recently this approach is being applied especially in predicting physical, chemical and thermodynamic properties plus interaction mechanism of potential ILs (*Palomar et al. 2009*). A recent study which employed COSMO-RS was carried out by Banerjee group, in which different or modified parameterization were used to predict potential ILs for diesel desulfurization, by means of selectivity and capacity at infinite dilution. They selectively screened out 168 suitable ILs (from 28 anions and 6 cations) mostly for extracting thiophene, BT and DBT from simulated diesel composition (*Anantharaj and Banerjee, 2011*). The attempted investigation via COSMO-RS showed that 4-ethyl-4-methylmorpholinium gave the best performance for desulfurization in combination with anions such as thiocyanate (CNS), acetate (CH_3COO), bis(trifluoromethylsulfonyl)imide (NTf_2) and triflate (CF_3SO_3). However, their predictions did not match well with the experimental results from the literatures; for instance Holbrey et *al*. (2008) who reported that (CF_3SO_3) and (NTf_2) anions showed poor results in removing DBT from *n*-dodecane phase, while Wang[b] et *al*. (2007) indicated that (CH_3COO) anion gave average performance in removing thiophene from *n*-heptane phase.

2.3.2 Experimental Approach

The screening of appropriate combination of cation/anion for ILs was first attempted by Bosmann and co-worker. They justified that from three types of cations ([emim],[bmim] and [omim]) with [BF_4] as anion and seven types of anions ([PF_6], [CF_3SO_3], [BF_4], [Cl], [$MeSO_4$], [$MeSO_3$] and [OSO_4]) with [bmim] as cation, [omim] and [OSO_4] depicted better extractability for DBT removal. It was later proved that the combination of these cation-anion, [omim][OSO_4] has high viscosity at ambient conditions. Further work was carried out which indicated that [bmim][OSO_4] has the best extractability of some sulfur compounds (*Eβer et al. 2004; Nie et al. 2006*). Later, Holbrey and co-worker screened out 20 ILs for extracting   DBT   and   revealed   that   1-butyl-dimethylpyridinium

bis(trifluoromethylsulfonyl)imide ([bdmpy][NTf$_2$]) yielded the highest DBT removal (83%) from *n*-dodecane. Recently, [bmim] tricyanomethane ([C(CN)$_3$] has been found to yield higher DBT removal (86%) as compared to previous works (*Hansmeier et al. 201*1). The result of both research studies are summarized in Table 2.2.

Table 2.2: Results of DBT removal using some ILs in extractive desulfurization

ILs	Experimental description	
	DBT	GC-analysis
[3-mebupy][N(CN)$_2$]	86%	
[bmim][C(CN)$_3$]	86%	Extraction condition;
[4-mebupy][N(CN)$_2$]	85%	Speed: 1200 rpm
[4-mebupy][SCN]	84%	Time: 15 min
[bmim][N(CN)$_2$]	77%	Vol. Ratio: 1/1
[bmim][SCN]	70%	
[emim][N(CN)$_2$]	57%	
[omim][BF$_4$]	70%	
[opy][BF$_4$]	66%	
[beim][DBP]	63%	
[bmim][DBP]	62%	
[eeim][DEP]	62%	
[hpy][BF$_4$]	59%	
[omim][DMP]	57%	
[emim][DEP]	57%	
[obim][DBP]	55%	
[beim][DEP]	54%	
[oeim][DEP]	54%	
[emim][DMP]	54%	
[hmim][DMP]	51%	
[hbim][DBP]	50%	
[bbim][DBP]	47%	
[heim][DEP]	47%	
[bmim][DMP]	41%	
[bpy][BF$_4$]	44%	
[mmim][DMP]	33%	
[emim][DBP]	32%	
[bmim][BF$_4$]	16%	
Hansmeier et *al*. (2011), Green Chemistry		
	DBT	GC-MS and HPLC
[C$_4$mim][BF$_4$]	47%	
[C$_4$mim][OcSO$_4$]	63%	Extraction condition;
[C$_4$mim][CF$_3$SO$_3$]	50%	Time: 60 min
[C$_4$mim][PF$_6$]	53%	Settling: 15 min
[C$_4$mim][NTf$_2$]	50%	Temp.: 40°C

