

CLEANING OF CONTAMINATED SOILS USING IONIC LIQUIDS AND
SUPERCRITICAL CARBON DIOXIDE

by

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ABSTRACT

CLEANING OF CONTAMINATED SOILS USING IONIC LIQUIDS AND SUPERCRITICAL CARBON DIOXIDE

The aim of this research was to utilize the ability of ionic liquids (IL) to dissolve contaminants at near ambient conditions from soil along with the ability of scCO_2 to recover the contaminants from the IL extract, in order to develop a process for the cleaning of contaminated soils. Naphthalene was used as the model component to represent a group of soil contaminants, and 1-n-butyl 3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) was used as the IL. The model component was extracted from soil by IL and then it was recovered from the IL extract by scCO_2 to recycle the IL. The feasibility of using scCO_2 to recover the naphthalene dissolved in the IL was investigated by the supercritical extraction experiments conducted at 25, 35, 40°C and 80, 100, 120, 140 bar to observe the effects of temperature and pressure on the naphthalene recovery. The supercritical extraction experiments were performed for two, four and six hours to study the influence of contact time. Finally, ILs cleaned by scCO_2 under different conditions were reused in the extraction of other soils samples to observe the efficiency of IL recycling. Results of soil extraction experiments demonstrated that soil contaminated with naphthalene was cleaned using [bmim][PF₆], and the naphthalene remaining in the soil was below the maximum allowable concentration limit given. Results of scCO_2 extraction experiments suggest that extraction pressure, temperature and time positively affect the naphthalene recovery from IL. At 140 bar and 40°C and four hours of extraction period, naphthalene recovery from IL by scCO_2 reached a value of 83.8 per cent, whereas at the low end of the pressure and temperature range studied, i.e. at 80 bar, 25°C and four hours of extraction period, the recovery was 12.0 per cent. This study is expected to be the first in the literature which investigates soil-model compound-IL- scCO_2 system. On the basis of this research a process flowsheet was suggested using IL extraction of contaminated soils and continuous scCO_2 extraction of the contaminants from IL extract.

ÖZET

KİRLİ TOPRAKLARIN İYONİK SIVILAR VE KRİTİKÖTESİ KARBON DİOKSİT İLE TEMİZLENMESİ

Bu araştırmanın amacı iyonik sıvıların normal şartlarda toprakta bulunan kirletici maddeleri çözme gücünden ve kritikötesi karbon dioksitin iyonik sıvıdaki çözünmüş olan bu maddeleri çekme gücünden faydalanarak kirli toprakların temizlenmesini hedefleyen bir işlem geliştirmektir. Bu çalışmada naftalin, toprak içerisindeki kirletici maddeleri temsilen model malzeme olarak, 1-n-bütül 3-metilimidazolyum hekzaflorofosfat ([bmim][PF₆]) ise iyonik sıvı olarak kullanılmıştır. Naftalin ile kirletilmiş olan toprak iyonik sıvı ile temizlenmiştir. Toprakta iyonik sıvı içerisinde geçen naftalin kritikötesi karbon dioksit kullanılarak iyonik sıvıdan çekilmiştir. Kritikötesi özütleme deneyleri 25, 35, 40°C sıcaklık, 80, 100, 120, 140 bar basınçlarda yapılmıştır. Kritikötesi karbon dioksit ile iyonik sıvının temas süresinin etkisini gözlemlemek amacıyla iki, dört ve altı saatlik deneyler yapılmıştır. Kritikötesi yöntemle temizlenen iyonik sıvı, naftalinle kirletilmiş toprakların temizlenmesinde tekrar kullanılmıştır. Toprak özütleme deneyleri sonucunda, naftalin ile kirletilen toprağın [bmim][PF₆] ile başarıyla temizlendiği, toprakta kalan naftalin derişiminin kaynaklarca kabul edilen sınırların altında olduğu görülmüştür. Kritikötesi özütleme deneylerinin sonuçları, basınç, sıcaklık ve özütleme süresi arttıkça, kritikötesi karbon dioksitin [bmim][PF₆] içerisinde naftalin çekme oranının arttığını göstermektedir. Dört saat süresince, 140 bar, 40°C’de yapılan deneylerde iyonik sıvı içerisinde çekilen naftalin oranı yüzde 83.8’e ulaşmakta iken, 80 bar ve 25°C gibi düşük basınç ve sıcaklıklarda dört saat süresince yapılan deneylerde, bu oran yüzde 12’ye düşmektedir. Bu çalışmanın, toprak-kirletici madde-iyonik sıvı-kritikötesi karbon dioksit sistemini araştıran ilk çalışma olması beklenmektedir. Bu araştırma temelinde, kirli toprakların iyonik sıvı ile özütlenmesini ve iyonik sıvıların karbon dioksit ile sürekli temizlenmesini sağlayan bir süreç akım çizelgesi önerilmiştir.

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LIST OF ABBREVIATIONS

ATR-IR	Attenuated total reflectance-Infra red
IL	Ionic liquid
K	Distribution coefficient between IL and scCO ₂ phases
RTIL	Room temperature ionic liquid
scCO ₂	Supercritical carbon dioxide
SCF	Supercritical fluid
SCFE	Supercritical fluid extraction
TSIL	Task specific ionic liquid
UV-Vis	Ultraviolet-Visible
VOC	Volatile organic compound

1. INTRODUCTION

Soil pollution has become an important environmental problem in every country of the world due to industrialization and to high degrees of utilization of modern agricultural methods. Soil contamination is due to either solid or liquid hazardous substances mixed with the naturally occurring soil. Solid and liquid wastes of industries, usage of commercial fertilizers to increase agricultural production yield, soil regulators and hormones, usage of waste water for agricultural irrigation, radioactive sprinkle and atmospheric precipitation are the main factors polluting the soil. Also, there have been some contaminants such as asbestos in the natural composition of soil (<http://www.cevreorman.gov.tr/toprak>). Heavy metals, hormones, organic composites, radioactive wastes can also mix with soil naturally or by human activities. Usually, contaminants in the soil are physically or chemically adhered to soil particles, or, if they are not attached, are trapped in the small spaces between soil particles. Since the soil has a dynamic structure, these contaminants are absorbed by colloidal surfaces and retained in the soil. The soil contaminants can threaten health of plants, animals and humans. Moreover, contaminated soil harms another essential natural source; water. These contaminants can pollute the underground water by leakage through the soil or they can pollute the surface water sources by flooding or soil erosion.

Usually, the contaminated soil is abandoned and it is not used due to low agricultural efficiency and productivity. The contaminated soil can be excavated from the ground to be treated or it can be left in the ground and treated in its place. Some precautions can be taken to prevent the pollution becoming more widespread and reaching plants, animals, or humans. The general approaches to clean up the contaminated soil are flushing the contaminants out of the soil using water, chemical solvents, air, steam; adding special materials to encapsulate the contaminants and prevent them from spreading; destroying the contaminants by incineration (<http://www.epa.gov/superfund/students/wastsides/soilspil.htm>).

Soil pollution has also become an important concern for chemical industries. The chemical processing industries are instrumental both in the contamination and offering solutions for remediation of contaminated soils. A wide range of technologies are used for the remediation of contaminated soil, including the technologies based on liquid extraction. In order to extract the contaminants from soils, volatile organic solvents such as toluene, benzene, methanol, ethanol etc. are used. Traditional methods, in which these organic solvents have high participation, although necessary and advantageous on processing level, are significant sources of environmental pollution via fugitive emissions (Blanchard and Brennecke, 2001). Since these solvents have narrow liquid ranges, they become volatile at process conditions. The evaporation of organic solvents to atmosphere has a harmful effect on human health and environment. Nearly twenty million tons of volatile organic compounds (VOCs) are discharged into atmosphere each year as a result of industrial processing operations (Allen and Shonnard, 2002). Some of these amounts are responsible for air and water pollution and the rest for soil contamination. Solvents comprise two thirds of all industrial emission and one third of all organic solvent emissions. These emissions are linked to serious negative effects including global climate change, poor urban air quality and human illness (Brennecke and Maginn, 2001). There have been increasing limitations and strict regulations on volatile organic emissions recently to prevent environmental pollution and to reduce working exposure hazards. Ionic liquids (ILs) are created as green solvents in order to satisfy these regulations for chemical process industries. Since the ILs have no measurable vapor pressure, they can be used as environmentally benign media for a range of industrial processes.

Supercritical Fluid Extraction (SCFE) technologies have some advantages over the conventional liquid extraction techniques such as the ability of supercritical fluids (SCFs) to dissolve organic contaminants from soil. The ability to change the solvent power of SCFs by varying the temperature and pressure may be advantageously used for these purposes. Moreover, the high solute diffusivities in SCFs give superior mass transfer properties. SCFs are environmentally acceptable compared to volatile organic liquids. However such processes require that the contaminated soil be processed at high pressures, where batch handling is a must due to the solid nature of the soil fed to the pressure vessel.

This present study was performed to clean the contaminated soil by using two environmentally benign technologies: extraction of the soil contaminants by IL and recovery of the contaminants from IL by supercritical fluid extraction to recycle the IL. The solubility of scCO_2 in IL and the insolubility of IL in scCO_2 give an interesting binary system. The advantages of two green solvents, IL and scCO_2 , are combined with this system. This work investigates the feasibility of using an IL- scCO_2 system for the separation of harmful contaminants from soil. Model component naphthalene was used to simulate the soil contaminant, since the behavior of naphthalene in scCO_2 is well documented in literature. As the IL, 1-n-butyl 3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), the most widely studied IL in the literature, was used. CO_2 was preferred as the SCF in this study since it is non-toxic, nonflammable, environmentally acceptable, cheap, readily available in large quantities and the most popular SCF used in the related supercritical industries in practice.

Definitely there could be other hazardous components than naphthalene in the soil. However, the soil-naphthalene pair can very well be a representative for a soil-contaminant-IL- scCO_2 system as long as the basic aspects of the envisioned process are investigated. In this study, the amounts of soil contaminant extracted from soil by IL, per cent recovery of the contaminant from IL by scCO_2 and dependence of these upon processing variables such as extraction pressure, temperature, and time were studied with the model component-soil system. Moreover, a process for the cleaning of the contaminated soils using ILs and scCO_2 , was suggested based on the principles set and the experimental results obtained in this study.

Chapter 2 gives a literature survey on fundamentals of ILs, their properties, structures and applications in detail since ILs are an extremely new topic for chemical engineers. Chapter 3 represents the IL- scCO_2 systems and their applications. The main methods used for remediation of contaminated soil, studies for remediation of soil using scCO_2 and characteristics of the model compound naphthalene as a soil contaminant are discussed in Chapter 4. The detailed description of the experimental methods, materials and apparatus used are explained in Chapter 5. The results obtained from the experiments and related discussions are stated in Chapter 6. Finally concluding remarks with possible new research directions and recommendations are provided in Chapter 7. In Appendix A, the structure and general

properties of [bmim][PF₆] are given. The calibration chart used for calculation of amount of model compound extracted from soil and IL is presented in Appendix B. Finally, the particle size distribution of soil sample is given in Appendix C and X-ray diffraction analysis of the soil samples are given in Appendix D.

2. IONIC LIQUIDS

A new green chemical revolution based on ILs excited both the academia and industry since this new chemical group can dramatically reduce the use of hazardous and polluting organic solvents. The terms room temperature ionic liquid (RTIL), nonaqueous ionic liquid, molten salt, liquid organic salt and fused salt have all been used to describe these salts in the liquid phase (Welton, 1999). In contrast to high temperature molten salts, ILs are salts that are liquid at room temperature.

ILs possess a unique array of physico-chemical properties which make them suitable in numerous task-specific applications such as extraction in which conventional organic solvents are insufficiently effective or not applicable. These applications will be discussed in following sections in detail.

2.1. History of ILs

The earliest IL in the literature was created intentionally in 1970s for batteries of nuclear warheads. During 1940s, aluminum chloride based molten salts were utilized for electroplating at temperatures of hundreds of degrees Celsius. In the early 1970s, Wilkes tried to develop better batteries for nuclear warheads and space probes which required molten salts to operate. These molten salts were hot enough to damage the nearby materials therefore, the chemists searched for salts which remain liquid at lower temperatures and eventually they identified one which is liquid at room temperature. Wilkes and his colleagues continued to improve their ILs for use as battery electrolytes and then a small community of researchers began to make ILs and test their properties. Finally in the late 1990s, the interest in these liquids skyrocketed (Gorman, 2001).

The first ILs in the past, such as organo-aluminate ILs were unstable to air and water and thus most probably limited their range of applications. Furthermore, these ILs were not inert

towards various organic compounds (Dupont, 2004). After the first reports on the synthesis and applications of air stable ILs such as 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), the number of air and water stable ILs has started to increase rapidly.

Recently, researchers have discovered that ILs are more than just green solvents and they have found several applications for them such as making new materials, conducting heat effectively, supporting enzyme-catalyzed reactions, hosting a variety of catalysts (Gorman, 2001).

Although the number of research on ILs and their applications is increasing exponentially in the literature, the study of ILs is a young field and researchers are still striving to evaluate the basic physical properties of these chemicals such as viscosity and density (Brennecke and Maginn, 2001). Until 2001, the cation 1-n-ethyl-3-methylimidazolium has been the most widely studied and nowadays, 1-3-dialkyl imidazolium salts are the most popularly used and investigated class of ILs. For the future of ILs, the aim of the research is the commercialization of ILs in order to use them as solvents, reagents, catalysts and materials in large scale applications.

2.2. Basic Properties of Ionic Liquids

ILs are salts which are liquid at ambient temperatures. They possess several advantages over conventional organic solvents, which make them environmentally compatible (Brennecke and Maginn, 2001; Gorman, 2001; Yang and Dionysiou, 2004; Zhao *et al.*, 2005):

- ILs have the ability to dissolve many different organic, inorganic and organometallic materials.
- ILs are highly polar.
- ILs consist of loosely coordinating bulky ions.
- ILs do not evaporate since they have very low vapor pressures.

- ILs are thermally stable, approximately up to 300°C.
- Most of ILs have a liquid window of up to 200°C enabling wide kinetic control.
- ILs have high thermal conductivity and large electrochemical window.
- ILs are immiscible with many organic solvents.
- ILs are non-aqueous polar alternatives for phase transfer processes.
- The solvent properties of ILs can be tuned for a given application.

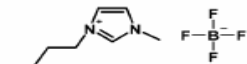
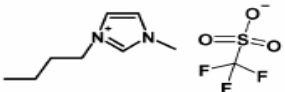
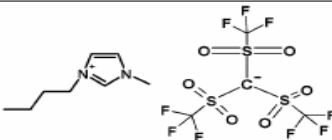
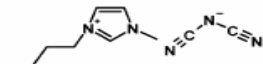
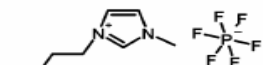
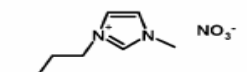
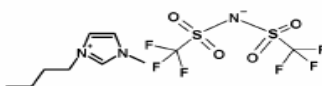
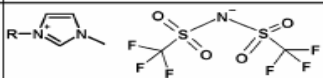
ILs exhibit the ability to dissolve a wide variety of materials including; salts, fats, proteins, amino acids, surfactants, sugars, polysaccharides. ILs can be customized, like organic solvents, to dissolve a wide range of organic molecules, including crude oil, inks, plastics, and even DNA (Renner, 2001).

ILs are made of positively and negatively charged ions whereas water and organic solvents such as toluene, dichloromethane are made of molecules. The structure of ILs is similar to the table salt such as sodium chloride which contains crystals made of positive sodium ions and negative chlorine ions, not molecules. While, salts do not melt below 800°C, most of ILs remain liquid at room temperature. The melting points of sodium chloride and lithium chloride are known as 801°C and 614°C, respectively. Since these conventional molten salts exhibit high melting points, their use as solvents in applications is severely limited. However, RTILs are liquid generally up to 200°C. ILs have a wide liquidus ranges (liquidus range is defined as the temperature range between the normal freezing point and the normal boiling point of IL). The adopted upper melting temperature limit for the classification as 'IL' is 100°C and higher melting ion systems are referred as molten salts.

Researchers investigating ILs believe that ILs remain liquid at room temperature since their ions do not pack well. Combination of bulky and asymmetrical cations and evenly shaped anions form a regular structure namely a liquid phase. The low melting points of ILs are a result of the chemical composition. The combination of larger asymmetric organic cation and smaller inorganic counterparts lower the lattice energy and hence the melting point of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in

lowering the melting point (Yang and Dionysiou, 2004). Most widely used ILs and their structures are given in Table 2.1.

Table 2.1. Most widely used ILs, their structures and short names (Aki *et al.*, 2004)

Ionic liquid	Structure	Short name
1-butyl-3-methylimidazolium tetrafluoroborate		[bmim][BF ₄]
1-butyl-3-methylimidazolium triflate		[bmim][TfO]
1-butyl-3-methylimidazolium methide		[bmim][methide]
1-butyl-3-methylimidazolium dicyanamide		[bmim][DCA]
1-butyl-3-methylimidazolium hexafluorophosphate		[bmim][PF ₆]
1-butyl-3-methylimidazolium nitrate		[bmim][NO ₃]
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide		[bmim][Tf ₂ N]
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide; R = C ₆ H ₁₃		[hmim][Tf ₂ N]

Two important groups of ILs are those based on imidazolium and pyridinium cations with PF_6^- and BF_4^- anions. Figure 2.1 and 2.2 illustrates the imidazolium and pyridinium derivatives of ILs and their possible anions which are investigated in literature very extensively.

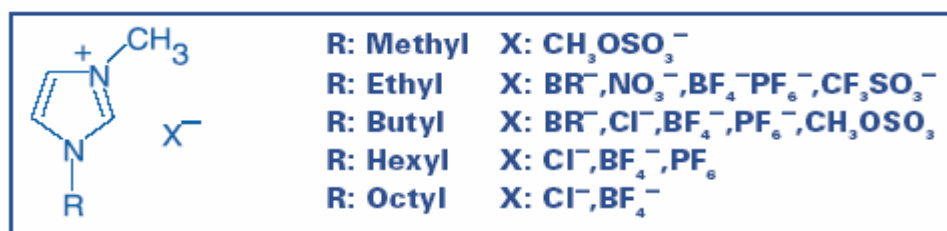


Figure 2.1. Imidazolium derivatives of ILs
(www.sigmaaldrich.com/img/assets/15469/chemfiles)



Figure 2.2. Pyridinium derivatives of ILs
(www.sigmaaldrich.com/img/assets/15469/chemfiles)

ILs tend not to give off vapors in contrast to traditional organic solvents such as benzene, acetone, and toluene. For example, Kabo *et al.* (2004) gave the vapor pressure of $[\text{bmim}][\text{PF}_6]$ at 298.15 K as 10^{-11} Pa. ILs are considered as green solvents because unlike the volatile organic compounds (VOCs) they replace, many of these compounds have negligible vapor pressure and they can be easily recycled and reused repeatedly. It is more convenient to work with ILs in the laboratory since the non-evaporating properties of ILs eliminate the hazardous worker exposure and air pollution problems.

ILs are known as ‘designer solvents’ since they give the opportunity to tune the specific properties for a particular need. The researchers can choose negatively charged small anions and positively charged large cations to make a liquid which can dissolve a certain chemical or extract a specific material from a solution. The fine-tuning of the structure provides tailor-designed properties to satisfy the specific application requirements. The physical and chemical properties of ILs are varied by changing the alkyl chain length on the cation and the anion. For example, density of ILs increases with a decrease in the alkyl chain length on the cation and an increase in the molecular weight of the anion (Huddleston *et al.*, 1998).

Some of the specific properties of ILs seem to break the rule of thumb of “like dissolves like”. For example, nonpolar benzene is up to 50 per cent soluble (by volume) in polar tetrachloroaluminate-based ILs (Renner, 2001). Therefore, studies on why ILs are able to dissolve uncharged covalent molecules are continuing.

Until recently, ILs have been considered to be rare but it is now known that many salts form liquids at or close to room temperature. There are literally billions of different structures that may form an IL. The composition and the specific properties of these liquids depend on the type of cation and anion. By combining various kinds of cation and anion structures, it is estimated that 10^{18} ILs can be designed.

2.2.1. Solvent Properties of ILs

ILs are good solvents for a wide range of molecules; organic, inorganic, organometallic. They are usually composed of poorly coordinating ions which makes them highly polar but non-coordinating solvents. ILs are immiscible with most of the organic solvents, thus they provide a nonaqueous, polar alternative for two-phase systems. Furthermore, ILs which are not miscible with water can be used as immiscible polar phases with water. Although all other conventional solvents evaporate to the atmosphere, ILs do not evaporate and their nonvolatility gives an opportunity to utilize them in high-vacuum systems. The negligible volatility is the basic property which characterizes them as green solvents. ILs can easily

replace other conventional organic solvents which are used in large quantities in chemicals processing industries to eliminate major environmental problems.