[C$_4$mim][SCN]	66%	(equal volume ratio)
[C$_4$mim][CH$_3$CO$_2$]	61%	
[C$_4$py][NTf$_2$]	55%	
[C$_4$py][BF$_4$]	43%	
[C$_4^4$mpy][NTf$_2$]	76%	
[C$_4^4$mpy][BF$_4$]	70%	
[C$_4^4$mpy][SCN]	79%	
[C$_4^4$mpy][CF$_3$SO$_3$]	72%	
[C$_4^3$mpy][NTf$_2$]	77%	
[C$_4^3$mpy][BF$_4$]	70%	
[C$_4^3$mpy][SCN]	83%	
[C$_4^3$mpy][CF$_3$SO$_3$]	69%	
[C$_4^{2,4}$dmpy][NTf$_2$]	83%	
[C$_4^{2,5}$dmpy][NTf$_2$]	81%	
[C$_4$mpyrr][NTf$_2$]	47%	
Holbrey et *al*. (2008), Green Chemistry	*n*-dodecane	

2.4 Extractive Desulfurization

When a separation by distillation is ineffective or very difficult, liquid-liquid extraction (LLE) is one of the main alternatives to be considered. Close boiling point mixtures or substances that are unstable at the temperature of distillation, even under a vacuum condition, may often be separated by extraction which utilizes the chemical differences instead of vapour pressure differences. One of the major uses of extraction is to separate petroleum products that have different chemical structures, but have about the same boiling range. In liquid-liquid extraction, two phases must be brought into good contact to permit transfer of solute and then be separated (*McCabe et al. 2001; Planeta et al. 2006*).

Extraction is a process in which a liquid mixture (of normally two species that contain the solute and the feed carrier) is contacted in a mixer with a third liquid (normally the solvent) that is immiscible or nearly immiscible with the feed carrier component. When the liquids are contacted, the solute is transferred from the feed carrier into the solvent. It is because during mixing process, bonds between solute and feed carrier are broken and possible new bonds are formed between solute and solvent. The energy, which may or may not be required in breaking the bonds

between the solute and feed carrier or in forming the bonds between the solute and solvent, depends on the type of interaction.

The combined mixture is then allowed to settle into two phases that are then separated by gravity in a decanter. When a solute transfers from one phase to another, the transfer rate generally decreases with time until the second phase is saturated with the transferred solute, holding as much as it can hold at the prevailing process condition. When the concentrations of the solute in each phase no longer changes with time, the phases are said to be at equilibrium. The effectiveness of any of the separation processes described depends on both how the solute is distributed between the phases at equilibrium and on the rate at which the system approaches equilibrium from its initial state. The extract is the layer of solvent plus extracted solute and the raffinate is the layer from which the solute has been removed from the feed carrier substance (*McCain, 1990; McCabe et al. 2001; Stanislaus et al. 2010*).

Recently, ILs has been applied in the petrochemical industry especially in catalytic processes, extractive distillation and LLE process for example upgrading heavy oils for desulfurization. Their negligible vapour pressure allows the extracted product to be separated from the ILs through low pressure distillation with potential energy savings. In addition, as a result of their negligible vapour pressure, they are able to be regenerated for reuse.

The use of ILs for selective extraction of sulfur compounds from diesel is first described by Bosmann et *al*. in 2001. Based on the initial idea to extract the sulfur compound by chemical interaction, the extraction of DBT with Lewis and Brønsted acidic ILs was majorly investigated. They indicated that such Lewis-acid based interactions enhance the extraction power of ILs that permit complex formation of sulfur compound and ILs. They also identified that extraction of actual diesel is much more complicated due to the complex chemical composition of diesel which includes many different sulfur compounds and other impurities like organic nitrogen and oxygen compounds (*Brennecke and Maginn, 2001; Eβer et al. 2004; Holbrey et al. 2008; Cassol et al. 2007*).

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2.4.1 Extractive Desulfurization on Model Oil

As mentioned previously, due to the limited efficiency of HDS towards aromatic sulfur compounds, a number of research have been focused on extracting them, mainly thiophene, BT, DBT and their derivatives. By using various types of ILs through various anion/cation combinations, some researchers have found that extraction process alone could remove up to 86% sulfur in model oil and 30% in actual diesel, which due to the steric hindrance of various sulfur compounds (*Eβer et al. 2004*). There are various types of model oil that have been investigated including aliphatics (*n*-hexane, *n*-heptane, *n*-octane, *n*-dodecane) and aromatics (toluene). In evaluating desulfurization performance, besides removal percentage, sulfur partition coefficient (K_N) gives a better insight in terms of explaining the relationship between ILs amount and its structure against desulfurization performance (*Eβer et al. 2004; Jiang et al. 2008*). K_N is defined as the ratio of sulfur concentration on weight basis in ILs to sulfur concentration in hydrocarbons, which the higher K_N the better the desulfurization performance of that ILs (*Nie et al. 2008*).

Zhang and Zhang (2002) in their report said that at ambient condition operation, sulfur compounds with C_5 aromatic ring were observed to favourably absorb over C_6 aromatics sulfur, while sulfur with non-aromatic structures were poorly absorbed by imidazolium-based ILs. Eβer and co-worker reported in their article that, even though the concept of extraction in desulfurization seemed feasible, but selective extraction of nitrogen-containing compounds and aromatic hydrocarbons still needs further investigation. Although quite a few researchers preferred pyridinium-based (*Wang[b] et al. 2007; Gao et al. 2008*) and ammonium based ILs (*Taib and Murugesan, 2011*) for extractive desulfurization, it seems that the extraction ability is less promising. Some have been noticed to be comparable to imidazolium-based ILs if the anions matchup is just appropriate (*Alonso[a] et al. 2008; Chu et al. 2008; Jiang et al. 2008; Nie et al. 2008; Hansmeier et al. 2011*).

2.4.1.1 Sulfur Species Study

Most of the research works have been focused on thiophene or DBT removal from model oil mixtures, and sometimes BT and 3-MT (*Huang et al. 2004; Wang[b] et al. 2007; Chu et al. 2008; Kuhlmann et al. 2009; Hansmeier et al. 2011; Wang et al.*

2011). At earlier stage, Zhang's group found that the extraction efficiency of sulfur species follow the order of TS > MT > isobutylthiol using imidazolium-based coupled with BF_4^- and PF_6^- as anions (*Zhang and Zhang 2002; Zhang et al. 2004*). Meanwhile, Eβer and co-worker also studied the effect of sulfur species using *n*-dodecane and [bmim][OSO₄], and found that alkylated DBTs showed a much lower extraction efficiency; and followed the order of DBT > BT > 4-MDBT > 4,6-DMDBT > TS > tetrahydrothiophene > dodecanethiol. They explained that these occurred due to the sterical hindrance, which increases with the degree of alkylation of the DBT (*Eβer et al. 2004*).

The findings by Gao et *al.* (2008) revealed that pyridinium-based ILs coupled with BF_4^- anion gave relatively better extraction efficiency toward DBT as compared to BT compound. By using imidazolium-based dialkylphosphate ILs, Nie's group discovered the removal selectivity order of DBT > BT > 3-MT. Mochizuki and Sugawara found that DBT showed better extraction efficiency as compared to diphenylsulfide and diphenyldisulfide compound using imidazolium-based alkylsulfate ILs. The influence of sulfur species was further expanded by Liu's group where they justified relatively low extraction efficiency for thiols, sulphides and similar species which followed the order of DBT > BT > 4-MDBT > 4,6-DMDBT > TS > MT > isobutylthiol (*Nie et al. 2006; Nie et al. 2007; Gao et al. 2008; Mochizuki and Sugawara, 2008; Nie et al. 2008*).

2.4.1.2 Alkyl Side-chain Study

The observation on alkyl side-chain length, whether the side chain is attached to the anion or cation was first attempted by Nie's group using imidazolium-based dialkylphosphates ILs. They identified that the solubility of sulfur compounds as well as hydrocarbon increases as the alkyl substitute in the imidazolium-based dialkylphosphate ILs increases from methyl to butyl. Then, these was further investigated by Mochizuki and Sugawara where they suggested that for imidazolium-based alkylsulfate ILs, alkyl side-chain attached to the cation gave more significant influence toward extractive desulfurization as opposed to when the side chain is attached to the anion. They also suggested that the performance on extractive

desulfurization linearly increases with an increase of the alkyl side-chain length (*Nie et al. 2006; Nie et al. 2008; Mochizuki and Sugawara, 2008*)