Many of the chemical reactions are carried out in conventional solvents. When the reaction is complete, chemical products must be taken out of the solvent. There are several techniques to recover a product from a solvent. Water soluble compounds may be extracted with water; distillation can be used for chemicals with high vapor pressures. On the other hand, for the chemicals with low vapor pressures, distillation must be performed at high pressures, which is not practical. In addition to this, there are some chemicals that can be decomposed as a result of heating, such as pharmaceuticals. Therefore, ILs are potentially good solvents for many chemical reactions.

Extraction is also a favorable separation technique and energy efficient technology which uses two immiscible phases such as an organic phase and an aqueous phase. Many organic solvents used in extractions are flammable and toxic. In order to improve the safety and environmental friendliness of this conventional technique, ILs may be used as ideal substitutes due to their stability, nonvolatility and adjustable miscibility and polarity (Zhao *et al.*, 2005).

The solvent properties of ILs are mainly determined by the ability of the salt to act as a hydrogen-bond donor and/or acceptor and the degree of localization of the charges on the anions (Dupont *et al.*, 2000). For example, imidazolium based ILs are highly ordered hydrogen-bonded solvents and they have strong effects on chemical reactions and processes.

2.2.2. Polarity of ILs

Polarity of chemicals is commonly used to classify the solvents. The terms used as polar, nonpolar and apolar are generally related to the values of dielectric constants, dipole moments, polarizabilities. If a solvent has the ability to dissolve and stabilize dipolar or charged solutes, it is defined as a polar solvent. Under this simple definition, ILs are highly polar solvents.

The existences of polar and nonpolar domains, believed to be associated with the unique “amphiphilic” solvent properties of ILs, are found in the structures of PF_6^- and BF_4^- salts (Kölle and Dronskowski, 2004). Since polarity is the simplest indicator of solvent strength, researchers compared polarities of ILs and conventional solvents. For example, [bmim][PF_6], [C_8mim][PF_6], [bmim][NO_3] and [N-bupy][BF_4] are more polar than acetonitrile and less polar than methanol and these ILs are expected to be at least partially miscible with water (Aki *et al.*, 2001). 1-alkyl-3-methylimidazolium ILs with anions [PF_6], [BF_4], [$(\text{CF}_3\text{SO}_2)_2\text{N}$], and [NO_3] are in the same polarity region as 2-aminoethanol and lower than alcohols such as methanol, ethanol and butanol (Carmichael *et al.*, 2000). Those ILs based on [PF_6] anion is preferred as solvent in most extraction application for forming biphasic systems due to its immiscibility with water.

2.2.3. Toxicology of ILs

The green character of ILs has been usually related with their negligible vapor pressure; however their toxicology data have been very limited until now. Although ILs will not evaporate and thus will not cause air pollution, most of ILs are water soluble and they may enter the environment in this way. Therefore, both toxicity and ecotoxicity information which provide metabolism and degradability of ILs are also required to label them as green solvents.

The impact of ILs on aquatic ecosystems is highly important since some of ILs have a high solubility in water. Brennecke and co-workers (2004) provided the LC_{50} levels (“lethal concentration” values refer to concentration of a chemical in air; concentration of a chemical in water in environmental studies) for two imidazolium based ILs with *Daphnia magna*. *Daphnia* are common fresh water crustaceans and they are filter feeders at the base of the aquatic food chain. Their responses to ILs are essential to assess how these new solvents would impact an environmental ecosystem. As ILs, 1-n-butyl 3-methylimidazolium cation with PF_6^- and BF_4^- anions are used. As Table 2.2 demonstrates, these two ILs are as toxic to *Daphnia* as benzene and even far more toxic than acetone.

Table 2.2. LC₅₀ values for certain solvent
(http://www.nd.edu/~ed/Research/ionic_liquids.htm)

COMPOUND	LC ₅₀ (mg/L)
[bmim][PF ₆]	250-300
[bmim][BF ₄]	225-275
acetone	30642
dichloromethane	310
toluene	60-313
benzene	203
chlorobenzene	5-86
phenol	5
ammonia	0.53-4.94
chlorine	0.028

Table 2.3. Toxicity classes (Hodge and Sterner Scale, 1956)

LC ₅₀ (mg/L)	TOXICITY RATE
10 or less	Extremely toxic
10-100	Highly toxic
100-1000	Slightly toxic
1000-10000	Practically non-toxic
10000-100000	Relatively harmless

2.2.4. Air and Moisture Stability of ILs

The stability of ILs is crucial for optimum process performance. Many of ILs are both air and moisture stable, some are even hydrophobic. On the other hand, most imidazolium and ammonium salts are hydrophilic and if they are used in open vessels, hydration will certainly occur. Despite their wide spread usage, ILs containing PF₆⁻ and BF₄⁻ have been reported to

decompose in the presence of water, giving off HF. The degree to which this hydration is a problem depends on the application. For instance, small amounts of highly reactive species which are used as catalysts may be deactivated by even very small amounts of water. For this kind of application, ILs must be handled under inert atmosphere. Moreover, the solutes used may be sensitive for air or moisture, thus an inert atmosphere is required for IL-solute systems.

The interaction between water and ILs and their degree of hygroscopic character are strongly dependent on anions. The amount of absorbed water is highest in BF_4^- and lowest in PF_6^- (Tran *et al.*, 2003). However, Tf_2N^- is much more stable in the presence of water as well as having the advantage of an increased hydrophobic character.

ILs immiscible with water tend to absorb water from the atmosphere. The results of infra-red (IR) studies demonstrated that the water molecules absorbed from the air are mostly present in the free state, bonded via H-bonding with PF_6^- and BF_4^- anions (Cammarata *et al.*, 2001). The presence of water may have dramatic effect on IL reactivity. Since water is present in all ILs, they are usually utilized after a moderate drying process which will be discussed in the following sections in detail.

The new ILs synthesized are more stable than the old halogenoaluminate systems. Certain ILs incorporating 1-3-dialkyl imidazolium cations are generally more resistant than traditional solvents under harsh process conditions, such as those occurring in oxidation, photolysis and radiation processes (Yang and Dionysiou, 2004).

2.3. Structure of ILs

There are a great number of different cation and anion combinations to synthesis IL. The most widely used cations are imidazolium, pyridinium, phosphonium and ammonium. The properties of ILs are determined by mutual fit of cation and anion, size, geometry, and charge distribution. Among the similar class of salts, small changes in types of ions influence the

physico-chemical properties. The overall properties of ILs result from the composite properties of the cations and anions and include those that are superacidic, basic, hydrophilic, water miscible, water immiscible and hydrophobic. Usually, the anion controls the water miscibility but the cation also has an influence on the hydrophobicity or hydrogen bonding ability (Huddleston *et al.*, 2001). The structures of most commonly used cations and some possible anion types are tabulated in Figure 2.3.

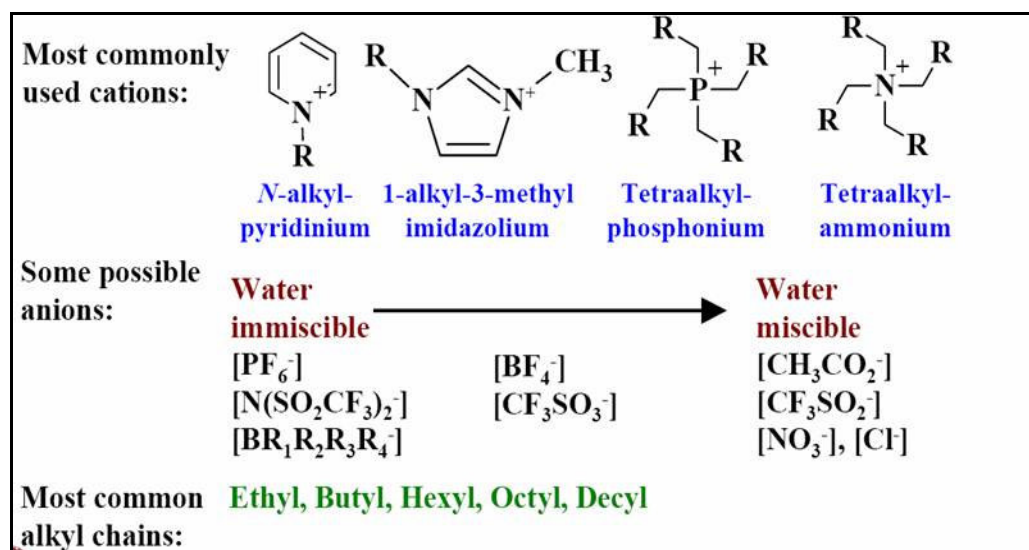


Figure 2.3. Most commonly used cation structures and possible anion types
(<http://lem.ch.unito.it/didattica/infochimica/Liquidi%20Ionici/>)

2.3.1. Anions

The properties of ILs are determined by the anion type. The introduction of different anions results in an increasing number of alternative ILs with various properties. The most commonly employed IL anions are polyatomic species:

- fluorous anions such as PF₆⁻, BF₄⁻, CF₃SO₃⁻, (CF₃SO₃)₂N⁻
- non-fluorous anions

In designing ILs usually fluorine anions are used. The most widely investigated ILs are the ones with anions PF_6^- and BF_4^- . Especially PF_6^- is the most prominent anion used in IL research. Since the anion chemistry has a large effect on the properties of IL, although the cations are the same, there are significant differences between ILs with different anions. For example IL with 1-n-butyl-3-methylimidazolium cation and PF_6^- anion is immiscible with water, whereas IL with same cation and BF_4^- anion is water soluble. This example represents the ‘designer solvent’ property of ILs: different ion pairs determine physical and chemical properties of the liquid. By changing the anion one can vary the hydrophobicity, viscosity, density and solvation of the IL system (Brennecke and Maginn, 2001).

Although these two anion types are utilized in most of IL applications, they have an important disadvantage: these two anions may decompose when heated in the presence of water and gives off HF. After the researchers realize production of HF in the presence of water, the bonding style of anion is altered and fluorine anions inert to hydrolysis are synthesized. The fluorine of the anion is bonded to carbon and C-F bond becomes inert to hydrolysis. In this way, ILs such as CF_3SO_3^- and $(\text{CF}_3\text{SO}_3)_2\text{N}^-$ are produced (<http://lem.ch.unito.it/didattica/infochimica/Liquidi%20Ionici>).

Fluorinated anions tend to be expensive and in response to cost and safety concerns new ILs with non-fluorine ions have been introduced. In the synthesis of these ILs, anions are derived from inexpensive bulk chemicals. Alkylsulfate anions are the most popular non-fluorine anions due to their non-toxic and biodegradable structures. The first commercially available IL for which toxicology data are available contains alkylsulfate anion (methosulfate). Another anion docusate is known to exhibit low mammalian toxicology and it is widely used in food, drug and cosmetic applications. Furthermore, non-fluorine docusate anion is miscible with hydrocarbons in contrast to other ILs. The structures of two mostly used non-fluorine anions are given in Figure 2.4.

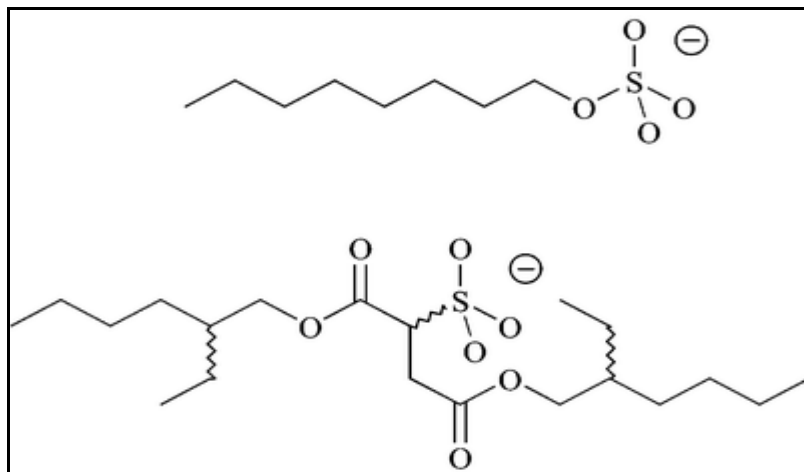


Figure 2.4. Structures of n-octyl sulfate (top) and docusate (bottom)
 (<http://lem.ch.unito.it/didattica/infochimica/Liquidi%20Ionici/>)

2.3.2. Cations

The cation of IL is generally a bulk organic structure with low symmetry. Those are based on ammonium, sulfonium, phosphonium, imidazolium, pyridinium, picolinium, pyrrolidinium, thiazolium, oxazolium and pyrazolium cations. The research mainly focus on RTILs composed of asymmetric N, N-dialkylimidazolium cations associated with a variety of anions. 1-n-butyl-3-methylimidazolium and 1-n-ethyl-3-methylimidazolium are the most investigated structures of this class.

By examining the properties of a series of imidazolium cation based ILs, it has been established that the melting point decreases when the size and asymmetry of the cation increase. Further an increase in the branching on the alkyl chain increases the melting point. The melting point of ILs is essential because it represents the lower limit of liquid gap and with thermal stability it defines the interval of temperatures within which it is possible to use ILs as solvents (Chiappe and Pieraccini, 2005).

2.3.3. Synthesis

There are three basic methods to synthesize ILs: metathesis reactions, acid-base neutralization, direct combination (Welton, 1999). Many alkylammonium halides are commercially available; they can also be prepared simply by the metathesis reaction of the appropriate halogenoalkane and amine. Pyridinium and imidazolium halides are also synthesized by metathesis reaction. On the other hand, monoalkylammonium nitrate salts are best prepared by the neutralization of aqueous solutions of the amine with nitric acid. After neutralization reactions, ILs are processed under vacuum to remove the excess water (Welton, 1999). Tetraalkylammonium sulfonates are also prepared by mixing sulfonic acid and tetraalkylammonium hydroxide (Poole *et al.*, 1989). In order to obtain pure IL, products are dissolved in an organic solvent such as acetonitrile and treated with activated carbon and the organic solvent is removed under vacuum. The final method for the synthesis of ILs is the direct combination of halide salt with a metal halide. Halogenoaluminate and chlorocuprate ILs are prepared by this method. Typical preparation routes are given in Figure 2.5.

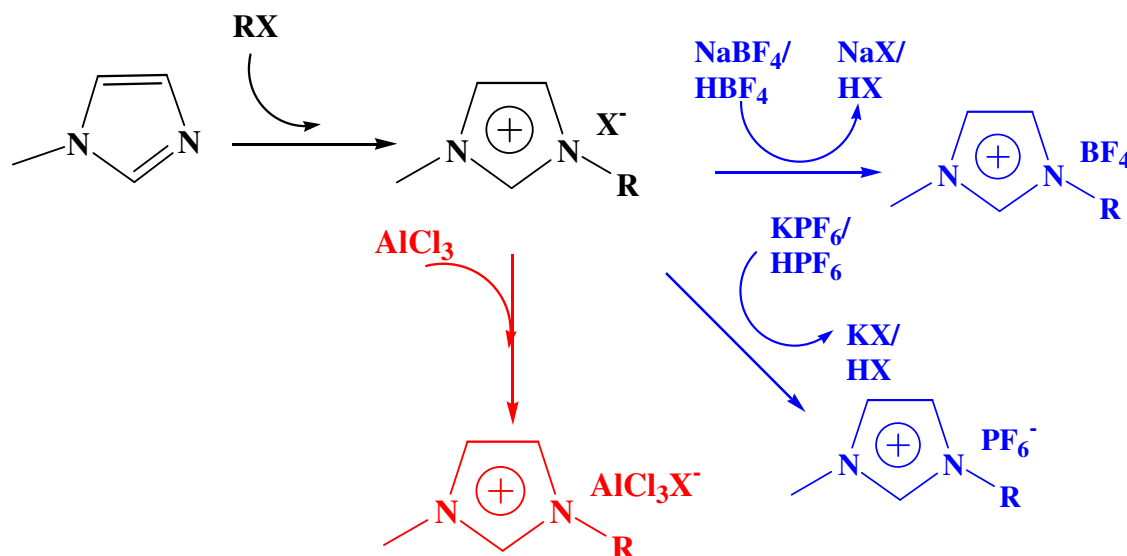


Figure 2.5. Typical preparation routes for ILs (www.chemada.com)

2.4. Applications of ILs

The unique chemical and physical properties of ILs bring about several application areas including reaction and synthesis media. The application areas of ILs can be expressed as solvents for organic, organometallic synthesis and catalysis; electrolytes in electrochemistry, in fuel and solar cells; lubricants; stationary phases for chromatography; matrices for mass spectrometry; supports for the immobilization of enzymes; in separation technologies; as liquid crystals; templates for synthesis nano-materials and materials for tissue preservation; in preparation of polymer-gel catalytic membranes; in generation of high conductivity materials (Dupont, 2004).

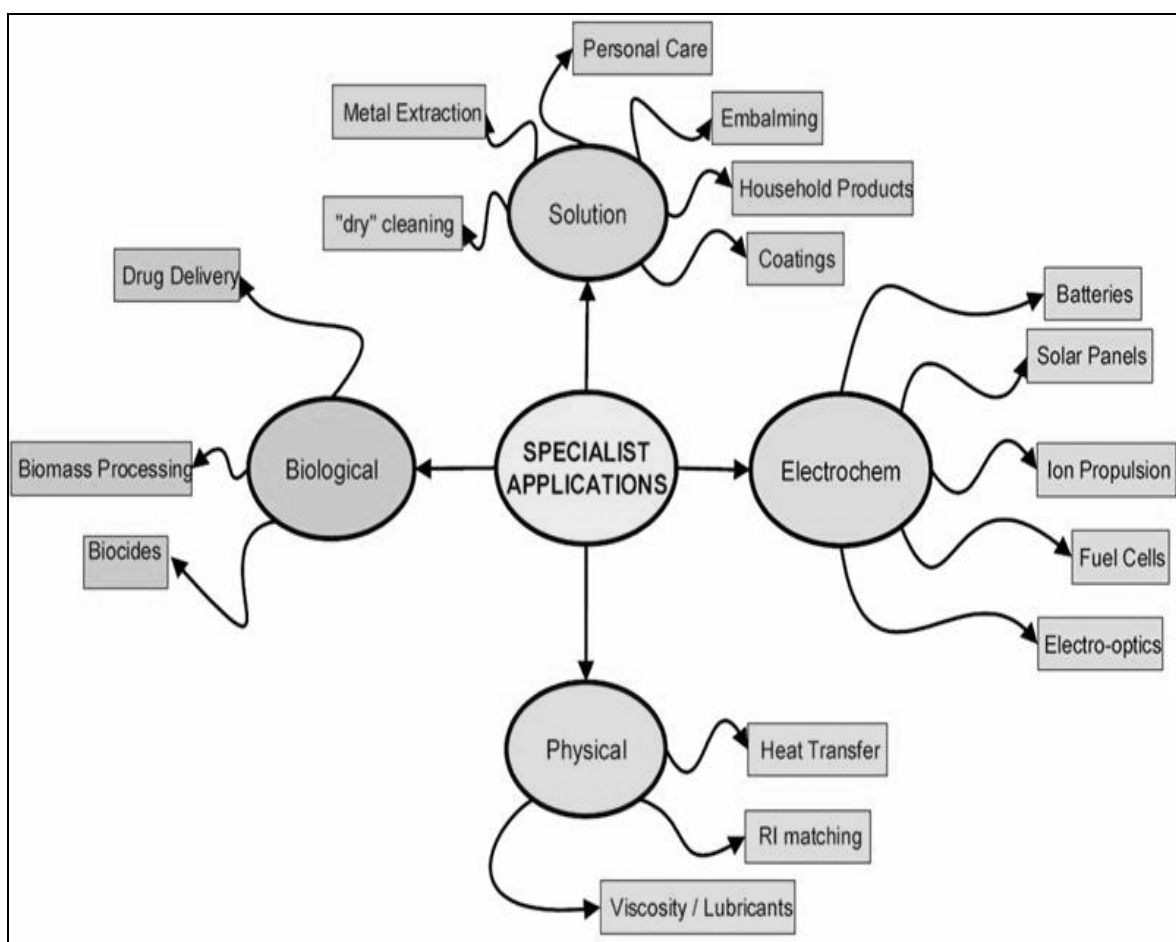


Figure 2.6. Application areas of ILs (<http://lem.ch.unito.it/didattica/infochimica/>)

2.4.1. Solvent Replacement

Despite their widespread use a majority of common solvents have potential health hazards. For example, approximately half of 189 hazardous air pollutants regulated by Air Act Amendment of U.S. (1990) are VOCs including solvents such as dichloromethane. The VOCs are the workhorses of industrial chemistry in the pharmaceutical and petrochemical areas. The use of VOCs by these industries can be assessed using the Sheldon E-factor. This factor is responsible to measure process by-products as a proportion of production on the mass basis. Table 2.4 demonstrates how VOC use is distributed across the chemical industry. The values on this table suggest that fine chemicals and pharmaceuticals industries use inefficient and dirty processes although on smaller scale compared to the oil and bulk chemicals industries. The oil and bulk chemicals industries which are commonly regarded as dirty are remarkably waste conscious when the E-factors are analyzed (Renner, 2001).