2.4.1.3 Stirring Speed Study

The trend or effect of stirring speed has not been discussed much in the open literatures. The stirring speed applied during extraction process is normally set at the optimum speed of the equipment. Usually the speed relies greatly on the equipment capability, stirrer type, sample amounts and extraction period. Stirring speed as low as 100 up to 1200 rpm has been applied in order to reach thermodynamic equilibrium (*Taib and Murugesan, Hansmeier et al. 2011*)

2.4.1.4 Extraction Time Study

The study on extraction time effect (also known as reaction time, stirring time, contact time, mixing time and absorption time) has been investigated by many researchers, in order to identify the optimum duration or equilibrium state for extracting sulfur compound. Equilibrium can be achieved in as fast as three minutes but usually in the range between five to 60 minutes, depending on the viscosity of ILs and extracting temperature (*Zhang et al. 2004; Gao et al. 2009; Yu et al. 2011*)

2.4.1.5 Water Content Study

The investigation on water content was studied by Nie's group which employed imidazolium-based phosphates ILs. They found that the extraction efficiency drastically decreased when water was added into ILs. They suggested that subsequent recycling by water dilution is feasible whereby hydrophilic ILs can easily repel and precipitate the sulfur compounds from ILs phase due to strong electrostatic interaction between water and hydrophilic ILs (*Nie et al. 2006; Nie et al. 2007; Nie et al. 2008*).

2.4.1.6 Mass Ratio Study

Mass ratio of IL to model oil is the most popular parameter that has been studied, and generally the extraction efficiency is found to increase with the increase of mass ratio (IL/model oil), with some depicting a linearity between mass ratio and extraction efficiency (*Mochizuki and Sugawara, 2008*). This effect has a strong influence on

extraction efficiency (*Wang[b] et al. 2007; Gao et al. 2008; Gao et al. 2009; Wang et al. 2011; Taib and Murugesan, 2011*)

2.4.1.7 Initial Concentration Study

The effect of initial sulfur concentration has received little attention by researchers as it has been found to have a minimum impact on extraction efficiency (*Mochizuki and Sugawara, 2008*). Nevertheless, various initial concentration have been studied ranging from 160 up to 1515 ppm of sulfur content, whilst 500 ppm and 1000 ppm are the most studied concentration (*Holbrey et al. 2008; Gao et al. 2009; Taib and Murugesan, 2011; Wilfred et al. 2012*).

2.4.1.8 Temperature Study

Basically, extraction process is conducted at ambient condition, but in order to identify optimum condition, the effect of temperature should be investigated. The extraction efficiency is found to increase with an increase in temperature up to 80°C (*Liu[b] et al. 2008*). Beyond 80°C, a stable trend is shown. This indicates that extraction efficiency slightly increases with temperature. Since extraction efficiency is not sensitive to temperature, extractive desulfurization can be performed at mild conditions, for example at or around room temperature (*Yu et al. 2011*).

2.4.2 Extractive Desulfurization on Model Fuel

Extractive desulfurization has been performed on model fuel containing up to 25% aromatics (*Eßer et al. 2004*). Basically naphthalene, methylnaphthalene, indole, pyridine and tetralin are the most common aromatics used for preparing model fuel. The extraction efficiency is relatively high, and competing removal of aromatics and sulfur compounds was not detected based on model fuel containing *n*-dodecane/indole/DBT using [BMIm][OSO⁻] as extractant (*Eßer et al. 2004*) . Further investigations showed that ILs gave higher removal of molecules that have higher density of aromatic π-electrons. Cross-miscibility of the studied aromatics in the ILs produced an unwanted effect, whereby high cross-miscibility will demonstrate a loss of fuel or at least contribute to an increase of process costs (*Gao et al. 2008; Gao et al. 2009; Hansmeier et al. 2011; Kedra-Krolik et al. 2011*). However, the effect of

aromatic hydrocarbons such as benzene and xylene needs further research in order to understand the selective extraction process.

2.4.3 Extractive Desulfurization on Actual Diesel

An approach based on extraction for removing sulfur compounds from actual diesel using ILs have been investigated by many researchers (*Bosmann et al. 2001; Liu[b] et al. 2008; Kedra-Krolik et al. 2011; Hansmeier et al. 2011*). Compared to model oil or model fuel, the extraction from actual diesel is much more complicated due to its complex chemical composition including many different sulfur compounds and other impurities such as nitrogen and oxygen-containing compounds. For example, the removal of sulfur from model oil is 64% but in actual diesel this percentage is drastically reduced to 24.3% when the same ILs is applied. The obvious or most sterically hindered sulfur species would still remain in the actual diesel even though after several extraction steps (*Gao et al. 2008*). However, it has been proven that extractive desulfurization of actual diesel with ILs is still possible, although the operating expenses such as the number of theoretical extraction steps may vary in order to reach ultra-low concentration of sulfur (*Zhang et al. 2004; Eβer et al. 2004; Chu et al. 2008; Schmidt et al. 2008; Gao et al. 2009*).

2.5 Optimization Studies

Design of Experiments (DoE) has been very useful in the study of complex processes in order to determine the optimum operating conditions for extraction process. In extractive desulfurization of model oil using ILs, the present practice of determining the optimal operating conditions is through one-variable-at-a-time method, which is time consuming (*Wilfred et al. 2012; Liu[b] et al. 2008*). Therefore to overcome this problem, optimization studies are usually carried out using Response Surface Methodology (RSM) for a better understanding of evaluating the optimum conditions for extractive desulfurization process.

2.5.1 Response Surface Methodology (RSM)

RSM is a set of techniques that encompasses designing up a series of experiments aimed to determine the mathematical model which best fits the data collected from the

experimental design and the optimal setting of the experiment factors that produced the optimum values of response (*Montgomery, 2001*). The first step in RSM is to approximate the mathematical model. Usually, this process employs a low-order polynomial in some region of the operating condition (independent variables). If the response is well modelled by a linear function of the independent variables, then the approximating mathematical model is a first-order model. If there is curvature in the system or in the region of the optimum, then polynomial of higher degree must be used to approximate the response. This analysis is to determine the optimum independent variables of the system being studied that satisfy the operating specifications. There are many useful RSM designs that are in practice such as Central Composite Design (CCD), Three-level Factorial, Pentagonal and others.

2.5.2 Central Composite Design (CCD)

CCD is the most used design technique, mostly for fitting a second order model. This might be because of its ability to run sequentially. It estimates linear interaction as well as curvature effects. As the design can provide much information on experimental variable effects and overall experimental error in a minimum number of required runs, it can be considered as a very efficient design. It also has the ability to be used under different experimental regions of interest and operability because of its accessibility to several varieties of CCD (*Montgomery, 2001*).

The three main varieties of CCD available in most statistical software programs by changing the alpha (α) are rotatable, face-centred and inscribed. As shown in Figure 2.7, which illustrates the three types of CCD, the rotatable design explores the largest process space. This design is used when the data range is not so vast. The inscribed design investigates the smallest process space. Both rotatable and inscribed are considered as rotatable design in which the $\alpha \neq 1$, but the face-centred design is when $\alpha = 1$ (*Montgomery, 2001*).
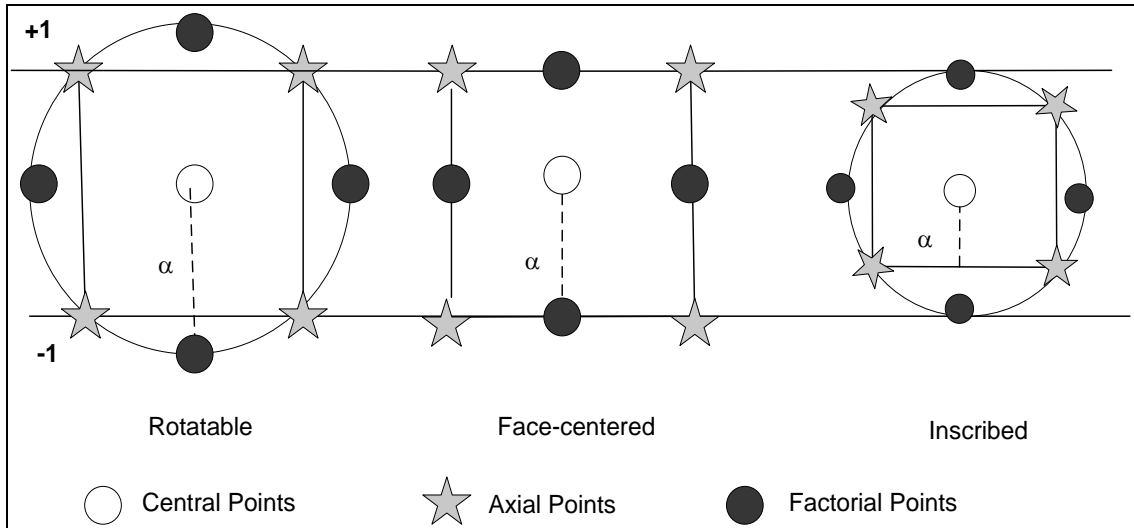
Figure 2.6: Three types of central composite designs