Table 2.4. By products as a proportion of production for the chemical industry
(Renner, 2001; adapted from Sheldon, 1993)

INDUSTRY	PRODUCTION (tons/year)	E-FACTOR
Oil refining	10^6 - 10^8	0.1
Bulk chemicals	10^4 - 10^6	1-5
Fine chemicals	10^2 - 10^4	5-50
Pharmaceuticals	10 - 10^3	25-100

As the introduction of cleaner technologies has become a major concern throughout both industry and academia, the search for the alternative solvents has become a high priority. Therefore, environmentally friendly ILs can easily replace the hazardous VOCs in large scale to reduce E-factors.

ILs are able to dissolve a variety of solutes. They can be used instead of traditional solvents in liquid-liquid extractions where hydrophobic molecules such as simple benzene derivatives will partition to the IL phase. Huddleston *et al.* (1998) showed that [bmim][PF₆]

could be used to extract aromatic compounds from water. Fadeev and Meagher (2001) demonstrated that two imidazolium ILs with PF_6^- anion could be used for the extraction of butanol from aqueous fermentation broths. Selvan *et al.* (2000) used ILs for the extraction of aromatics from aromatic/alkane mixtures, whereas Letcher *et al.* (2003) used ILs for the extraction of alcohols from alcohol/alkane mixtures. Moreover, binary temperature-composition curves of ILs with alcohols, alkanes, aromatics and water; ternary temperature-composition curves of ILs with alcohols and water; solubilities of some organics and water in ILs are all investigated by various groups to completely benefit from the solvent properties of ILs (Wu *et al.*, 2003; Wagner *et al.*, 2003; Domanska and Marciniak, 2003).

2.4.2. Purification of Gases

Reliable information on the solubility of gases in ILs is needed for the design and operation of most of the processes. Process using ILs to purify gas streams are developed after the solubility of various gases in ILs are noticed by the researchers (Camper *et al.*, 2004; Scovazzo *et al.*, 2004; Baltus *et al.*, 2004). The experimental studies show that some gases, especially CO_2 is highly soluble in IL. The simulations performed explain that the anion of the IL is responsible for high gas solubility. With this property ILs can be used as replacement solvents for reactions involving gaseous species.

Anthony *et al.* (2002) investigated solubility of nine different gases: carbon dioxide, ethylene, ethane, methane, argon, oxygen, carbon monoxide, hydrogen, and nitrogen in $[\text{bmim}][\text{PF}_6]$. These gases were chosen for several reasons: CO_2 solubility is important due to the possibility of using scCO_2 to extract solutes from ILs; ethylene, hydrogen, carbon monoxide, and oxygen are reactants in several types of reactions studied in IL such as hydroformylations, hydrogenations, and oxidations. Due to the nonvolatile nature of IL, the gas solubilities in IL were measured using a gravimetric technique, usually with a microbalance. The study of Anthony and co-workers (2002) showed that CO_2 has the highest solubility and strongest interactions with $[\text{bmim}][\text{PF}_6]$, followed by ethylene and ethane. Argon and oxygen had very low solubilities and immeasurably weak interactions. Figure 2.7

demonstrates the solubility of various gases (CO_2 , C_2H_4 , C_2H_6 , CH_4 , Ar, O_2) in $[\text{bmim}][\text{PF}_6]$ at 25°C and at different pressures. Except for CO_2 , all gases remained in the Henry's Law regime up to 13 bar. However, CO_2 showed some non-linearity, indicating some degree of saturation. Henry's constants of these gases in various organic solvents and in $[\text{bmim}][\text{PF}_6]$ were compared and the results showed that the gases that are less soluble in the IL are less soluble in the other solvents as well. However, CO_2 is more soluble in the IL than in the other solvents. The relatively high solubility of CO_2 was explained as a result of its large quadrupole moment. The solubility of CO_2 in $[\text{bmim}][\text{PF}_6]$ at different temperatures is demonstrated in Figure 2.8.

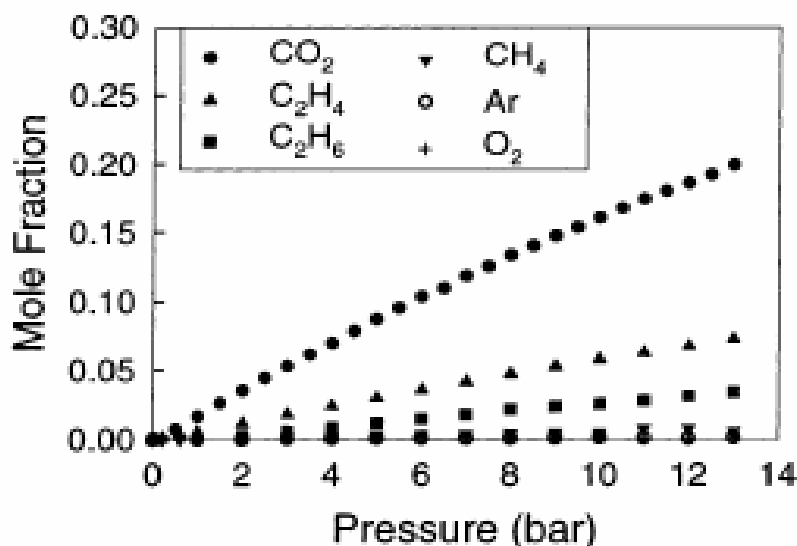


Figure 2.7. Solubility of various gases in $[\text{bmim}][\text{PF}_6]$ at 25°C
(Anthony *et al.*, 2002)

Recently, the results of solubility of hydrogen in $[\text{bmim}][\text{PF}_6]$ was presented for temperatures from 313 to 373 K and pressures up to 9 MPa. The results demonstrated that the solubility of hydrogen in $[\text{bmim}][\text{PF}_6]$ is low and increases slightly with temperature (Kumelan *et al.*, 2006). The gases which have low solubilities in ILs may be used to strip ILs to recover the products.

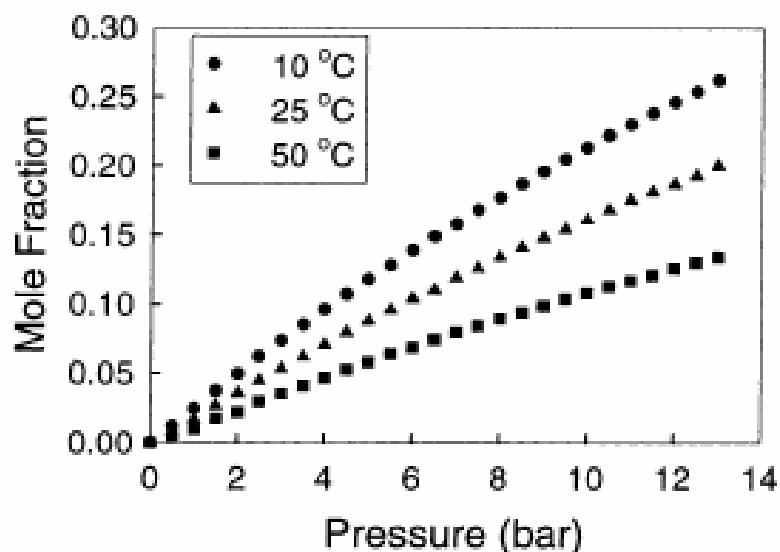


Figure 2.8. Solubility of CO₂ in [bmim][PF₆] at different temperatures
(Anthony *et al.*, 2002)

Since IL can dissolve certain gaseous species, it may be used in conventional gas absorption applications. The non-volatility of ILs prevents any cross contamination of the gas stream by the solvent during the process. Moreover, regeneration of the solvent may be performed easily by a simple flash or distillation to remove the gas from the solvent without any cross contamination. The other advantages of ILs as separating agents are no solvent loss and no air pollution. Figure 2.9 demonstrates a simple gas absorption unit where the four streams associated with the operation are shown in their conventional terminologies as well as in the application for IL absorption of gases. The contaminated gas stream, rich gas, is fed to the bottom of the absorber and IL, as the lean solvent is fed in at the top. The lean gas treated with IL is removed from the column. The absorbed gas is removed in the liquid effluent, rich solvent, and treated in another separation unit. Currently, researchers are interested in examining the potential of ILs for the separation of CO₂ from flue gases emitted from fossil-fuel combustion operations.

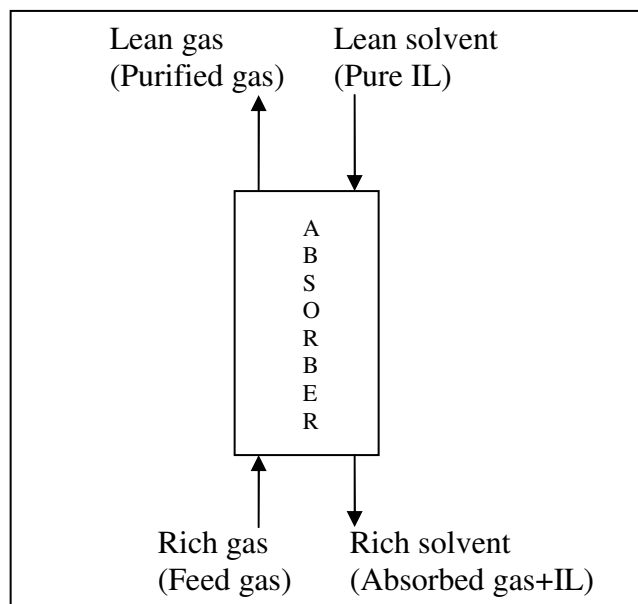


Figure 2.9. A gas absorption set-up to treat contaminated gas streams with ILs

ILs may also be utilized as supported liquid membranes. In conventional membranes, gas dissolves in liquid but then the liquid in which the gas dissolved evaporates rendering the membrane useless (<http://lem.ch.unito.it/didattica/infochimica/Liquidi%20Ionici>). Due to the non-volatility of ILs, they can be immobilized on a support and used in supported liquid membrane.

2.4.3. Homogenous and Heterogeneous Catalysis

One of the most important targets of modern chemistry is to combine the advantages of both homogenous (catalyst modulation) and heterogeneous (catalyst recycling) catalysis. Homogenous catalysis imparts much greater selectivity than its heterogeneous counterparts, but separation of the catalyst from the product or from the extract stream is a problem. ILs offer the advantages of both homogenous and heterogeneous catalysts, since the selected IL can be immiscible with the reactants and products but dissolve the catalysts. ILs have the advantages of a solid for immobilizing the catalyst, and the advantages of a liquid for allowing the catalyst to move freely (Morland, 2001). The ionic nature of the IL solvent gives an

opportunity to control reaction chemistry either by participating in the reaction or stabilizing highly polar or ionic transition states (Brennecke and Maginn, 2001).

ILs have an active role in chemical reactions and catalysis, some of the examples where ILs are utilized are given below:

- Reactions of aromatic rings: clean polymerization (Abuabdoun, 1989); Friedel Crafts alkylation (Wasserscheid, 2003); reduction of aromatic rings (Ota, 1987); carbonylation (Nemeth *et al.*, US Patent 6288281); sulfonation (Earle and Katdare, Patent WO2002030878); nitration (Earle and Katdare, Patent WO2002030865); oxidation (Earle and Katdare, Patent WO2002030862), halogenation (Earle and Katdare, Patent WO2002030852).
- Solvents for transition metal catalysis : immobilization of charged cationic transition metal catalysis in IL phase without need for special ligands (Olivier-Boubigou and Magna, 2002).
- In-situ catalysis directly in IL rather than aqueous catalysis followed by extraction of products from solution: this process eliminates washing steps, minimizes losses of catalysis and enhances purity of the products (Cornils and Herrmann, 2003).

ILs have been used successfully for hydrogenations, hydroformylations, isomerizations, dimerizations, alkylations, Diels-Alder reactions and Heck and Suzuki coupling reactions, and in general researchers have concluded that the reaction rates and selectivities are as good or better in ILs than in conventional organic solvents (Brennecke and Maginn, 2001).

2.4.4. Biological Reactions Media

ILs are used in biological reactions such as the synthesis of pharmaceuticals due to the stability of enzymes in ILs, and in separation processes such as the extraction of amino acids

(Zhao *et al.*, 2005). IL biphasic systems are used to separate many biologically important molecules such as carbohydrates, organic acids including lactic acid (Liu *et al.*, 2005; Matsumoto *et al.*, 2004). Carbohydrates are renewable and inexpensive sources of energy and raw material for the chemical industry. The underivatized carbohydrates are soluble in water but not in almost any other solvents. Their insolubility in most solvents prevents the transformation of carbohydrates. Therefore, ability of ILs to dissolve carbohydrates enables the possibility of transformations (Zhao *et al.*, 2005).

Swatloski *et al.* (2002) showed that ILs can be used as non-derivatizing solvents for cellulose, the most abundant biorenewable material. Cellulose, which is insoluble in water and in most of the common organic solvents, has many derivitized products in many applications of the fiber, paper, and polymer industries. ILs incorporating anions which are strong hydrogen bond acceptors are most effective solvents for cellulose, whereas ILs containing non-coordinating anions including PF_6^- and BF_4^- are not effective. Furthermore, Przybysz *et al.* (2005) examined the influence of ILs on a cellulose product, paper and found that the wettability of paper is improved whereas the strength decreased as a result of weakening of cellulose hydrogen bonds.

2.4.5. Removing of Metal Ions

Davis and Rogers (2002) designed and synthesized several ILs to remove cadmium and mercury from contaminated water. The hydrophobic ILs come into contact with contaminated water and they snatch the metal ions out of water. Task specific ionic liquids (TSIL) concept is introduced in order to synthesize IL with desired properties to extract metal ions.

In traditional solvent extraction technologies, adding extractants that reside quantitatively in the extracting phase increases the metal ion partitioning to the more hydrophobic phase. The added extractant molecules dehydrate the metal ions and provide a more hydrophobic environment enabling their transport to the extracting phase. In TSIL, attaching a metal ion coordinating group directly to the imidazolium cation makes the

extractant an integral part of the hydrophobic phase and greatly diminishes the chance for loss to the aqueous phase. Therefore, TSILs serve as the hydrophobic solvent and the extractant at the same time. However, the cost of TSIL is generally high. Furthermore, they are not limited to extraction processes; they can be also used as versatile solvents in organic catalysts, solid phase synthesis and even in production of liquid Teflon (Zhao *et al.*, 2005).

Davis and Roger (2002) produced TSIL cations by appending different functional groups (namely thioether, urea and thiourea) to imidazolium cations. These IL cations can be considered as a new class of IL or novel class of IL extractants. Synthesized TSIL cations were combined with PF_6^- anion and used alone or in a mixture with [bmim][PF_6]. The results of the study gave significant distribution ratios for mercury and cadmium in liquid-liquid separations and minimized the reliance on traditional organic solvents for this process.

The extraction of radioactive metals (lanthanides and actinides) has particular industrial significance among IL extraction of metal ions for the handling of nuclear materials. The behavior of uranium species in various ILs were investigated in early studies. Recently, researchers have focused on the fundamental understanding of ILs in nuclear chemistry such as radiochemical stability of ILs (Baston *et al.*, 2002).

Moreover, Dai *et al.* (1999) studied the effects of ILs (with PF_6^- and Tf_2N^- anions) on improving the ability of crown ethers to remove metal ions from aqueous solutions. Strontium nitrate, a fission product for which there is no available extraction technique for its removal from radioactive waste sites, was used in this study. Recently, Nakashima *et al.* (2005) examined the feasibility of stripping of rare earth metals from ILs into aqueous phase by complexing agents and they successfully accomplished to recycle the extracting ILs phase.

Table 2.5. Some examples of IL extractions of metal ions

Metal Ion	Substances	IL	References
Alkali metals	Li ⁺ , Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺	[C _n mim][PF ₆] (n = 4-9)	Chun <i>et al.</i> , 2001
	Na ⁺ , Cs ⁺	[C _n mim][PF ₆] (n = 4,6,8)	Visser <i>et al.</i> , 2000
	Cs ⁺	[C _n mim][Tf ₂ N] (n = 2,3,4,6,8)	Luo <i>et al.</i> , 2004a
	Na ⁺ , K ⁺ , Cs ⁺	[C _n mim][Tf ₂ N] (n = 2,4,6,8)	Luo <i>et al.</i> , 2004b
Alkaline earth metals	Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺	[C _n mim][PF ₆] (n = 4-9)	Bartsch <i>et al.</i> , 2002
	Sr ²⁺	[C _n mim][PF ₆] (n = 4,6,8)	Visser <i>et al.</i> , 2000
	Sr ²⁺	[C _n mim][Tf ₂ N] (n = 2,4,6,8)	Luo <i>et al.</i> , 2004
Heavy and radioactive metals	Pb ²⁺	[C _n mim][PF ₆] (n = 4-9)	Bartsch <i>et al.</i> , 2002
	Cu ²⁺ , Ag ⁺ , Pb ²⁺ , Zn ²⁺ , Cd ²⁺ , Hg ²⁺	[C _n mim][PF ₆] (n = 4)	Wei <i>et al.</i> , 2003
	Hg ²⁺ , Cd ²⁺	TSILs	Visser <i>et al.</i> , 2001

2.5. Challenges of ILs

The unique properties of ILs and the ability to design their properties by choice of anion, cation and substituents create many more processing options alternative to ones with conventional solvents. However, high cost, lack of physical property and toxicity data restrict the advantages of ILs.

The challenges in the use of ILs must be addressed as well as their advantages. The major challenge is the cost. A kilogram of IL costs about 30000 fold greater than a common

organic solvent such as acetone. This cost could be reduced to approximately 1000 fold greater depending on the composition of IL and the scale of production (Renner, 2001).

The second problem is associated with the manufacturing method of ILs. Environmental issues also need to be tackled since some VOCs are used to manufacture ILs. Recently, some advanced methods have been developed in the solventless syntheses of ILs. For example, 1-alkyl-3-methylimidazolium halides have been synthesized in open containers in a microwave oven without any VOCs by Varma and Namboodiri at the Environmental Protection Agency of U.S. (2001).

Researchers need to find alternative ways to recycle ILs due to the reason that many processes for cleaning up ILs involve washing with water or VOCs which creates another waste stream. This problem has been solved by adopting supercritical extraction technologies to recover the dissolved organic compounds from ILs or using membrane separation processes. However, there are other solid matrixes which adsorb some part of IL. Thus, a second rinse would be required and this would create an aqueous waste stream that contains IL. Despite this disadvantage there may be some cleaning applications where ILs would be attractive (Brennecke and Maginn, 2001).

Incomplete physico-chemical data are another challenge for the application of ILs. At present most of data available are focused on bulk physical properties such as viscosity, density, phase transitions. Relatively little is known about the microscopic physical properties of ILs. After these properties are investigated properly and the influence of ILs on chemical reaction rates is found, new ILs with precisely tailored properties can be synthesized.

Another barrier to the large scale application of ILs arises from the high viscosity. The viscosity of IL is higher than most organic solvents and water, usually similar to viscosity of oils. This high viscosity may be responsible to produce a reduction in the rate of many organic reactions and even a reduction in the diffusion rates of species. Also, handling of ILs with high viscosities is difficult however; increasing temperature, changing anion-cation combinations may give ILs with low viscosities. To overcome mass transfer limitations resulting from high

viscosity reactions using ILs may be run at high pressures and in efficient gas-liquid contacting equipment.

In chemical processing, pharmaceuticals, fine chemicals, petroleum refining, metal refining, polymer processing, pulp and paper, textiles where a nonvolatile liquid with a wide liquidus range could work better, ILs are the best choice however, the challenges of turning ILs into useful and environmentally benign fluids must be overcome.

3. IONIC LIQUIDS AND SUPERCRITICAL CARBON DIOXIDE

Green chemistry, also known as sustainable chemistry, describes the search for reducing or even eliminating the use of substances in chemical products and reactions which are hazardous to human health and environment. The goal of green chemistry is to create a cleaner and more sustainable chemistry and it has received more and more attention in recent years. Green chemistry searches for alternative, environmentally friendly reaction media (as compared to the traditional organic solvents) and at the same time aims at increased reaction rates, lower reaction temperatures as well higher selectivities.

The ideal situation for a safe and green chemical process is using no solvent, however most of the chemical processes depend on solvents. Some of these solvents are soluble in water and therefore they must be stripped from water before it leaves the process not only for ecological but also for economic reasons. Solvents must be recovered for recycle and reuse for an economically viable process. Water, perfluorinated hydrocarbons and SCFs are alternative solvents which may be used in green chemistry. Among these, the most promising elements of green chemistry are ILs and scCO_2 .

The low volatility of ILs is the key property that makes them green solvents. However, this advantage also causes a problem for product separation and recovery. Several techniques for solute recovery from ILs exist: Volatile products can be extracted from IL with distillation or evaporation. However, nonvolatile or thermo-sensitive products can not be separated from ILs with these methods. ILs exhibiting immiscibility with water can be extracted with water to separate water soluble solutes from IL into aqueous phase; but this method is not suitable for hydrophilic ILs. Of course, organic solvents such as hexane and toluene may be effective to recover the products from IL but this approach obviously compromises the ultimate goal of 'green' technologies (Zhao *et al.*, 2005). Furthermore, the cross contamination between the phases presents another problem. Finally, another green solvent is discovered which solves all the problems and recovers various kind of solutes from ILs without cross contamination: SCF.

SCFs are compounds which are above their critical temperature and pressure and they can be manipulated from gas like to liquid like densities due to their unusual properties near the critical point. They are commercially viable solvents in several applications such as dry cleaning and polymer impregnation. scCO_2 is the most widely used SCF as a result of nontoxic and nonflammable characteristics. scCO_2 has low critical temperature and pressure and it is not expensive.

The advantages of using SCFs as extraction medium include low cost, nontoxic nature, recoverability and ease of separation from the products. SCFs have been adapted for product recovery from ILs and SCFE is shown to be a viable technique with the additional benefits of environmental sustainability and pure product recovery (Blanchard and Brennecke, 2001). Among the SCFs, inexpensive and readily available one, scCO_2 has become a partner of IL and two environmentally benign solvents are utilized in several applications together. The volatile and nonpolar scCO_2 forms different two phase systems with nonvolatile and polar ILs. The product recovery process with these systems is based on the principle that scCO_2 is soluble in ILs and ILs are not soluble in scCO_2 . With the high solubility of scCO_2 in ILs, the products are transferred from IL to supercritical phase.

3.1. Solute Recovery from ILs with scCO_2

Researchers found that nonvolatile organic compounds can be extracted from ILs using scCO_2 , which is widely used to extract large organic compounds with minimal pollution. Brennecke and Blanchard (1999) showed that CO_2 can be used to extract naphthalene, a low volatility model solute, from an IL. They synthesized $[\text{bmim}][\text{PF}_6]$ which was stable in the presence of water and oxygen. The model compound naphthalene was readily soluble in $[\text{bmim}][\text{PF}_6]$ (maximum solubility of 0.30 mole fraction at 40°C) and in CO_2 . Their study investigated the phase behavior of $[\text{bmim}][\text{PF}_6]$ with CO_2 , as well as with naphthalene and finally that of the $[\text{bmim}][\text{PF}_6]$ - CO_2 -naphthalene ternary system. The results showed that CO_2 rich phase was not significantly contaminated by IL as would be expected during contact of CO_2 with any conventional organic solvent.

Brennecke and Blanchard (1999) demonstrated that CO₂ is highly soluble in [bmim][PF₆] reaching a mole fraction of 0.6 at 8 MPa. After extracting IL with CO₂ at 13.8 MPa and 40°C there was no detectable [bmim][PF₆] in the extract, which indicates that the solubility is less than 10⁻⁵ mole fraction. In contrast to this result, a mixture of CO₂ with conventional organic liquid results in significant solubility of the liquid in the CO₂ phase. A mixture of 0.12 mole fraction naphthalene in [bmim][PF₆] was extracted with CO₂ at 13.8 MPa and 40°C with recoveries of 94-96 per cent and therefore it was concluded that it is possible to quantitatively extract an organic solute having a reasonable molecular weight from IL using scCO₂ without any cross contamination. Furthermore, the dissolution of scCO₂ in IL was completely reversible and pure IL remained after the extraction of naphthalene and depressurization.

Subsequent work showed that a wide variety of solutes can be extracted from [bmim][PF₆] with scCO₂ with recovery rates greater than 95 per cent (Blanchard and Brennecke, 2001). Their study investigated the feasibility of using scCO₂, another environmentally benign solvent for the separation of organic solutes from an IL. Hexane and benzene were chosen as the roots to which numerous substituents groups were added to explore the effect of chemical structure on the solubility and extractability of an organic solute in and from an IL. The substituent groups represented were halogen, alcohol, ether, amide, ketone, carboxylic acid, ester, and aldehyde.

The solubility studies of organics in [bmim][PF₆] were carried out under ambient, 22°C and 0.98 bar (Blanchard and Brennecke, 2001). During the solubility studies, the mixtures of IL-solute were stirred in closed containers to avoid contamination with air and water vapor. The results of the study demonstrated that organics with the potential for strong intermolecular interactions, those with a large dipole moment for example, generally exhibited complete miscibility or a large degree of solubility in [bmim][PF₆].

Table 3.1 expresses the solubilities of organic compounds in IL and the methods of analysis. Blanchard and Brennecke (2001) analyzed the organics exhibiting strong absorption in the UV-Visible (Ultra Violet-Visible) range with UV-Visible spectroscopy. Solubilities of

the organics not absorbing in the UV-Visible range were determined by the gravimetric method. Solubility measurement results indicated that aromatic compounds are more soluble in [bmim][PF₆] than non-aromatic compounds of equivalent molecular weight and polarity.

Table 3.1. Organic solutes solubilities in [bmim][PF₆] at 22°C along with solute dipole moments (Blanchard and Brennecke, 2001)

solute ^a	solubility (solute mole fraction)	dipole moment (Debye)	analysis method (wavelength (nm))
benzene	0.66	0	UV-vis (255, 261)
chlorobenzene (s) (halogen)	0.58	1.69	UV-vis (258, 271)
phenol (alcohol)	0.69	1.45	UV-vis (273)
anisole (ether)	miscible	1.38	UV-vis (271, 278)
aniline (amine)	miscible	1.53	UV-vis (236, 286)
acetophenone (ketone)	miscible	3.02	UV-vis (241)
benzoic acid (s) (carboxylic acid)	0.07	1.00	UV-vis (231)
methyl benzoate (ester)	miscible	2.55	UV-vis (273)
benzamide (s) (amide)	0.04	3.60	UV-vis (225)
benzaldehyde (aldehyde)	miscible	2.80	UV-vis (245)
hexane	miscible	0	gravimetric
1-chlorohexane (halogen)	0.25	1.99	gravimetric
1-hexanol (alcohol)	0.26	1.65	gravimetric
butyl ethyl ether (ether)	0.06	1.22	gravimetric
cyclohexane	0.21	0	gravimetric
2-hexanone (ketone)	miscible	2.68	UV-vis (278)
hexanoic acid (carboxylic acid)	0.13	1.57	UV-vis (219)
methyl pentanoate (ester)	0.59		UV-vis (209)
hexanamide (s) (amide)	0.06	3.90	UV-vis (203)
1,4-butanediol	0.51	2.58	gravimetric

^a Solids are indicated by (s).

[bmim][PF₆] was doped with twenty different organic solutes not only to determine the extent of solute recovery from the IL but also to explore the possible trends regarding the amount of CO₂ necessary for extraction. For scCO₂ extraction experiments, a high pressure extraction apparatus was used and all supercritical extraction experiments were conducted at 40°C and 138 bar. Benzene and chlorobenzene which exhibited phase immiscibility with [bmim][PF₆] required the least amount of CO₂ for recovery. Phenols, benzoic acid and benzamide which are solids at room temperature, required the largest amount of CO₂. Figures 3.1 and 3.2 illustrates per cent recovery of solutes as a function of molar ratio of CO₂ passed

through the extractor to organic solute loaded in the reactor (Solute dipole moments are also given in these figures in terms of debye).

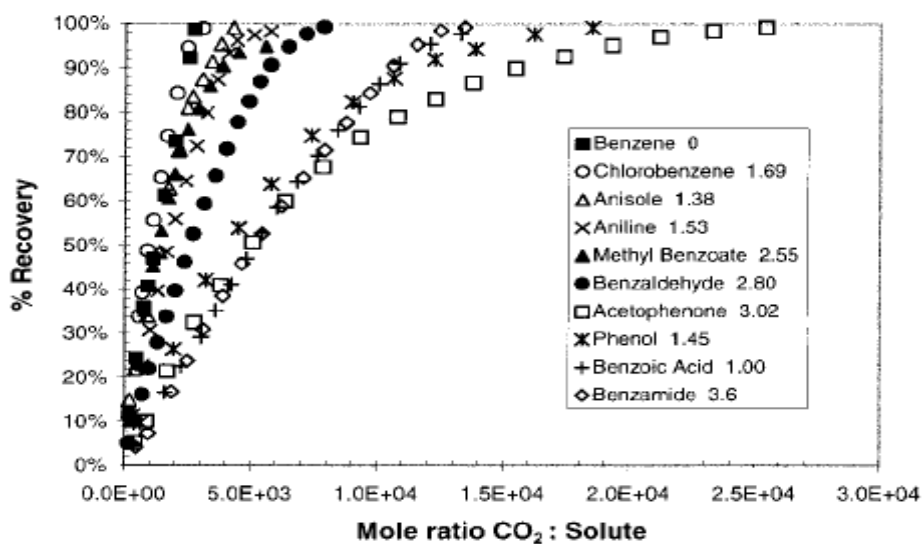


Figure 3.1. Extraction of aromatic solutes from [bmim][PF₆] with scCO₂ at 40°C and 138 bar (Blanchard and Brennecke, 2001)

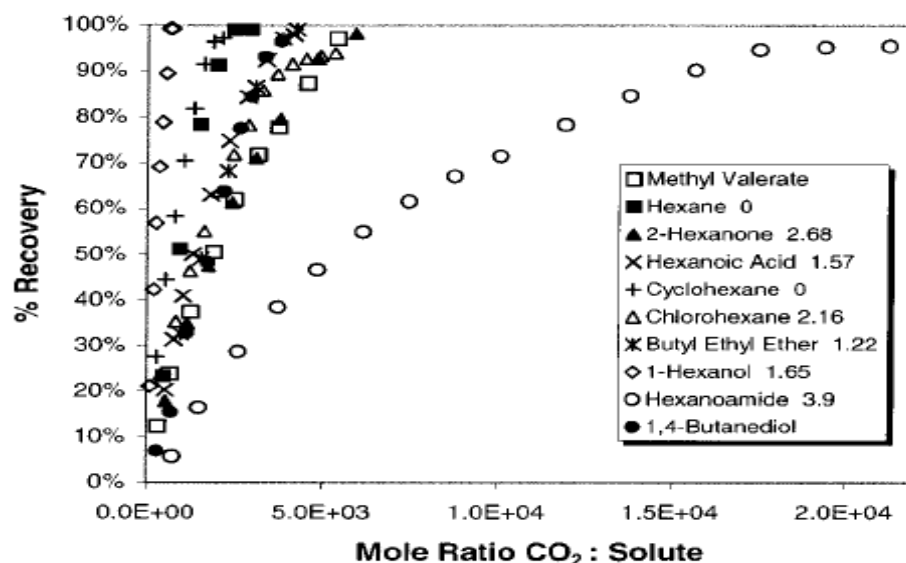


Figure 3.2. Extraction of aliphatic solutes from [bmim][PF₆] with scCO₂ at 40°C and 138 bar (Blanchard and Brennecke, 2001)

The experimental work of Blanchard and Brennecke (2001) provided a significant step to visualize the partnership of IL-CO₂ system. One of the essential problems of ILs, namely product recovery was solved by applying the SCFE technique. With this study, it was seen that organic compounds including polar, nonpolar, aromatic, aliphatic, volatile and nonvolatile compounds, dissolved in IL can be recovered with a recovery rate higher than 95 per cent which is a clear indication that although the ionic nature of IL might lead to an interaction with a solute, it does not limit the extent of extraction. Furthermore, for some of the organic solutes, scCO₂ extraction achieved greater than 98 per cent recovery rate before the extraction test was terminated.

Distribution coefficient (K), may be defined as the ratio of solute mole fractions in the supercritical and in the IL phases respectively. Since ILs do not dissolve in scCO₂ appreciably, supercritical phase is essentially CO₂ and organic solute. The distribution coefficient is an important thermodynamic property to comprehend IL-scCO₂-solute systems. Theoretically, one can anticipate the trend of distribution coefficient between IL and scCO₂ phases by considering the volatility and polarity characteristics of the solute. For example, a solute with a high volatility and low polarity will have a large affinity for CO₂, whereas a solute with high polarity and aromaticity will have a large affinity for the IL rich liquid phase. Therefore, solutes with high polarities give a small K value due to high affinity for IL and low affinity for CO₂. Conversely, nonpolar solutes give large K values as a result of high affinity for CO₂. With this discussion, it is clear that the compounds that have high affinity for CO₂ can be more easily extracted from the IL mixture.

There is a relation between the dipole moments of solutes and the amount of CO₂ required for extraction. Figure 3.3 illustrates the number of CO₂ per mole of organic solute as a function of dipole moment. Blanchard and Brennecke (2001) concluded that the organics with a dipole moment of zero (benzene, hexane, cyclohexane) are easily extracted compared to solutes with nonzero dipole moments.

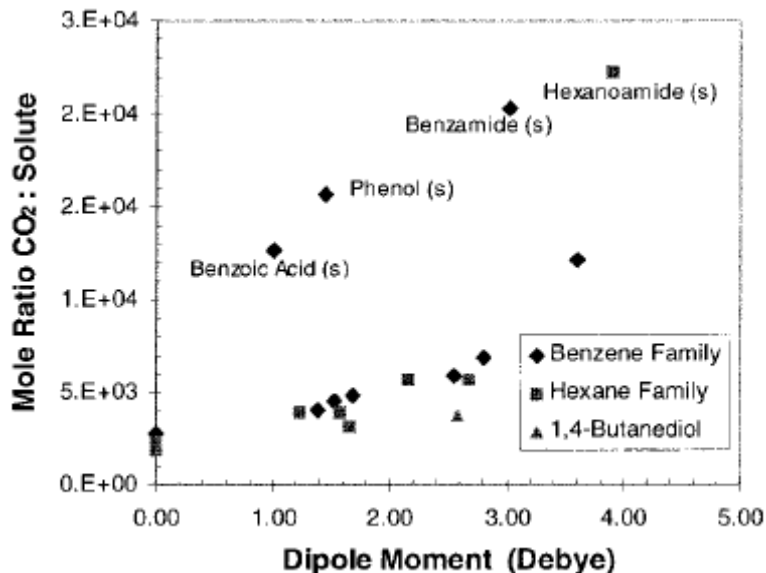


Figure 3.3. Effect of solute dipole moment on ease of extraction of [bmim][PF₆] with scCO₂ at 40°C and 138 bar (Blanchard and Brennecke, 2001)

The ease of extraction of compound from ILs with scCO₂ is also affected by the phase behavior of organic solute-CO₂ binary systems. A measure of affinity of compounds for CO₂ can be determined from liquid phase data at low pressures. For example, compounds in which CO₂ readily dissolves at low pressures have a greater attraction for CO₂. Table 3.2 gives information about the phase behavior of CO₂ and some liquid organic solutes.

Using scCO₂ to recover products from IL is a good alternative if the products are thermally sensible or nonvolatile. A high boiling point solute can also be recovered from IL with scCO₂, where distillation is not a desirable option. Blanchard and Brennecke (2001) extracted a high boiling point (230°C) organic liquid namely 1,4-butanediol from [bmim][PF₆]. This high boiling point solute followed the same solubility and extractability trend as the other liquid solutes. Therefore, SCFE technology is readily applicable for the recovery of various kinds of compounds from ILs.

Table 3.2. CO₂-liquid organic solute binary phase behavior
(Blanchard and Brennecke, 2001)

Binary System	Pressure (bar)*	Mole ratio CO ₂ :solute for 95 per cent recovery	Reference
CO ₂ -hexane	54.1	2.34E+03	Ohgaki and Katayama, 1976
CO ₂ -benzene	59.6	2.75E+03	Ohgaki and Katayama, 1976
CO ₂ -anisole	60.8	4.00E+03	Park <i>et al.</i> , 1991
CO ₂ -cyclohexane	64.8	1.84E+03	Al-Sahh Hof <i>et al.</i> , 1989
CO ₂ -chlorobenzene	66.7	4.77E+03	Walther and Maurer, 1992
CO ₂ -methyl benzoate	71.0	5.87E+03	Bamberger and Maurer, 1994
CO ₂ -acetophenone	75.4	2.03E+04	Weng and Lee, 1992
CO ₂ -benzaldehyde	77.8	6.85E+03	Walther and Maurer, 1992

* Pressure required to dissolve 70 mol per cent CO₂ in the liquid phase at 40°C

3.2. High Pressure Phase Behavior of IL-CO₂ Systems

Preliminary works have shown that scCO₂ extraction is a viable method for solute recovery from an IL. However, the knowledge of phase behavior of IL-CO₂ systems is an essential aspect of this methodology. scCO₂ dissolution in IL phase is not only necessary for contact with the solute but also it reduces the viscosity of IL and therefore enhancing the mass transfer process.

Early studies of IL-CO₂ phase behavior indicated that these systems are very unusual biphasic systems. No measurable amount of [bmim][PF₆] was soluble in the CO₂ rich phase, although a large amount of CO₂ dissolved in the IL rich phase, reducing the viscosity of IL (Blanchard *et al.*, 2001). Blanchard and Brennecke (2001) concluded that the system remained as two distinct phases even under pressures up to 400 bar. Therefore, high pressure phase behavior of [bmim][PF₆]-CO₂ is totally different from that of any normal organic liquid-CO₂

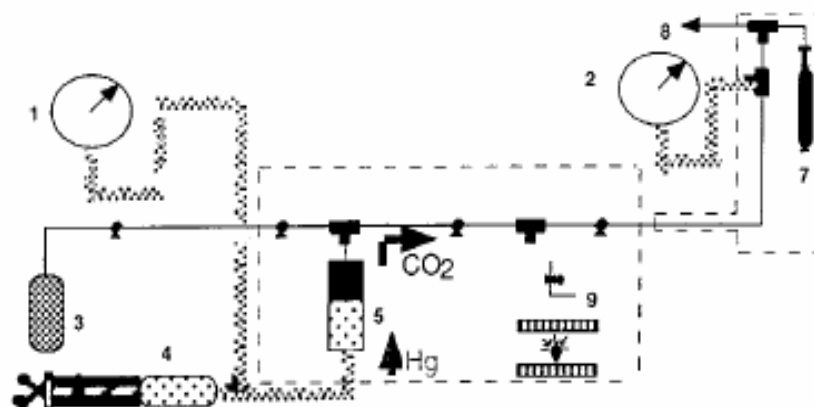
systems. This different phase behavior is the key phenomena which makes extraction of solutes from IL with CO₂ attractive.

3.2.1. [bmim][PF₆]-CO₂ System

Since [bmim][PF₆] is the most widely studied IL in the literature, most of the researchers developed high pressure phase behavior of [bmim][PF₆]-CO₂ system (Blanchard *et al.*, 2001; Kamps *et al.*, 2003; Lu *et al.*, 2003; Aki *et al.*, 2004; Cadena *et al.*, 2004, Shariati and Peters, 2005).

High pressure vapor-liquid phase behavior of [bmim][PF₆]-CO₂ was measured by using a static high pressure phase equilibrium system and a dynamic flow apparatus (Blanchard *et al.*, 2001). In the static high pressure vapor-liquid equilibrium apparatus, a glass cell was loaded with a known amount of IL sample and known amounts of CO₂ were metered into the cell while the sample within was vigorously stirred to ensure equilibrium. The composition of the IL rich liquid phase was calculated on the basis of the known amount of CO₂ added to the cell, with the assumption of a pure CO₂ vapor phase. At the end of the equilibration period, CO₂ was completely removed from IL phase upon depressurization.

In Figure 3.4 the static high pressure phase equilibrium system is demonstrated and in Figure 3.5 schematic diagram of general experimental apparatus is given which was used to measure the solubility of CO₂ in ILs by research groups.