The rotatable design is the original form of CCD in which some of the design point will occur outside the range of the factor as can be seen in Figure 2.6. These points are named as axial points. They are at α distance from the centre. It is based on the number of factors (k) in the design, where α is equal to $\sqrt{k}$. The rotatable design requires 5 levels of each factor and 3-5 centre points are required. The factorial points will range between -1 and +1 while the axial points would range between $-\alpha$ and $+\alpha$. The face-centred design is not considered as rotatable design. The design requires 3 levels of each factor and 1-2 centre points are required. The factorial and axial points would range between -1 and +1. In the inscribed design, the factorial points would range between $-\alpha/2$ and $+\alpha/2$ and the axial points would range between -1 and +1 (*Montgomery, 2001*).

2.5.3 Data Analysis

Analysis of experimental data based on selected RSM design is done by fitting the data obtained to the second order polynomial as shown in Equation 2.1.

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i \chi_i + \sum_{i=1}^{k} \beta_{ii} \chi_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} \chi_i \chi_j + \varepsilon \qquad (2.1)$$

where

Y   is the response (dependent variables).

β_o is constant coefficient.

β_i, β_{ii} and β_{ij} are coefficients for the linear, quadratic and interaction effect.

χ_i and χ_j are factors (independent variables).

ε is the error.

2.5.4 Model Fitting and Validation

The statistical significance of the predicted quadratic models is evaluated by the Analysis of Variance (ANOVA). The ANOVA determines which of the factors significantly affect the response variables in the study using Fisher's Statistical Test (F-Test). The F-Test analysis computed with P-value approach is employed to reveal the statistical significance of the regression coefficients. The F-Test value explains the ratio between the variations in the data to the pure error. The factors studied will appear to have a significant effect on the response if a large ratio in the F-Test value is obtained. On the other hand, the P-value is a level of significance that is used to determine how significant the data is at any specified level of significance. The smaller the magnitude of the P-value, the more significant is the corresponding coefficients. The significance and magnitude of the effect of estimates of each variable and all their possible linear and quadratic interactions on the response variables will be determined. The effect estimate of each variable represent the improvement in the response variable, which is expected as the variable setting is changed from low to high. The significance of the model can be evaluated by considering either the F-Test or P-value of the model and the lack-of-fit. The effects with less than 95% of significant that are effect with a P-value higher than 0.05, will be discarded and pooled into the error term (residual error) and a new ANOVA will be performed for reduced model. The P-value represents a decreasing index of reliability of the results (*Montgomery, 2001; Beg, 2003*).

Meanwhile, the regression models will be accepted when the P-value of the model is lower than 0.05 (ideally lower than 0.001) and the lack-of-fit is higher than 0.05. However, if any one of these conditions is not fulfilled, the model is only accepted

when the model correlation coefficient, R^2 is higher than 0.05, meaning that 95% of the data is explained by the model (*Montgomery, 2001*).

2.6 Ternary Diagram Studies

Ternary diagrams are used for a wide variety of applications including rock classification schemes in depicting chemical compositions on certain types of phase diagrams. Normally, ternary diagrams are used to represent or explain the relative fraction of three components present in a mixture. In liquid-liquid extraction process, the separation of the mixture is often illustrated by ternary diagrams. For construction of ternary diagram, besides experimental measurement, theoretical modelling for predicting mixture composition are becoming more essential especially for designing the processes involving that mixture. From a ternary diagram, the composition of sulfur compound (solute), ILs (solvent) and oil (feed carrier) composition can be determined clearly including the solute distribution coefficient/ratio, ILs selectivity and capacity (*Marsh et al. 2004; Arce[a] et al. 2006; Arce[b] et al. 2006; Arce[a] et al. 2007; Cassol et al. 2007; Shiflett and Yokozeki, 2007; Huo et al. 2008; Shiflett and Yokozeki, 2008; Domanska and Krolikowski, 2010; Shiflett and Niehaus, 2010; Marciniak, 2011*). In order to use ILs as solvents, it is necessary to be able to predict their behaviour in terms of their miscibility with the solute and feed carrier, which in this case is solely hydrocarbon.