- | | |
|---|---------------------|
| 1. CO ₂ reservoir pressure gauge | 6. Heat source |
| 2. Cell pressure gauge | 7. Pressure cell |
| 3. CO ₂ tank | 8. Exhaust line |
| 4. CO ₂ ruska pump | 9. Calibration line |
| 5. CO ₂ reservoir | |

Figure 3.4. Typical static high pressure vapor-liquid equilibrium apparatus
(Blanchard *et al.*, 2001)

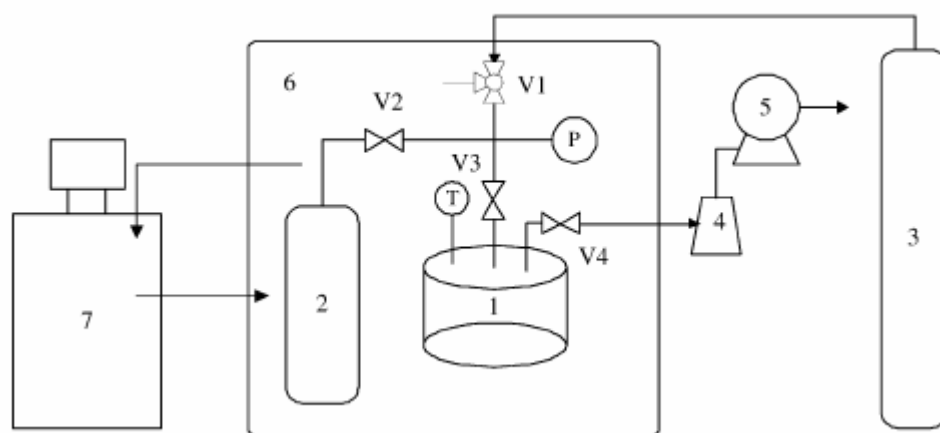


Figure 3.5. Apparatus for measurement of solubility of CO₂ in ILs:
(1) equilibrium cell; (2) gas reservoir; (3) CO₂ bomb; (4) water trap; (5) vacuum pump;
(6) water bath; (7) circulator (Kim *et al.*, 2004)

The solubility of CO₂ in [bmim][PF₆] was determined at 40, 50 and 60°C and pressures up to 93 bar (Blanchard *et al.*, 2001). The phase behavior of the [bmim][PF₆] is illustrated in Figure 3.6. In this figure, the mole fraction of CO₂ in the IL rich phase is plotted as a function of pressure. As the pressure increases, the solubility of CO₂ in IL rich phase increases dramatically and the solubility value reaches a mole fraction of 0.72 at 40°C and 93 bar. A general rule suggests that an increase in temperature results with a decrease in the solubility of gases in liquids. As expected, the solubility of CO₂ in [bmim][PF₆] rich phase decreases with temperature. However, the figure indicates that the temperature dependence of the solubility is quite small in this temperature and pressure range. Another crucial point is the effect of large degree of CO₂ solubility on the viscosity of IL. The viscosity of IL decreases when a certain amount of CO₂ is dissolved in IL and this effect can easily be observed by the reduced drag on the stirring magnet when a static high pressure vapor-liquid equilibrium set-up is used. This reduction in viscosity of the liquid facilitates the solution process.

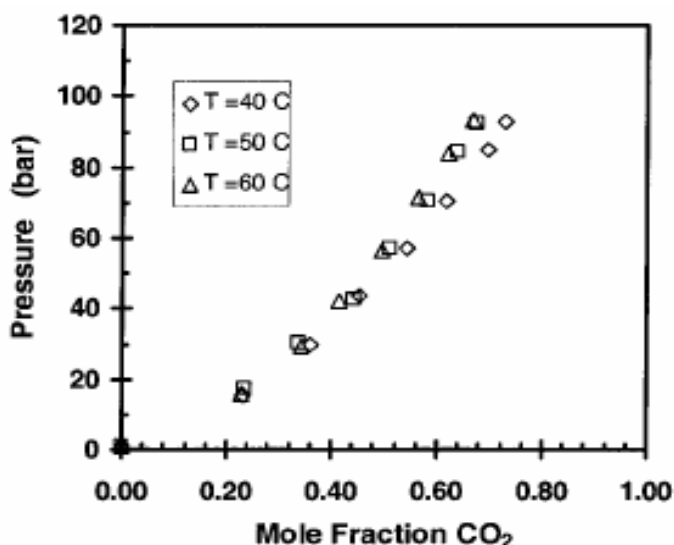


Figure 3.6. [bmim][PF₆]-CO₂ liquid phase compositions at 40, 50 and 60°C
(Blanchard *et al.*, 2001)

Kamps *et al.* (2003) presented the solubility of CO₂ in [bmim][PF₆] for temperatures 293 to 393 K in 20 K intervals and pressures up to about 9.7 MPa. The total pressure is plotted versus the stoichiometric molality of the gas (number of moles per kilogram of the IL) in

Figure 3.7. The total pressure increases linearly with increasing amount of the gas in IL. The solubility data represented by Kamps and co-workers (2003) differ from the previously reported solubility data of Blanchard and co-workers (2001). The comparison of experimental data of two studies is given in Figure 3.8.

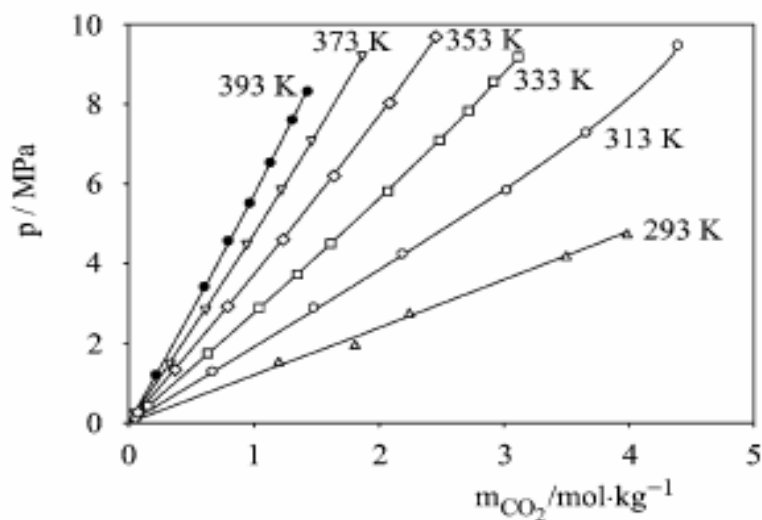


Figure 3.7. Total pressure versus molality of gas for [bmim][PF₆]-CO₂ system (Kamps *et al.*, 2003)

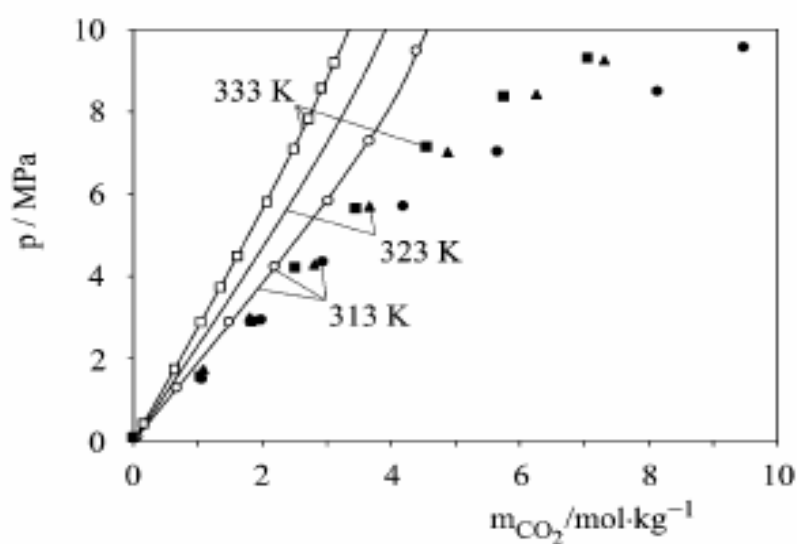


Figure 3.8. Comparison of experimental data for [bmim][PF₆]-CO₂ system: (Blanchard *et al.*, 2001 (• ■ ▲); Kamps *et al.*, 2003 (○ □))

There are several [bmim][PF₆]-CO₂ high pressure vapor-liquid equilibrium data sets available in the literature. However, these sets differ from each other considerably in the values they report for similar conditions. The reason of different solubility data may be due to the small amounts of water dissolved in IL sample used. For example, Blanchard *et al.* (1999) presented a solubility data of CO₂ in [bmim][PF₆] which is different than the data reported by the same group in 2001. In the first study, this group used [bmim][PF₆] which was saturated with water at 22°C, containing 2.3 weight per cent water. In the second study, they used [bmim][PF₆] which was dried to approximately 0.15 weight per cent water. Drying of IL has a dramatic effect on the phase behavior with CO₂. In Figure 3.9, [bmim][PF₆]-CO₂ liquid phase compositions are given for dried and wet IL samples.

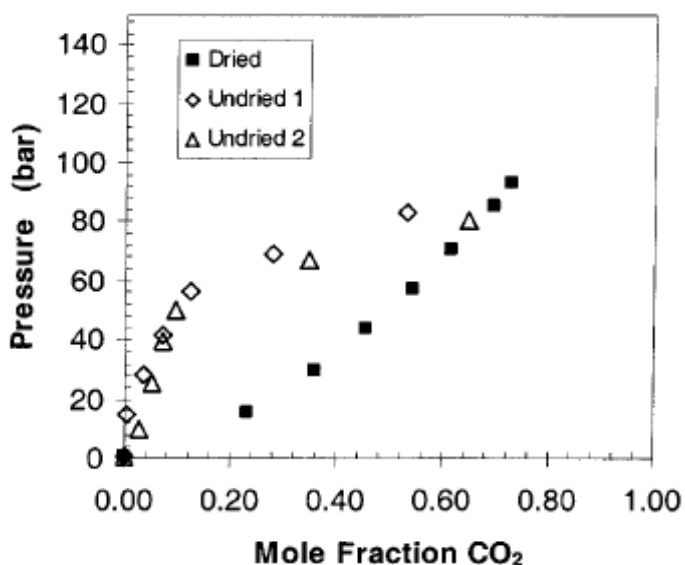


Figure 3.9. [bmim][PF₆]-CO₂ liquid phase compositions for dried and wet IL samples at 40°C (Blanchard *et al.*, 2001)

In order to observe the effect of water impurity in IL, phase behaviors of two IL samples (dry and wet) with CO₂ are compared. The effect of water impurity in IL is significant at 57 bar. For dried IL sample, the mole fraction of CO₂ is 0.54, whereas for the wet (water saturated) IL sample it is only 0.13. The effect of water in IL can be explained by CO₂-phobic nature of water. Even at high pressures, mutual solubilities of water and CO₂ are very low

(King *et al.*, 1992). Another point is the formation of carbonic acid from the reaction of CO₂ with water that can result in a reduction of the aqueous phase pH to as little as 2.80 (Toews *et al.*, 1995).

Rubero and Baldelli (2004) investigated gas-liquid interface of imidazolium ILs using surface-sensitive vibrational spectroscopy sum frequency generation. The results indicated that when the IL is dry, the cation is oriented with the imidazolium ring parallel to the surface plane for both hydrophilic and hydrophobic ILs. But the cation reorients itself with respect to the surface for the hydrophobic liquid when water is added, while the orientation in the hydrophilic liquid is unaffected.

After the influence of water is noticed, researchers have started to dry and degas all ILs under vacuum at room temperature for several days prior to use. After ILs are dried and degassed, the water contents are estimated by the Karl Fischer analysis before solubility data are taken. Measurements show that most widely studied IL; [bmim][PF₆] absorbs a couple weight per cent water when left to the atmosphere. The estimated water content of [bmim][PF₆] after drying was approximately 0.15 weight per cent water as measured by Karl Fischer analysis (Blanchard *et al.*, 2001).

A number of high and low pressure [bmim][PF₆]-CO₂ solubility studies have appeared in the literature. Although consistent results have been established for low pressure solubility data of CO₂ in [bmim][PF₆], there are large discrepancies among high pressure solubility data of several researchers (Kamps *et al.*, 2003; Blanchard *et al.*, 2001; Aki *et al.*, 2004; Shariati and Peters, 2005). These large solubility differences in the literature are most probably due to the differences in the purities of the ILs used.

Since the behavior of IL-CO₂ systems are different from other organic liquid-CO₂ systems, full phase diagram of IL-CO₂ systems are investigated. Blanchard and co-workers (1999) found two-phase immiscibility regions with three cloud point measurements of 1.31, 4.92 and 7.15 mole per cent IL mixtures with the balance being CO₂. However, these experiments were conducted with water saturated ILs.

Finally, Blanchard *et al.* (2001) gave a qualitative phase behavior of [bmim][PF₆]-CO₂ system with dry IL samples over a wide pressure range. Figure 3.10 demonstrates the phase behavior where a large miscibility gap exists even at extremely high pressures. As a complementary work, McHugh and co-workers studied [bmim][PF₆]-CO₂ at higher pressures up to 3100 bar and found two distinct phases at all conditions. This type of behavior is not expected for organic liquid-CO₂ systems and the existence of two distinct phases is explained by the following discussion: At high pressures density of pure CO₂ phase increases but since the liquid phase does not expand, the two phases will never become identical and a mixture critical point will never be reached. Therefore, the IL-CO₂ system remains two phase even at very high pressures, although the CO₂ solubility is quite high, the mixtures never become single phase.

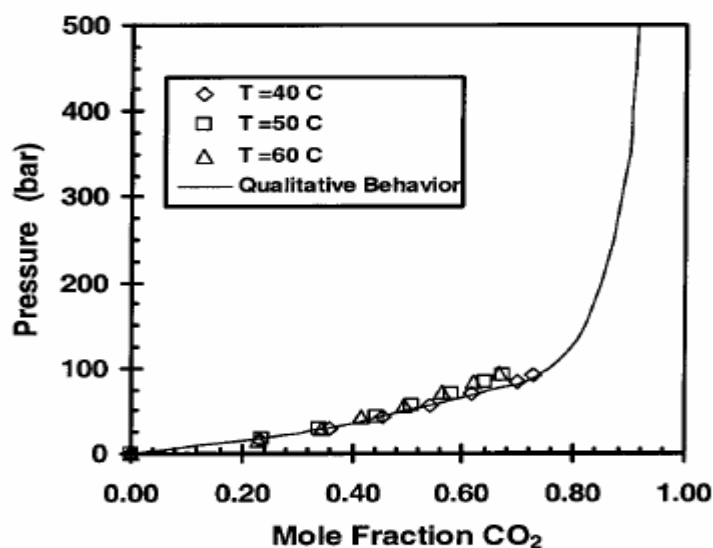


Figure 3.10. Qualitative phase behavior of [bmim][PF₆]-CO₂ system
(Blanchard *et al.*, 2001)

3.2.2. Other IL-CO₂ Systems

High pressure phase behavior of different types of ILs are similar to that of [bmim][PF₆]. Blanchard *et al.* (2001) investigated the high pressure phase behavior of CO₂ with six different ILs. The focus of the work was to develop an insight into physical interaction between CO₂

and ILs with different cation-anion configurations. The solubility of CO₂ in the IL rich phase was greatest for ILs with fluorinated anions, followed the trend of [bmim][PF₆] and [C₈-mim][PF₆] > [C₈-mim][BF₄] > [N-bupy][BF₄] > [bmim][NO₃] > [emim][EtSO₄]. The solubility of CO₂ was the greatest in ILs with PF₆⁻ anion. Aki *et al.* (2004) also presented the solubility of CO₂ in ten different imidazolium based ILs at different temperatures and pressures up to 150 bar.

The solubility of CO₂ in most of ILs increases with increasing pressure but the exact amount of CO₂ dissolved in the liquid phase varies significantly. For example, at 70 bar the solubility of CO₂ in [emim][EtSO₄] is 0.36 mole fraction whereas, it is 0.63 mole fraction in [C₈-mim][PF₆] (Blanchard *et al.*, 2001). The solubility of CO₂ in the IL rich phase changes slightly with the temperature as in the case of [bmim][PF₆]-CO₂ system.

The liquid phase compositions of different IL-CO₂ systems are demonstrated in Figure 3.11. Changing the anion from PF₆⁻ to BF₄⁻ in the [C₈mim] salts results in an approximately eight per cent decrease in CO₂ solubility at 40°C over the range of pressures shown in the Figure 3.11. Although there are some numerical differences in the mole fraction of CO₂ dissolved, the general trend of phase behavior is nearly identical for all ILs. From this point of view, it can easily be concluded that scCO₂ can be used to recover solutes not only from [bmim][PF₆] but also from all kind of ILs.

Experimental and molecular simulation studies found that the anions of IL dominate the interaction with CO₂, with the cation playing a secondary role. Cadena *et al.* (2003) concluded that the changes in the imidazolium cation involving alkyl groups have relatively little influence on the solubility of CO₂ in IL.

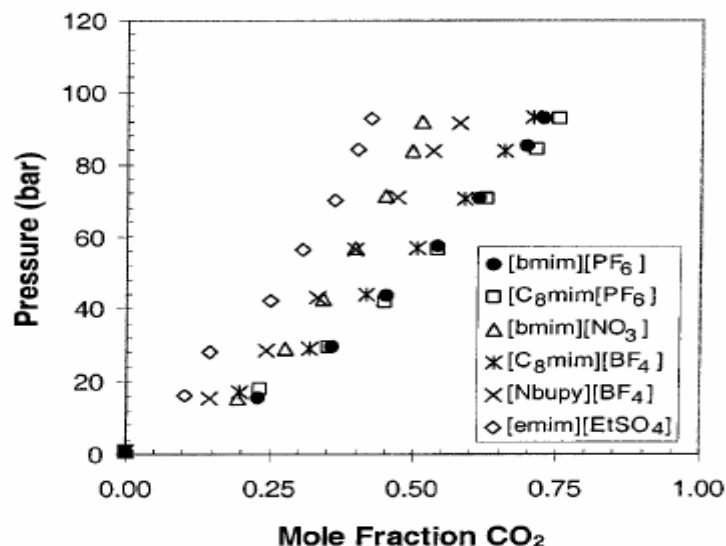


Figure 3.11. Liquid phase compositions of different IL-CO₂ systems
(Blanchard *et al.*, 2001)

Shariati and Peters (2004) studied the phase behavior of binary system, [emim][PF₆]-CO₂ experimentally by measuring its bubble point pressures at different temperatures and compared it with [bmim][PF₆]-CO₂ system to understand the effect of the length of alkyl chain on the solubility of CO₂. The solubility of CO₂ in [bmim][PF₆] is higher than in [emim][PF₆]. Since the butyl group in [bmim][PF₆] is bulkier than the ethyl group in [emim][PF₆], it can be expected that CO₂ can dissolve better in [bmim][PF₆] than in [emim][PF₆], the latter component being denser.

In general when a gas is dissolved in a liquid phase, dilation of the liquid occurs. ILs show only slight dilations in volume with CO₂ dissolution. This behavior is different than normal liquid-CO₂ systems. In fact, the dissolution of CO₂ in liquids to expand them and reduce their solvent strength is a well known phenomena and it is the basis of gas anti-solvent (GAS) process to precipitate solutes from liquids (De la Fuente Badilla, 2000). However, ILs do not follow this trend due to the strong Coulombic forces associated with the ionic nature of ILs. The lack of expansion of ILs seems to derive from the fact that dissolved CO₂ does not greatly affect the strength of interionic interactions in IL. Therefore, the IL-CO₂ system is

extremely different from other organic liquid-CO₂ systems with the large immiscibility region and lack of dilation of the liquid phase.

The experimental solubility data of CO₂ in ILs ([bmim][BF₄] and [bmim][PF₆]) have been successfully correlated for the first time using a simple cubic equation of state by Shiflett and Yokozeki (2005). A generic Redlich-Kwong equation of state predicts high pressure phase behavior as well as miscibility gaps for high concentrations of CO₂ in ILs and found in a good agreement with those reported in the literature.

3.2.3. IL Solubility in CO₂

The majority of the research focus on the solubility of CO₂ in IL, on the other hand the concentration of IL in CO₂ rich phase is also important. A dynamic apparatus, a high pressure cell, was used to measure the solubility of [bmim][PF₆] in the CO₂ rich phase (Blanchard *et al.*, 2001). The solubility of [bmim][PF₆] in CO₂ was determined at 40°C and 137.9 bar by flowing 0.5866 mole of CO₂ through a cartridge loaded with [bmim][PF₆]. UV-Visible analysis gave no appreciable IL absorption peak, indicating [bmim][PF₆] solubility of less than $5 \cdot 10^{-7}$ (mole fraction of [bmim][PF₆]) of in the CO₂ rich phase. Due to the fact that no measurable IL dissolves in CO₂, a solute dissolved in an IL can be easily recovered with scCO₂ without any cross contamination. The lack of solubility of IL in CO₂ phase can be attributed to two reasons: extremely low vapor pressure of IL and inability of CO₂ to adequately solvate ions in the gaseous phase.