In the open literature, predominantly imidazolium-based ILs combined with anions like NTf_2^-, PF_6^-, $EtSO_4^-$ and BF_4^- are described as the solvents for the extraction of hydrofluoroethers, alcohols, aliphatic/aromatic hydrocarbons, phenol and including sulfur compounds (thiophene/DBT/4-MDBT) mostly from hydrocarbon systems. Their measured experimental data were then correlated either using non-random two liquids (NRTL) or UNIQUAC activity coefficient model or both (*Alonso[c] et al. 2007; Arce[b] et al. 2007; Revelli et al. 2010; Kedra-Krolik et al. 2011; Oliveira and Aznar, 2011*).

Alonso and co-worker focused on removing thiophene (TS) from various systems (aliphatic, acyclic and aromatic hydrocarbon) using imidazolium-based ILs coupled

with NTf$_2^-$, BF$_4^-$ and ESO$_4^-$ as anions. From their studies, it can be concluded firstly that the extraction of TS increases with the increase of aliphatic chain length. Secondly, imidazolium-based ILs coupled with NTf$_2^-$ give better TS extraction, and lastly when involving aromatic system partial or total miscibility with ILs is expected (*Alonso[a] et al. 2007; Alonso[b] et al. 2007; Alonso[a] et al. 2008; Alonso[b] et al. 2008; Alonso[c] et al. 2008; Alonso[d] et al. 2008; Alonso[e] et al. 2008*). Arce[a] and co-worker investigated ([C$_n$mim][NTf$_2$] + hexane + benzene) ternary system, with *n* taking the values of 4, 8, 10 and 12 at 25°C. They found that short alkyl side-chains on the imidazolium-based ILs led to a better extractive separation of benzene and hexane. These finding provides insight on how modification of alkyl side-chain on cation of imidazolium-based ILs influences the ability of ILs to extract aromatic from aliphatic hydrocarbon mixtures (*Arce[b] et al. 2007*).

Meanwhile, Revelli and co-worker investigated the separation of benzene and TS compound from *n*-heptane at 25°C using [bmim][BF$_4$], 1,3-dimethylimidazolium methylphosphonate ([dmim][MP]) and [bmim] thiocynate ([SCN]) as solvents. A ternary diagram was constructed to evaluate the ability of the studied solvents. The diagram revealed that [bmim][SCN] is a good solvent amongst the other solvents for the extraction of benzene or TS from *n*-heptane (*Revelli et al. 2010*). Recently, Oliveira and Aznar used ternary diagram approach while focusing more on DBT and DBT derivatives separation from aliphatic hydrocarbon systems whereby ILs acted as solvent. They used 1-ethyl-3-methylimidazolium diethylphosphate ([emim][DEP]) and 1-ethyl-3-methylimidazolium ethylsulfate ([emim][ESO$_4$]) ILs to selectively extract DBT and 4-MDBT from *n*-dodecane. Based on the constructed ternary diagram, distribution coefficients and solvent selectivities, [emim][DEP] gave better extraction for both DBT and 4-MDBT for that studied ternary systems (*Oliveira and Aznar, 2010; Oliveira and Aznar, 2011*).

2.7 Regeneration Studies

Besides being efficient for extraction process, regeneration or recycibility of spent ILs is equally important since ILs has been recognized as environmentally benign solvent. Since ILs is quite expensive as compared to some conventional organic

solvents, finding an alternative way to recycle spent ILs is the key for cost effectiveness in order to ensure the feasibility of using ILs at a larger scale application.

Undoubtedly, regeneration has become a fundamental issue from economic point of view. However, this is not only limited to the operating cost, but also concerning environmental issues such as disposal, biodegradable and toxicity. In general, ILs has a higher density compared to organic solvents or water; therefore, many ILs form separate phases when mixed with organic or aqueous solution. This behaviour makes ILs as feasible for regeneration, which in turn presents potential economic viability of desulfurization process using ILs. In addition, the process is considered as being environmental benign since no waste is generated (*Davila et al. 2007*).

Most published literatures have mentioned that ILs can be easily regenerated, however mostly at lab scale only. Various successful methods have been studied, some of which are listed below.