Although the solubility of IL in scCO₂ is extremely low and not measurable, in industrial applications, the scCO₂ phase may contain some other component such as reactants, products which may act as cosolvents to enhance the ability of scCO₂ to dissolve IL significantly. In this case, the amount of IL dissolved in CO₂ rich phase may not be negligible under some conditions. In order to decide on the conditions to avoid cross contamination, solubility of IL in scCO₂-organic compound mixtures must be known. Wu *et al.* (2003) conducted the first study in the literature to observe the effect of organic compounds in scCO₂ on the solubility of

an IL in CO₂ phase. The solubility of [bmim][PF₆] in scCO₂, and in scCO₂-ethanol, scCO₂-acetone, scCO₂-n-hexane mixtures are investigated quantitatively. The solubility of IL in scCO₂ is extremely low as the earlier studies suggested, however by addition of ethanol and acetone, the solubility of IL increases dramatically as the concentration of the organic compounds in scCO₂ exceeds 10 mole per cent. This enhancement of the IL solubility by addition of ethanol and acetone results mainly from strong interaction of the two compounds with the IL due to their strong polarity. The polarity of acetone is stronger than ethanol; therefore the solubility of IL is higher in the scCO₂-acetone system than in the scCO₂-ethanol system. Since n-hexane is a nonpolar substance its influence on the solubility of IL in scCO₂ phase is very limited. A further study of Wu *et al.* (2004) also showed that the ability of cosolvents to increase the solubility of ILs ([bmim][PF₆] and [bmim][BF₄]) in scCO₂ follows the order: acetonitrile > acetone > methanol > ethanol > n-hexane. This order is same with the order of dipole moments of cosolvents. With this discussion, it is clear that the polarity of the organic compound is a dominant factor in influencing solubility. Figure 3.12 represents the solubility of [bmim][PF₆] in mole fractions in scCO₂-organic compound mixtures where x_2 and x_3 represent mole fractions of the organic compounds and IL in scCO₂ rich phase, respectively. This figure illustrates that the amount of IL dissolved in scCO₂ rich phase may be significant if the system contains enough polar organic compounds.

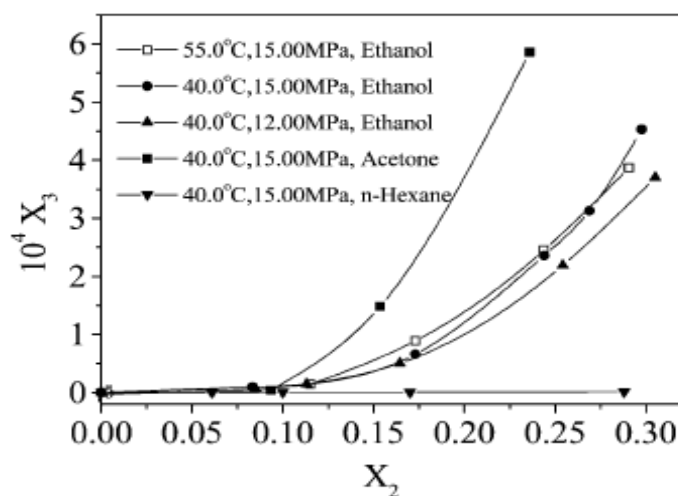


Figure 3.12. Solubility of [bmim][PF₆] in scCO₂ + organic compounds system
(Wu *et al.*, 2003)

3.3. IL-CO₂ Interaction in the Molecular Level

An in situ ATR-IR (Attenuated Total Reflectance-Infra Red) study of CO₂ dissolved in two ILs ([bmim][PF₆] and [bmim][BF₄]) at high pressures has demonstrated the effects of anionic species of the ILs on the molecular state of the dissolved CO₂. Kazarian *et al.* (2000) showed that CO₂ forms weak Lewis acid-base complexes with the anions in [bmim][PF₆] and [bmim][BF₄]. Furthermore, they demonstrated that this interaction is stronger with [bmim][BF₄]. BF₄⁻ acts as a stronger Lewis base towards CO₂ than PF₆⁻. In addition to this, as the size of anion increases the strength of interaction decreases. However, the solubility data of various group indicated that CO₂ has a higher solubility in [bmim][PF₆] than in [bmim][BF₄]. Thus, the strength of these interactions can not be solely responsible for the solubility of CO₂ in these ILs and presumably, a free volume contribution in IL plays a significant role (Gu *et al.*, 2000). The strength of the anion-cation interactions in IL affects the available free volume and one can expect that a weaker interacting anion leads to more free volume being available.

ILs are generally distinguished with their low melting points. Another in situ ATR-IR spectroscopic study of Kazarian *et al.* (2002) showed that high pressure CO₂ reduces the melting temperature of ILs. This possibility of reducing melting temperature of ILs further under high pressure CO₂ provides a new opportunity to use ILs as solvents at milder temperatures. Kazarian *et al.* (2002) investigated the effect of CO₂ pressure on phase behavior of 1-hexadecyl-3-imidazolium hexafluorophosphate. The data presented indicated that 70 bar CO₂ reduces the melting point of this IL from 75 to 50°C. This result was assigned to a weak Lewis acid-base type interaction between anion and CO₂, with the P-F bonds perpendicular to O = C = C axis thereby reducing the rather stronger interactions between the P-F bonds and the cations. CO₂ disrupts the cation-anion and the tail-tail interactions in IL rather than simply playing an impurity role in the mechanism of induced melting. Preliminary results obtained by Kazarian *et al.* (2002) also indicated that melting temperatures of other analogous ILs decrease by high pressure CO₂ allowing their use in many applications at mild temperatures.

4. REMEDIATION OF CONTAMINATED SOILS

Soil systems have developed over many millions of years and they can be influenced by numerous natural and nowadays human-induced factors. The soil characteristics in a given geographical area at a given point in time are a function of both natural influences and human activities. Soil contamination is usually defined as solid and/or liquid hazardous substances mixed with the naturally occurring soil. The crucial contaminant groups from various sources (Canter, 1996;<http://www.epa.gov/superfund/students/wastsides/soilspil.htm>) are tabulated in Table 4.1.

Table 4.1. Examples of soil contaminant groups

Contaminant Groups	Examples
Semi-Volatile Constituents	Polychlorinated Biphenyl (PCB), Polynuclear Aromatic Hydrocarbons (PAH), Crude Oil, Dioxin, Pesticides, Herbicides etc.
Heavy Metals	Arsenic, Barium, Cadmium, Cesium, Cobalt, Copper, Iron, Lead, Nickel, Titanium etc.
Radionuclides	Uranium, Radium etc.
Organometallics	Mercury, Nickel Carbonyl, Tetraethyl Lead etc.
Reactive Inorganics	Bromine, Chlorine, Chromates etc.
Aliphatic and Cyclic Hydrocarbons	Cyclohexane, Cyclopentane, Dicyclopentadiene, Heptanes, Octanes etc.
Organics with Carbon-Oxygen Bonds	Ethanol, Methanol, Acetone, Acetophenone, Methyl Ethyl Ketone, Ethylene Glycol etc.
Organics with Carbon-Nitrogen Bonds	Acetonitrile, Aniline, Benzidine etc.
Acids	Nitric Acid, Sulfuric Acid etc.

These hazardous contaminants may be spilled onto or buried directly in the soil; they may migrate to soil from a spill that has occurred elsewhere or they may be carried by ground or underground waters from another contaminated area and deposited in the soil. Contamination of soil is most frequently due careless industrial activity or careless handling of some industrial products.

Contaminated soils are a major concern since the contaminants of the soil can be transported to groundwater sources and into the air. Therefore, remediation of the soil to remove the contaminants resulting from spreading of hazardous substances, pesticides and fertilizer usage, industrial and chemical processes is essential. Because of the attention directed towards the cleanup of contaminated soils, identification of necessary constituent concentrations requisite to establishing that cleanup has been achieved is a key issue (Canter, 1996). No uniform soil concentration level has been established, standards are developed for generic or site specific levels to address the ways to protect soil in the world.

4.1. Conventional Soil Remediation Techniques

In order to clean up contaminated areas, soil can be excavated from the ground to be treated or can be left in the ground and treated in situ. The methods for remediation of contaminated soils vary because there are hundreds types of different contaminants needing different methods of cleaning. Furthermore, the nature of the soils and geology differ from place to place (Canter, 1996). In the past, various soil cleaning techniques such as soil venting, bioventing, steam stripping and thermal desorption have been developed and implemented at field scale with varying successes. Usually, these methods involve desorption of contaminants from the soil particles (<http://www.epa.gov/superfund/students/wastsides/soilspil.htm>).

Soil washing generally incorporates particle size separation during washing. Since many of the soil contaminants have a tendency to bind to clay, silt particles, particle size separation is considered as an effective treatment. With the washing step, fine clay and silt particles are separated from the coarser soil particles and therefore contaminants are concentrated into a smaller volume consisting of clay and silt fraction. Finally, this fraction is managed by further

soil washing treatment systems (www.art-engineering.com/Soil~Treatment.htm). Soil washing treatment systems are based on standard chemical and physical separation processes. Soil treatment may include any combination of technologies involving soil separation, density separation (effective for metal separation), flotation (effective for PAHs), surfactant washing, chemical extraction using acids, and complexing agents. Among these technologies, using surfactants is the newest one for in situ remediation of soils. The surfactants can cause contaminants to move more rapidly through the 'vadose zone' (which is a lower water content zone above the water table) and to reach the water table more quickly. The researchers are investigating the effects of surfactants on the flow of contaminants to help reduce the time and money associated with cleaning the subsurface environment (www.art-engineering.com/Soil~Treatment.htm). Encouraging natural organisms in the soil to break down contaminants, destroying contaminants by incineration and encapsulating the contaminants by adding special materials are other attractive and latest methods for soil remediation. However, the main approach is still flushing contaminants out of soil using water or chemical solvents, i.e. leaching (<http://www.epa.gov/superfund/students/wastsides/soilspil.htm>).

In order to extract the contaminants from soils, volatile organic solvents such as toluene, benzene, methanol, ethanol etc. are commonly used. These solvents become volatile at process conditions. However, the evaporation of such organics to atmosphere has a harmful effect on human health and environment. These traditional methods utilizing organic solvents are significant sources of environmental pollution via fugitive emission (Blanchard and Brennecke, 2001). There have been increasing limitations and strict regulations on volatile organic emissions recently to prevent environmental pollution and to reduce working exposure hazards.

4.2. Soil Treatment with scCO_2

Supercritical Fluid Extraction (SCFE) has been suggested for soil remediation in the past (Akgerman *et al.*, 1991; Erkey *et al.*, 1993). SCFE methods for soil remediation offer advantages over conventional liquid extraction techniques. The SCFE method for soil remediation, as in all other SCFE applications, takes advantage of the ability of SCFs to

dissolve organic contaminants from soil, the ability to vary the solvent power of SCF near the critical point by changing temperature and pressure, low viscosities of SCFs compared to liquid solvents and high solute diffusivities in SCFs which increase mass transfer rates (Erkey *et al.*, 1993). Furthermore, SCFs have very low surface tensions which enable facile penetration into microporous materials such as soils (McHugh and Krukonsis, 1986).

scCO₂ is a desirable fluid to be used in removing pollutants from soil. Unlike other organic solvents (methanol, ethanol etc.) used in remediation of contaminated soils, it is nontoxic. It is nonflammable unlike the other solvents (ethane, propane, ethylene etc.) and therefore, it does not introduce a safety hazard during the remediation process. In processes where liquid extraction technologies are used, soil has to undergo another treatment in order to remove residual solvent. However, CO₂ can be recycled after the decontamination process and it does not leave any residue on the treated soil.

Various studies demonstrated that pentachlorobenzene (PCB), dichloro diphenyl trichloroethane (DDT), phenol and hexachlorobenzene (HCB) can be removed from soil by scCO₂ (Dooley *et al.*, 1987; Akgerman *et al.*, 1991; Erkey *et al.*, 1993). These model compounds represent polyaromatic hydrocarbons and polychlorinated compounds which are known as important soil pollutants. Organic soil contaminants can exist in two states: deposited state or adsorbed state. Some of the contaminants are deposited as a separate phase on the solid surface and these contaminants can be extracted by simple dissolution in the supercritical phase. The extraction of contaminants adsorbed on the solid phase is likely to be controlled by the adsorption-desorption equilibrium.

Akgerman *et al.* (1992) studied extraction of HCB from soil at 8.3-27.6 MPa and 298-323 K by CO₂. Erkey *et al.* (1993) determined the adsorption isotherms and desorption profiles for naphthalene, phenanthrene, hexachlorobenzene and pentachlorophenol as model compounds on soil in the presence of scCO₂ using an experimental technique based on frontal analysis chromatography at 10 MPa and 308-328 K.

Besides its various advantages mentioned above, direct SCFE for remediation of contaminated soils has a big disadvantage: This process requires that the contaminated soil to be processed at high pressures, where batch handling is a must. Thus, continuous cleaning of contaminated soils is not economically feasible if the contaminant is removed from soil directly by scCO₂ extraction. Batch handling, pressurization and depressurization of large soil quantities possess an economic problem which may be hard to solve. On the other hand, various disadvantages of using VOCs to remediate soil were explained in previous section. Therefore, a new process to be conceived combining the advantages of liquid extraction with the environmentally benign properties of scCO₂ may have high economic viability.

4.3. Naphthalene as Soil Contaminant

Naphthalene is a very common, relatively light, semi-volatile, two-ring, low molecular weight PAH found in numerous by-products, petroleum products, cigarette smoke, wood smoke, tar, asphalt and it is a priority pollutant according to Environmental Protection Agency (EPA) of the U.S. It is a bicyclic aromatic hydrocarbon with the chemical formula C₁₀H₈ and in purified form; it is a white crystalline solid that is sparingly soluble in water (0.031 g/L).

Naphthalene is known as a toxic release inventory chemical. Since it is a toxic pollutant, it is subject to effluent limitations. Naphthalene can bind weakly to soils and sediments and easily passes through sandy soils to reach groundwater. Naphthalene may be adsorbed by the soil to a moderate extent; 10 per cent (Irwin *et al.*, 1997). The extent of naphthalene sorption depends on the organic carbon content of the soil and a rapid movement is expected through sandy soils.

Naphthalene is not particularly water soluble compared to other chemicals, but it is a relatively water soluble among the PAHs. Therefore, a soil polluted with naphthalene may cause the contamination of groundwater. Soil with naphthalene contaminant causes the pollution of another natural resource; water. Limiting the concentration of naphthalene pollutant in soil is crucial because the magnitude of soil contamination provides insight about likelihood of contamination of groundwater sources. Furthermore, like other contaminants

naphthalene is harmful for human health. Humans may be exposed to naphthalene in soil by inhalation of airborne soil particles, by ingestion of food-borne soil residues, by ingestion of household dust or by direct ingestion of soil (U.S. EPA, 2003).

Since PAHs are one of the most important pollutant groups in soil and naphthalene is a member of this group, there are some regulations for remediation of soils to reduce the harmful effects of naphthalene. Facilities are required to report the amounts per year of naphthalene released into the environment both on and off site. The on site quantity is subdivided into air emission, surface water discharges, underground injections, and releases to land (U.S. EPA, 2003).

The interim remediation criteria considered as protective for human and environmental health for naphthalene in soil is 0.1 $\mu\text{g/g}$ for agricultural land, 5 $\mu\text{g/g}$ for residential parkland and 50 $\mu\text{g/g}$ for commercial-industrial land where $\mu\text{g/g}$ is defined as ppm (Irwin *et al.*, 1997). There are several soil criteria for evaluating the severity of contamination: For example, according to the Dutch Soil Cleanup Act (1982), 0.1 ppm naphthalene indicates a background concentration; 5 ppm naphthalene indicates a moderate soil contamination; 50 ppm indicates a threshold value which requires immediate cleanup (Irwin *et al.*, 1997).

Naphthalene was used as a model compound to simulate hazardous PAHs in soil in an earlier study (Erkey *et al.*, 1993). As discussed in the previous section, naphthalene may be extracted from soil by the scCO_2 extraction technique. Therefore, it is essential to understand the solvent power of scCO_2 and the solubility of naphthalene in dense CO_2 . The solubility of the naphthalene in scCO_2 depends on the system temperature and CO_2 pressure. Figure 4.1 shows the solubility of naphthalene in CO_2 as a function of temperature and pressure. If the pressure is replaced by density as the independent parameter, the solubility relation becomes simpler as demonstrated in Figure 4.2. At low pressures, density decreases dramatically with an increase in temperature; whereas at higher pressures, changes in temperature have much less effect on density. Thus density, not pressure, to a first approximation is proportional to the solvent power of the supercritical fluid. Solubility measurements show that the solvent power

of scCO₂ increases with density at constant temperature and the solvent power of scCO₂ increases with temperature constant density.

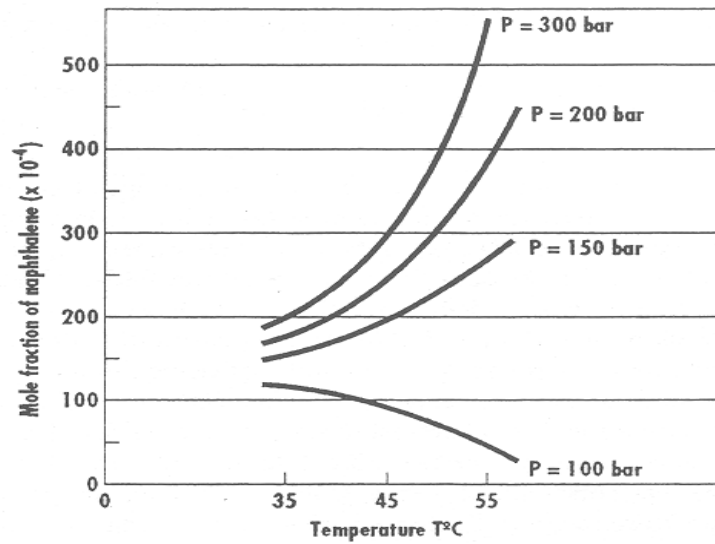


Figure 4.1. Solubility of naphthalene in CO₂ vs. temperature at various pressures (Taylor, 1996)

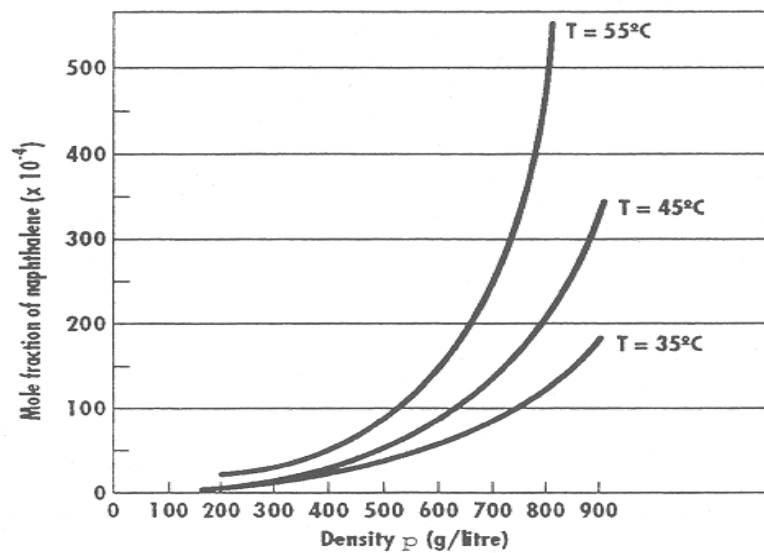


Figure 4.2. Solubility of naphthalene in CO₂ vs. density at various temperatures (Taylor, 1996)

4.4. A New Process Suggested for Cleaning of Soils

As explained in the previous sections, besides various advantages, a direct SCFE for soil remediation process has a crucial disadvantage since it requires batch feeding of soil to high pressure extraction vessel. Soil has to be processed at high pressures where expensive batch handling is a must. Therefore, in this thesis work, a new process is suggested which can combine the advantages offered by liquid solvents and scCO_2 . Liquid solvents can be used to extract contaminants from soil continuously, and scCO_2 can be utilized to recover the contaminants from liquid solvent in order to recycle the solvent. Therefore, this study suggests a process to clean contaminated soils by a powerful and nonvolatile liquid solvent, an IL, and to recover contaminants from the IL extract by scCO_2 extraction to recycle the IL. The suggested process employs high pressure only in the processing, i.e. SCFE of the IL-contaminant stream, which is a fluid. Thus, continuous processing at high pressures is easily possible.