1. Heating spent ILs in order to vaporize the sulfur compounds.
2. Precipitating the sulfur compounds by water dilution process.
3. Back extraction of sulfur compounds with low boiling point hydrocarbon such as *n*-pentane or *n*-hexane.
4. Re-extraction through supercritical CO_2.
5. Hydrogen gas stripping.
6. Inert gas stripping.
7. Vaporization at reduced pressure.
8. Oxidation of spent ILs.
9. Electrochemistry method.

However, the selection of regeneration method depends on the type of ILs, interaction mechanism (whether involving physical interaction or chemical interaction, where no reaction occurs between sulfur, ILs and hydrocarbon in physical interaction) and cross-miscibility of the solvent with ILs. The regeneration process involves a simple heating process where a spent ILs is heated in air at $100^{o}C$ for 30

minutes. No traces of sulfur compounds (thiophene) were detected after the distillation. Thus, the heat treatment process is feasible due to low boiling points of the sulfur compounds as compared to the ILs. As experimentally recorded by Jiang et *al*. in 2008, heating or vaporization method is less effective for long chain alkyl substituted BT and it derivatives as the boiling point may exceed the stable temperature range of ILs.

Back extraction generally suffers from lack of solvent efficiency, and re-extraction through supercritical CO_2 is restricting with high energy expenses (*Planeta et al. 2006*). The regeneration method using electrochemical approach is less effective if and only if the ILs is low in conductance. Nefedieva et *al.* (2010) studied the electrochemical approach for purifying ILs from BT and DBT, which revealed that redox reactions of BT and DBT occur with the formation of new polymers, at the same time decreasing the concentration of BT and DBT in ILs.

From the literatures and previous studies, most of the methods have explained the regeneration of spent ILs for sulfur compounds, but the study on hydrocarbons is limited. Also, from previous studies it has been proven that cross solubility of hydrocarbon in ILs is significantly present that may reduce the extraction efficiency for the long run processes.

2.8 Summary

The literature survey has shown that not much work has been reported on the interaction mechanism of ILs with sulfur in model oil system. In recently published work, the interaction was predicted using COSMO-RS where the strength of hydrogen bond of anion should be reduced in order to increase thiophene extraction capacity. On the other hand, the same researchers also found that the smaller sized cations would lead to higher selectivity, which could lower the capacity and vice versa (*Kumar and Banerjee, 2009*). While others have reported that the absorption capacity of sulfur compounds in ILs are strongly dependent on the chemical structures, physical properties and compactness between the cation and the anion of the ILs

(*Boschetti et al. 2007; Chu et al. 2008; Zhou et al. 2008*). However, these conclusions lead to a broad selection of ILs for extractive desulfurization process.

From the above discussion, it is clear that a systematic study is required to address the issue of selecting the suitable ILs for extracting sulfur from diesel in order to meet the stringent sulfur requirements. Firstly, the existing method of predicting or screening potential ILs for desulfurization using COSMO-RS is inconsistent with the literature results whereas this method solely relies on the results obtained from COSMO-RS in which the parameterizations have been fixed. These parameterizations are not suitable for screening potential ILs in desulfurization. Besides that, due to the major interaction mechanism involving π-electron density which also not covered by COSMO-RS, a new approach should be introduced for better ILs selection for desulfurization, where by estimating the aromaticity index (AI) for cation and double bond equivalent (DBE) for anion, which being identified to be closely related to π-electron density, are used to preliminarily select the suitable ILs for extractive desulfurization purposes have been explored.

Secondly, cross-miscibility between hydrocarbon and ILs has not been well studied and reported especially involving aromatic hydrocarbons. In addition, there is also no established relationship or correlation for desulfurization from the physical properties of ILs. In this study, the relationships between the physical properties of ILs against desulfurization performance are generated and discussed. Besides, by developing the ternary diagram between ILs, hydrocarbons (both aliphatic and aromatic) and sulfur compound (BT) is essential in discussing the cross-miscibility matter for extractive desulfurization on model fuel and actual diesel, especially toward miscibility and extractability of ILs.

In conclusion, extractive desulfurization process using selective ILs as the extractant is still in need of further research, starting from screening of suitable ILs for desulfurization, synthesis of ILs, physical property analysis of ILs, single batch extraction study encompassing process optimization up to actual diesel application, and including regeneration of spent ILs.