The suggested process for cleaning of contaminated soils combines several advantages of two green solvents; IL and scCO_2 : Unlike the other volatile organic solvents, ILs are nonvolatile, therefore they do not have harmful effects on human health and environment. Furthermore, the solvent power of ILs is extremely high and they are capable of dissolving a variety of contaminants present in the soil. For economic reasons, the solvent of a process must be recycled. The contaminants are recovered by scCO_2 from IL in the suggested process and, both IL and CO_2 are recycled. Thus, a soil remediation process combining the advantages of ILs and SCFE, where high pressure batch handling of soils is not necessary comprising of the following main steps may be suggested. These steps are given below:

- Drying and sieving of the contaminated soil
- Mixing of the contaminated soil with the extraction solvent, IL
- Draining of the extraction solvent, IL (initial IL extract recovery)
- Recovery of the remaining IL extract from soil by a solvent (second IL extract recovery)

- Recovery of the cleaned soil after total IL extract recovery
- Extraction of the contaminants from IL by scCO_2
- Recycle of the scCO_2 treated (stripped) IL
- Separation of the contaminants dissolved in scCO_2
- Recycle of the cleaned scCO_2 to supercritical extraction column

By considering the aim to design a process for cleaning of contaminated soils using ILs and scCO_2 , the main steps of the suggested process were studied experimentally and explained in detail in Section 5.

5. EXPERIMENTAL WORK

The aim of this work was to study in some detail a process suggested for cleaning of contaminated soils using ILs and scCO_2 . The experimental work for this objective consists of four major parts:

- A- preliminary cleaning of soil
- B- doping of the cleaned soil with the model compound
- C- extraction of the contaminated soil by IL
- D- supercritical extraction of the model compound from IL

In the soil extraction part, the model component, naphthalene was extracted by an IL, [bmim][PF₆], from the soil, and in the supercritical extraction part scCO_2 was used to recover the naphthalene from [bmim][PF₆] to be able to recycle the IL. The amount of model component extracted from the soil by [bmim][PF₆] and the amount of model component recovered from [bmim][PF₆] by scCO_2 were measured using UV-Visible spectroscopy. This laboratory procedure was devised to study the industrial cleaning process suggested in Section 4.4 above.

Section 5.1 explains the materials used in the experiments. In Section 5.2, the experimental set-up used in the study is described and depicted. Detailed explanation of the experimental procedure is given in Section 5.3. The program of experimental work performed is tabulated in Section 5.4. Finally, the methods used for the analysis of experimental products are discussed in Section 5.5.

5.1. Materials Used

The materials used were 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆], Fluka, ≥ 96 per cent pure) to represent the IL, crystalline naphthalene flakes

and soil. Naphthalene was used as the model compound representing the contaminants in the soil and it was used as received. [bmim][PF₆] was used as the solvent to clean contaminated soil without any further purification. CO₂ (99.7 per cent pure) was obtained in cylinders equipped with dip tubes from Habaş Inc., İstanbul.

5.2. Experimental Set-up

In soil extraction experiments, a 10 ml volume empty injector barrel with a needle was used as the solid-liquid extraction set-up. The injector was carefully chosen so that the needle outlet of the injector was located at the center of its base; therefore uniform solution flow was obtained. Clean soil of known particle size distribution with or without the model compound was placed inside the injector. The injector was put into a graduated cylinder containing a 1.5 ml microcentrifuge tube (eppendorf tube) to collect the draining IL. The base of the injector was covered with a wire mesh (150 mesh size) to prevent the flow of soil with IL. The soil extraction set-up is presented in Figure 5.1.

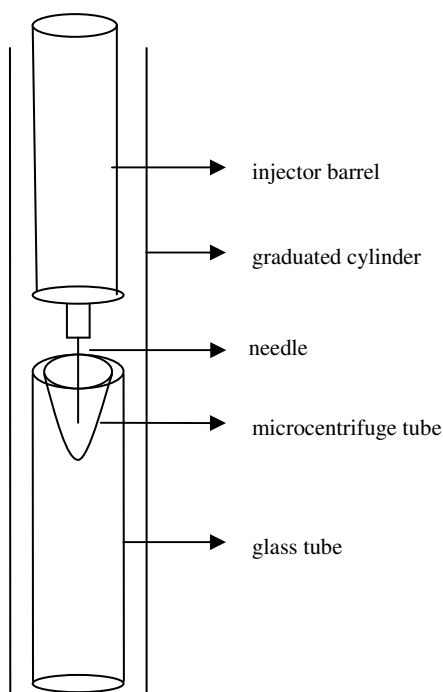


Figure 5.1. Soil extraction set-up

All supercritical extraction experiments were performed in a high pressure stainless steel cell used earlier in various works in the same laboratory (Mercangöz, 2002; Saygı, 2004). The cell had a three-valve sampling system, where all valves (Swagelok Co.) were capable to withstand pressures up to about 200 bar. The volume of the cell was 230 cm³, having 12 cm height, 8 cm OD and 6 cm ID. The cell had a bolted type head with two inlets and was manufactured from 316 SS. The pressure in the cell was measured with a range of 0-160 bar (Pakkens Instruments). The 250 bar tight sealing was provided with the Teflon gasket installed between the head and the cell body. To keep the cell and its contents at constant temperature, the high pressure cell was immersed in a constant temperature water bath equipped with a thermostat (Heto Instruments) of 0.1°C accuracy. The walls of the constant temperature water bath were made of 8 mm thick glass. [bmim][PF₆] solution obtained from soil extraction experiments was placed into the high pressure cell in the glass bottle, having a 4.3 cm height and 1.5 cm ID. This bottle was vertically positioned in the cell using a metal bottle holder to prevent falling down. The high pressure cell is depicted in Figure 5.2.

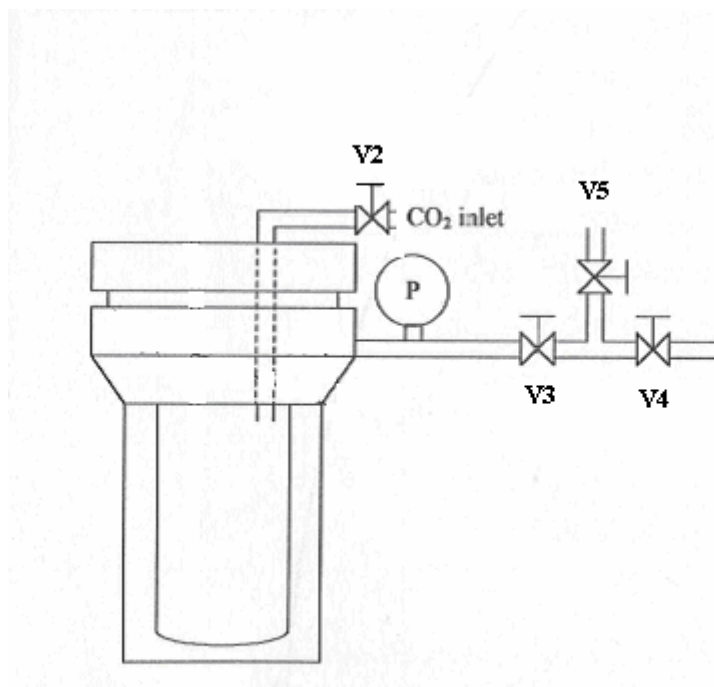


Figure 5.2. High pressure cell

The experimental set-up used for supercritical extraction experiments is depicted in Figure 5.3. A gas cylinder with a dip-tube attachment at a pressure of 60 bar at 15°C was used to supply CO₂ to the high pressure cell. As seen in Figure 5.3, the on-off valve V1 enabled flow of CO₂ to the system. In the experimental set-up, a drier (silica gel bed, 6.15 cm ID and 25 cm length) removed the water vapor that might be present in the CO₂. The gas was then cooled to -12.5°C in refrigerated bath (Heto, CB7) containing water/monoethylene glycol mixture to prevent bubbling causing cavitation in the diaphragm pump (Lewa, type EK). Liquid CO₂ was then compressed to the desired operating pressure by the diaphragm pump, the head of which was also cooled by the circulated refrigerant. The reason for cooling the gas was that the compressibility of CO₂ increases dramatically at the critical point reducing the pump efficiency to a degree where no pumping occurs effectively. The diaphragm pump used was capable of compressing the gas up to 400 bar, and the pressure gauge placed after the pump outlet allowed the pressure of the compressed CO₂ to be monitored. The diaphragm pump used was capable of compressing the gas up to 400 bar, and the pressure gauge placed after the pump outlet allowed the pressure of the compressed CO₂ to be monitored.

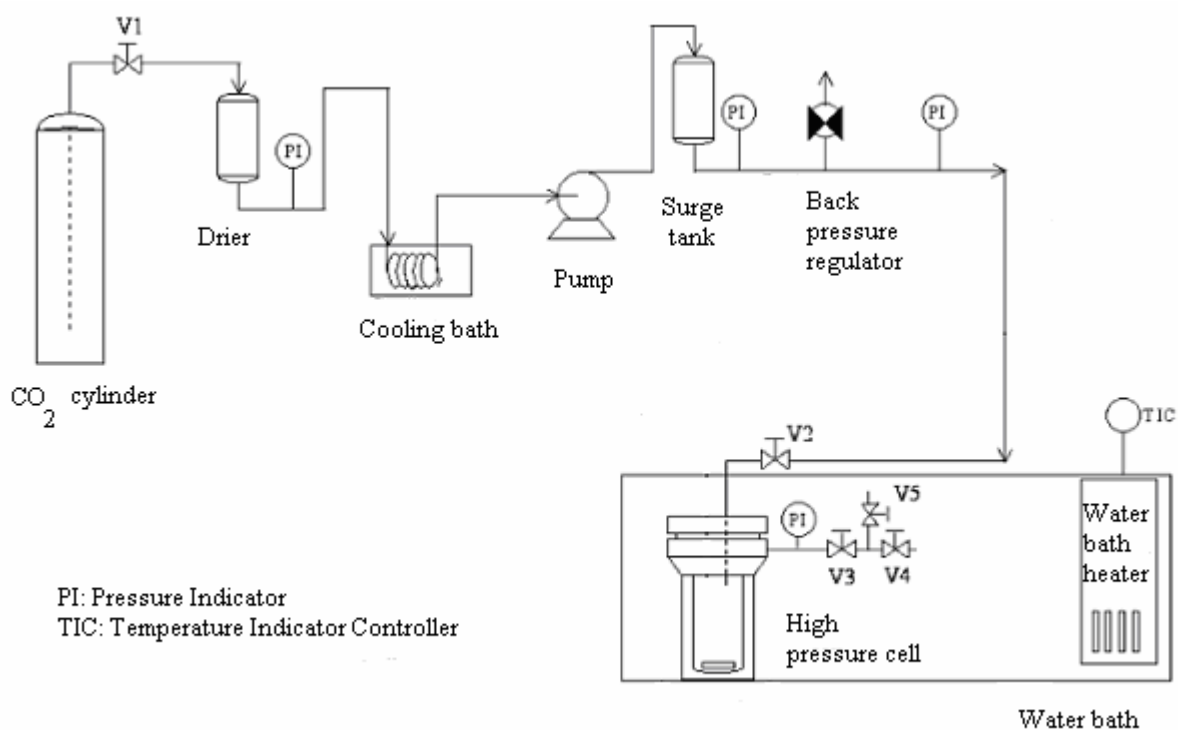


Figure 5.3. Supercritical CO₂ extraction set-up

After compression, CO₂ was introduced into a surge tank (6.15 cm ID and 25 cm length) to dampen any fluctuations generated by the pump. The surge tank was manufactured by Erikman Kardeşler Sanayii, İstanbul. In order to maintain a constant pressure within the system, a hand adjustable back-pressure regulator with a stated accuracy of ± 1 per cent of the relief pressure range (Tescom Co.) was used. The regulator was kept slightly open in order to keep the pressure of the compressed gas in the lines at a maximum pressure of 140 bar, which was selected for experimental safety.

5.3. Experimental Procedure

As already mentioned earlier, the experimental work consists of four parts: preliminary cleaning of the soil; doping of the cleaned soil with the model compound (naphthalene); extraction of the contaminated soil by IL; supercritical extraction of the model compound from IL. Experimental procedures of these parts and determination of the model compound are explained in detail in the following sections.

5.3.1. Determination of the Model Component Used

In order to choose a model component to represent soil contaminants, following requirements must be satisfied:

- The model component chosen must represent an important soil contaminant group such as polyaromatic hydrocarbons or polychlorinated compounds.
- The model compound must be soluble in [bmim][PF₆] to be extracted from the soil by this IL.
- The model component must be soluble in scCO₂ to be recovered from [bmim][PF₆] with scCO₂.

- The model component is preferred to be insoluble in water, otherwise there is no need to use [bmim][PF₆]-scCO₂ system and model compound can be easily extracted from soil by water.

In the preliminary experiments, different chemicals were experimented with to choose a proper model compound. First of all, a yellow food coloring insoluble in water but soluble in [bmim][PF₆] was used. After the food coloring was extracted from the soil sample, supercritical extraction experiments were conducted. These experiments indicated that food coloring can be extracted from [bmim][PF₆] with scCO₂. Although the solubility requirements were satisfied, food coloring was not considered as a model component for soil contaminants since its chemistry was not known, and it does not belong to a contaminant group such as PAHs or PCBs. Therefore, this chemical was not used further in our study.

Secondly, aniline was used as the model soil contaminant. Aniline is a hazardous chemical and may be present in soils as a pollutant. It is insoluble in water and usually organic solvents are used to extract it from soil. The preliminary experiments demonstrated that it is soluble in [bmim][PF₆]. However, supercritical extraction experiments carried out were not satisfactory in recovering aniline from [bmim][PF₆]. This result may be explained as the higher preferential solubility of aniline in [bmim][PF₆] than in scCO₂. Since [bmim][PF₆] could not be cleaned by scCO₂, this model component was also abandoned. At different temperatures and pressures scCO₂ may act probably as a solvent for aniline extraction. Using some entrainers like methanol or ethanol may enable scCO₂ extraction of aniline from the IL, but this was not tried.

Thirdly, dioxane was chosen as the possible model compound. Dioxane is a hazardous compound and known as a strong pollutant for the soil. However, it is soluble in water and therefore, soil can be simply washed with water to remove this hazardous chemical. Thus, dioxane was not chosen as the model contaminant.

Finally, naphthalene was used as the model component. Naphthalene is a member of PAHs. It may be present in soil as contaminant and there is a maximum concentration limit for

naphthalene. Naphthalene is sparingly soluble in water, soluble in [bmim][PF₆] and scCO₂ and its behavior in scCO₂ is well known. Thus, naphthalene was chosen as the model compound to represent the PAH contaminants in the soil.

The maximum allowable limit for the naphthalene in soil is given in literature as 50 µg naphthalene in 1 g soil (Canter, 1996; Irwin *et al.*, 1997; U.S. EPA, 2003). In the soil extraction experiments, 0.005 g naphthalene, hundred times more than the maximum allowable limit, was used to see whether [bmim][PF₆] could clean the contaminated soil.

5.3.2. Preliminary Cleaning of Soil

The soil obtained from campus garden was dried and sieved. It was then washed vigorously with water, hexane and acetone respectively. First, it was washed with water, drained and dried, and the same procedure was applied by using hexane and acetone. The aim of these extractions was to remove any organic contaminant in order to observe the extraction of naphthalene. In all soil extraction experiments, this cleaned soil was used.

5.3.3. Soil Extraction Using IL

As noted earlier, the maximum allowable naphthalene concentration in commercial-industrial lands is given in literature as 50 µg naphthalene in 1 g soil (Canter, 1996; Irwin *et al.*, 1997; U.S. EPA, 2003). In soil extraction experiments, 0.005 g naphthalene, which is hundred times more than the maximum allowable limit, was added to a sample of previously cleaned soil.

In preparing the doped soil sample, 0.005 g naphthalene and 1 g previously cleaned soil were weighed separately in an electronic balance (Precisa Instruments Ltd. XB 220A) and, put into the solid-liquid extraction set-up (injector) and mixed vigorously. Then, 1.9 ± 0.1 ml [bmim][PF₆] was poured on the doped soil and the soil-naphthalene-[bmim][PF₆] mixture was stirred for two minutes. The amount of [bmim][PF₆] was determined in preliminary experiments and 1.9 ml was found sufficient to completely wet the soil. Soil extraction

experiments were conducted in an injector at atmospheric pressure and at 50°C. The 50°C was chosen since the solubility of naphthalene in [bmim][PF₆] is at a maximum at this temperature.

As [bmim][PF₆] passed through the soil, it dissolved naphthalene particles and drained out of the needle of the injector. The draining time for [bmim][PF₆]-naphthalene solution was approximately twenty minutes and during this time the head of the open injector was kept closed with a parafilm layer to prevent air contamination. The [bmim][PF₆]-naphthalene solution, which drained out, was collected into a microcentrifuge tube (eppendorf tube). During the flow of [bmim][PF₆] through the soil, a very small portion of the soil particles were also carried out. In order to separate these soil particles, [bmim][PF₆]-naphthalene solution obtained, i.e. the extract was centrifuged (Eppendorf Centrifuge 5415C) for five minutes at 10000 min⁻¹. The extract of these experiments were labeled as sample solutions (SS) and these experiments were labeled as sample runs.

In soil extraction experiments, precleaned soil which was previously washed by water, hexane and acetone was used. Although water, hexane and acetone soluble compounds were removed from the soil, there may be some soil constituents which are not soluble in all of these solvents but soluble in [bmim][PF₆]. Since the solvent power of [bmim][PF₆] is high, it can dissolve some soil compounds which are not soluble in water, hexane and acetone. In order to eliminate the effect of these soil compounds, soil without naphthalene was also extracted by pure [bmim][PF₆]. Thus, a blank solution (BS) was obtained which was used as a reference solution in UV-Vis spectrophotometric analysis.

For the blank runs, no naphthalene was added to precleaned soil. The remaining procedure was totally the same with that of the sample runs. In these runs too, the same amount of [bmim][PF₆] (1.9 ± 0.1 ml) was poured on the soil and the soil-[bmim][PF₆] mixture was stirred. Blank run experiments were conducted under the same conditions with the sample runs, atmospheric pressure and 50°C. The [bmim][PF₆] drained from the needle of the injector and it was collected into a microcentrifuge tube. As in the sample runs, the head of the injector was also closed with parafilm layer to prevent air contact of [bmim][PF₆]. During the flow of [bmim][PF₆] through the soil, a very small portion of the soil particles were also carried out. In

order to separate these soil particles, the collected extract was centrifuged for five minutes at 10000 min^{-1} . The resulting [bmim][PF₆] extracts were used as BSs and analyzed using UV-Visible spectrophotometric analysis.

Some of the IL used for extraction of the model compound from the soil sample was adsorbed by the soil, and when 1.9 ml [bmim][PF₆] solvent was used, about 1.5 ml was collected which was enough to fill the quartz cell for spectrophotometric analysis. This result demonstrated that nearly twenty per cent of [bmim][PF₆] is adsorbed by the soil. The resulting [bmim][PF₆]-naphthalene samples were analyzed using UV-Visible spectrophotometer (Analytikjena, Specord 200) and quartz cells (Helma, 1.75 ml, 10 mm path length) at 310 nm which is the wavelength naphthalene in [bmim][PF₆] gives maximum absorbance as demonstrated in Appendix B. 1 ml [bmim][PF₆]-naphthalene solution, i.e. sample solution, was taken out of 1.5 ml solution and transferred to quartz cells. The absorbance of the SS was determined by referring to the BS and its naphthalene concentration was calculated by using calibration chart.

At the end of the soil extraction, as explained above, some of [bmim][PF₆] was adsorbed by the soil and not released. Since [bmim][PF₆] is soluble in acetone, acetone (Merck, >99 per cent purity) was used to recover the remaining [bmim][PF₆] from the soil sample. In order to be sure that all of the IL in the soil sample was removed from the soil, a spectrophotometric analysis method was again used. The soil was washed with acetone until the collected extract gives the same absorption value as the pure acetone. Then, the acetone-[bmim][PF₆] mixture, i.e. extract, was heated to 75°C to evaporate the acetone and recover the [bmim][PF₆]. Since IL has no vapor pressure at this condition, it was assumed that it does not evaporate.

In some runs, experimental problems occurred, for example; large soil particles blocked the needle and the draining of [bmim][PF₆] was stopped. In these situations, a new run was started.

As noted above, in soil extraction runs, two different solutions were used in order to make UV-Vis analysis; solutions and BS. The methods of preparation of these solutions are

pictorially presented in Figures 5.4 and 5.5. Furthermore, the labeling of the soils and extracts are given in Table 5.1.

Table 5.1. Labeling of soil and extracts

Sample	Label
Soil; dried, sieved extracted by water, dried extracted by hexane, dried extracted by acetone, dried	Precleaned soil (PCS)
Extract; obtained after extraction of precleaned soil by [bmim][PF ₆]	Blank solution (BS)
Precleaned soil doped with model compound (naphthalene)	Doped soil (DS)
Extract; obtained after extraction of doped soil by [bmim][PF ₆]	Sample solution (SS)

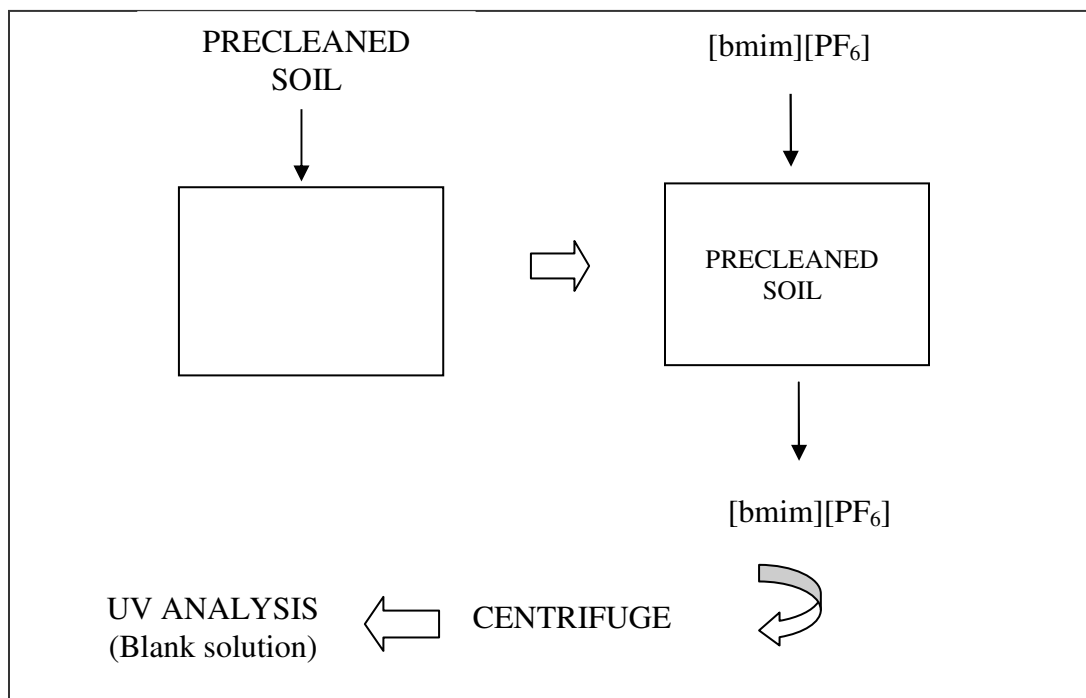


Figure 5.4. General view of soil extraction (Blank solution)

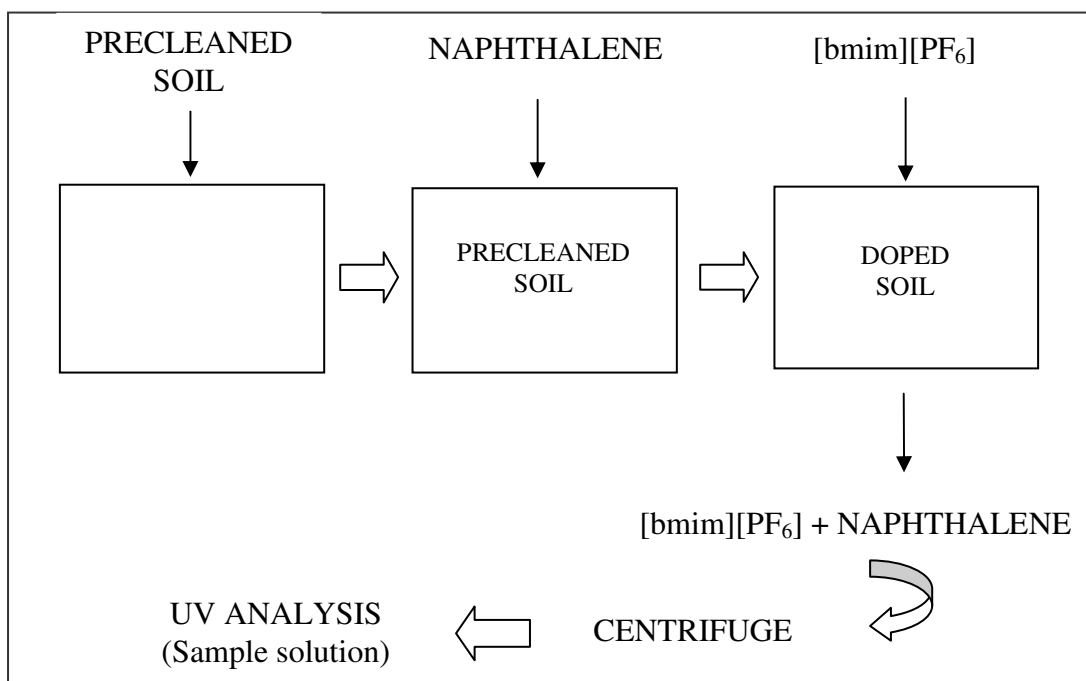


Figure 5.5. General view of soil extraction (Sample Solution)

5.3.4. scCO₂ Extraction

As in all liquid-liquid extraction processes, the recycle of the extraction solvent is essential for the economic feasibility of the process. Similarly in the process suggested in this work, the recycle of the IL, i.e. [bmim][PF₆], is considered to be a very important factor in the economic feasibility of this process. Thus, scCO₂ was used to recover the naphthalene dissolved in [bmim][PF₆]. Supercritical extraction experiments were conducted at 25, 35 and 40°C, and 80, 100, 120 and 140 bar. Prior to beginning a run, the refrigerated bath, which is used to cool CO₂ before entering the diaphragm pump and to provide pump head cooling was brought to -12.5 °C. The pump head was cooled with water-ethylene glycol mixture supplied from the cooling bath. The pump head cooler was turned on an hour before a run. The constant temperature water bath was also brought to its run temperature beforehand. The jacket type electrical heater of the back pressure regulator was turned on an hour before a run.

Supercritical extraction experiments were performed in a high pressure stainless steel cell. Both the blank and the sample solution obtained after soil extraction was placed into small glass bottles. Every time the glass bottle containing the sample solution was inserted into a bottle-holder and this bottle-holder was placed inside the high pressure cell with the same orientation in all experiments. The high pressure cell was then submerged into the constant temperature water bath and connected to the system. Before CO₂ was pumped, the cell remained in the water bath for a sufficient time about twenty minutes in order to obtain a constant cell temperature.

Initially, the on-off valves, V1, V2, V3, V4 and V5 were all kept closed. After the thermal equilibrium was reached, the valve of CO₂ tube (V1) was opened and CO₂ was allowed to fill the extraction unit. The inlet valve V2 was opened and high pressure cell was filled. Since the solubility of CO₂ in [bmim][PF₆] is affected by the water vapor dissolved in [bmim][PF₆], the air inside the high pressure cell must be removed. Thus, when the cell pressure reached 15-20 bar, the inlet valve V2 was closed and the valves V3 and V5 were opened to discharge the high pressure cell to ensure that no air remained in the cell and CO₂ was again pumped to the desired experimental pressure.

The cell and its contents were contacted with CO₂ for four hours for most runs at the specified experimental temperature and pressure. After this period was over, the valves V3 and V4 were opened and the cell was discharged. In order to observe the effect of contact time on the extraction efficiency, this CO₂ extraction period was varied as two hours and six hours in some runs.

At the end of each run, blank and sample solutions were taken out of the high pressure cell as soon as possible and the bottles were tightly closed. Due to the high dissolution of CO₂ in [bmim][PF₆], blank and sample solutions had high amounts of gas bubbles. Since these gas bubbles made the solutions turbid, samples were stored in closed bottles at room temperature for one night, and the next day they were analyzed using the UV-Visible spectrophotometer which was turned on an hour before analysis.

To determine the feasibility of reusing the used [bmim][PF₆] was treated with scCO₂. This scCO₂ treated [bmim][PF₆] was reused for soil extraction experiments to observe the efficiency of recycling. The [bmim][PF₆] cleaned with scCO₂ under different conditions (different temperatures and pressures) were again used to extract naphthalene from soil and the amount of naphthalene extracted from soil with the recycled [bmim][PF₆] was analyzed by UV-Visible spectrophotometer. For the soil extraction experiments, the same procedure explained in Section 5.3.3 was applied.

5.4. The Experimental Program

All soil extraction experiments with [bmim][PF₆] were conducted under the same conditions (50°C and atmospheric pressure). However, [bmim][PF₆] samples obtained after these soil extraction experiments were cleaned with scCO₂ under different conditions. The main variables of supercritical extraction experiments were extraction pressure, temperature and extraction time. In order to understand the effect of pressure and temperature of scCO₂, four different pressures and three different temperatures were chosen, making a total twelve experimental points. Furthermore, the preliminary experiments showed that the absorbance of pure [bmim][PF₆] decreases slightly after contacting with scCO₂. In order to eliminate the

effect of scCO₂ on the absorbance of [bmim][PF₆], pure [bmim][PF₆] was extracted with scCO₂ and the resulting solution was used as blank for these experiments. Therefore, for each of these twelve experimental points, a blank run with pure [bmim][PF₆] was also carried out, giving a total of twenty four experiments. Furthermore, to investigate the effect of contact time on the efficiency of the scCO₂ extraction process, three experiments were conducted at the same temperature and pressure with different extraction times. The necessary information on experiments including their conditions, types and experiment durations are tabulated in Table 5.2 in the order they were conducted.

Table 5.2. Experimental runs, their conditions and types

	Pressure (bar)	Temperature (°C)	Total time (h)	Type
Run 1	140	40	4	Blank Solution
Run 1	140	40	4	Sample Solution
Run 2	120	40	4	Blank Solution
Run 2	120	40	4	Sample Solution
Run 3	100	40	4	Blank Solution
Run 3	100	40	4	Sample Solution
Run 4	140	35	4	Blank Solution
Run 4	140	35	4	Sample Solution
Run 5	120	35	4	Blank Solution
Run 5	120	35	4	Sample Solution
Run 6	100	35	4	Blank Solution
Run 6	100	35	4	Sample Solution
Run 7	140	25	4	Blank Solution
Run 7	140	25	4	Sample Solution
Run 8	120	25	4	Blank Solution
Run 8	120	25	4	Sample Solution

Table 5.2. Experimental runs, their conditions and types (Cont'd)

	Pressure (bar)	Temperature (°C)	Total time (h)	Type
Run 9	100	25	4	Blank Solution
Run 9	100	25	4	Sample Solution
Run 10	80	40	4	Blank Solution
Run 10	80	40	4	Sample Solution
Run 11	80	35	4	Blank Solution
Run 11	80	35	4	Sample Solution
Run 12	80	25	4	Blank Solution
Run 12	80	25	4	Sample Solution
Run 13	140	40	2	Blank Solution
Run 13	140	40	2	Sample Solution
Run 14	140	40	6	Blank Solution
Run 14	140	40	6	Sample Solution
Run 15	140	35	2	Blank Solution
Run 15	140	35	2	Sample Solution
Run 16	140	25	2	Blank Solution
Run 16	140	25	2	Sample Solution

For the recycling of IL, [bmim][PF₆] treated with scCO₂ was reused for soil extraction experiments 1, 2, 3, 4, 5, 6, 7, 8 and 9. Supercritical extraction parts of experiments 1, 2, 4, 5 and 9 were repeated two times at the same conditions to ascertain the reproducibility of the measurements. Since sixteen soil extraction experiments were performed under same conditions without changing any of the processing parameters, these experiments were also found to be reproducible.

5.5. Spectrophotometric Analysis of Samples

The amount of naphthalene extracted from soil by [bmim][PF₆] and the amount of naphthalene recovered from [bmim][PF₆] by scCO₂ were measured using UV-Visible spectroscopy. Soil samples without naphthalene were extracted by [bmim][PF₆] and then the [bmim][PF₆] solution obtained was extracted by scCO₂. This solution was used as the blank solution. Soil samples doped with naphthalene were also extracted by [bmim][PF₆] and then the [bmim][PF₆]-naphthalene solutions obtained were also extracted by scCO₂. This solution was used as sample solution. Since identification of blank and sample solutions may be complicated, a general scheme is given in Figure 5.6.

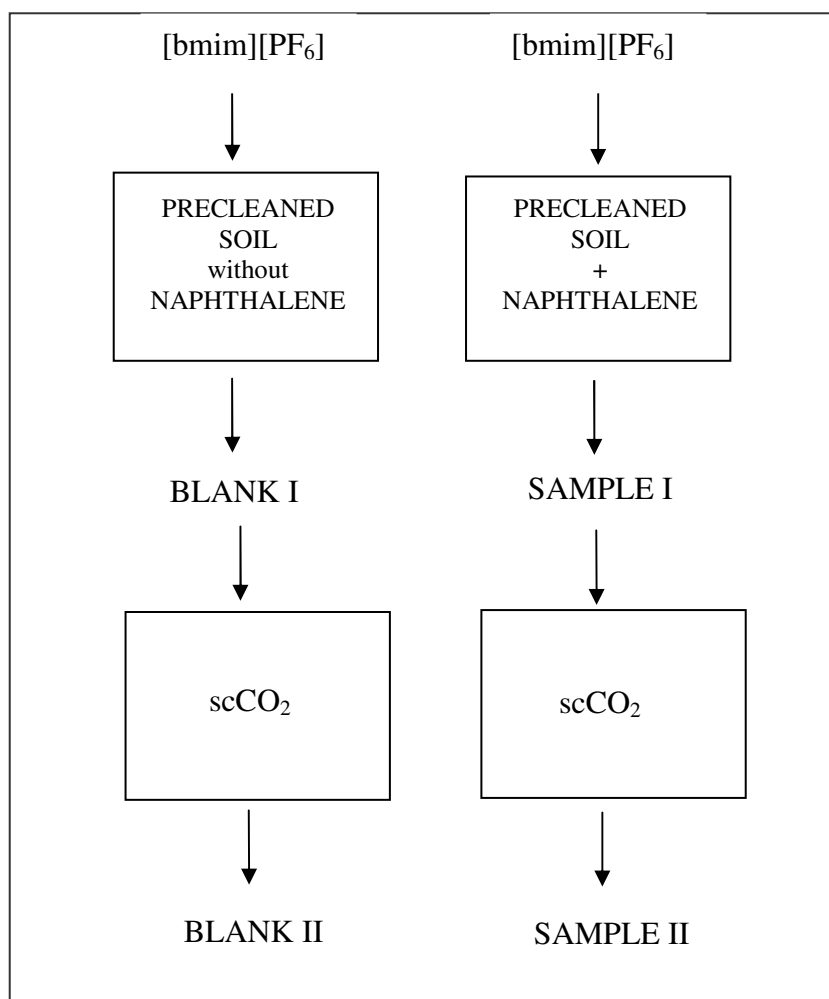


Figure 5.6. Identification of blank and sample solutions

A calibration chart was prepared to determine the amount of naphthalene extracted from soil and the amount of naphthalene recovered from [bmim][PF₆] by scCO₂. First of all, the wavelength at which naphthalene in [bmim][PF₆] gives maximum absorbance was decided. A wavelength scan was performed at spectrophotometer for [bmim][PF₆]-naphthalene solution. 310 nm was found as the wavelength at which maximum optical density (OD) value was obtained. The result of spectrophotometric scan is given in Figure B.1. Then, known amounts of naphthalene; 1, 2, 3, 4 and 5 mg were dissolved in 1 ml [bmim][PF₆] and OD values of these samples were recorded. These solutions were read as sample solutions, whereas pure [bmim][PF₆] without naphthalene was taken as the blank solution. The absorbance and concentration data are given in Table B.1. A line was fitted to data points and the equation of the line was determined by linear regression technique using Excel. Finally, a calibration chart was prepared demonstrating the OD values (absorbance values) vs. concentration (g naphthalene dissolved in 1 ml [bmim][PF₆]). The calibration chart is given in Figure B.2 in Appendix B. All the absorbance values of experiment samples were converted to concentration values by this calibration chart.

5.6. Identification of Soil Samples

The particle size distribution of the precleaned soil was determined by using sieves of size 0.180 mm, 0.400 mm and 0.800 mm (Retsch Vibratronic Type VE1 Instrument) and is given in Appendix C. Moreover, total pore volume of the precleaned soil was determined as 0.0129 cm³/g (Flowsorb 2300 Instrument). Pores in a soil sample were filled with condensed liquid when the soil was exposed to a condensable gas at a sufficiently high relative pressure. Pore filling was achieved with 95 per cent volume nitrogen at liquid nitrogen temperature.

After soil extraction experiments, precleaned soil sample which was not exposed to [bmim][PF₆] and a soil sample extracted by [bmim][PF₆] and acetone were analyzed by X-ray diffraction. The results were given in Appendix D. The only difference between two diffraction results was the disappearance of the aluminum silicate peak which clearly shows that [bmim][PF₆] also dissolved it. No other difference was noticed between the two samples.

6. RESULTS AND DISCUSSION

The aim of this research was to obtain the basic laboratory data towards the development of a proposed process to clean contaminated soils using ILs and scCO₂. Naphthalene was used as the model component to represent the soil contaminant, [bmim][PF₆] was used as the IL and scCO₂ was used as SCF. Previously Erkey *et al.* (1993) used naphthalene as a model compound to represent PAHs in the soil and cleaned the soil by using scCO₂. On the other hand, [bmim][PF₆] was used in almost all research investigating ILs. Among the SCFs, scCO₂ (T_c: 31.1°C, P_c: 73.8 bar) was chosen because it is an environmentally benign medium that has undergone the most intensive investigation as an alternative to undesirable organic solvents in the past three decades (Eckert *et al.*, 1996).

Recent research works have shown that since scCO₂ is very soluble in [bmim][PF₆], it has the potential as an effective medium for quantitatively extracting a wide variety of organic compounds from a RTIL phase with no solvent loss. The significance of CO₂ extraction operations is highlighted by both the environmental advantages of CO₂ and complete elimination of the problem of cross contamination which is commonly encountered in liquid-liquid extractions. Brennecke and Blanchard (1999) showed that CO₂ can be used to extract naphthalene, a low volatility model solute, from [bmim][PF₆]. The model compound naphthalene was readily soluble in [bmim][PF₆] (maximum solubility of 0.30 mole fraction at 40°C) and in CO₂. Moreover, solubility of naphthalene in scCO₂ is a very thoroughly studied subject (Taylor, 1996).

In the related literature Erkey *et al.* (1993) studied naphthalene-soil-scCO₂ system to determine the adsorption isotherm and desorption profile for naphthalene on soil in the presence of scCO₂. Naphthalene-[bmim][PF₆]-scCO₂ system was first investigated by Brennecke and Blanchard (1999). A great number of studies investigated [bmim][PF₆]-scCO₂ systems (Blanchard *et al.*, 2001; Kamps *et al.*, 2003; Lu *et al.*, 2003; Aki *et al.*, 2004; Shariati

and Peters, 2005). To our knowledge, there is no reported study based on the soil-naphthalene-[bmim][PF₆]-scCO₂ system in the literature.

The contaminated soil remediation process proposed in this thesis aims to utilize the ability of IL to dissolve contaminants at near ambient conditions from the contaminated soil and the ability of scCO₂ to recover these contaminants from the IL extract in order to recycle the IL solvent. The model compound naphthalene, which represents the PAH contaminant group in the soil, was extracted from soil by [bmim][PF₆]. The [bmim][PF₆] extract was further treated with scCO₂ and the naphthalene dissolved in [bmim][PF₆] was recovered by scCO₂. Since scCO₂ is soluble in IL and naphthalene is soluble in scCO₂, solute extraction was performed without any cross contamination. The [bmim][PF₆] extract cleaned by scCO₂ was recycled to clean other contaminated soil samples.

The process proposed combines the advantages of two green solvents, ILs and scCO₂, to clean contaminated soils. Moreover, this suggested process permits the use of continuous processing of the soil contaminant-IL-scCO₂ system at high pressures. In earlier suggestions where soil was cleaned by scCO₂ (Akgerman *et al.*, 1992; Erkey *et al.*, 1993), processes were forced to be in the batch mode due to the difficulty of feeding soil at high pressures. In this study, soil was first remediated with IL, and then the IL extract was treated with scCO₂. Therefore a continuous scCO₂ extraction process was possible.

6.1. Soil Extraction Using IL

After the soil extraction experiments were completed, the sample solutions were analyzed by UV-Vis spectrophotometer. Optical density (OD) values of sample solutions were converted to concentration values by using the calibration chart prepared and the amounts of naphthalene extracted from soil by [bmim][PF₆] were thus determined. Since the amount of naphthalene added to the soil at the beginning of the experiments was known, the amount of naphthalene remained in the soil was calculated from the results of these analysis.

The maximum allowable naphthalene concentration in commercial-industrial lands is given in various different sources in the literature as 50 μg naphthalene in 1 g soil (Canter, 1996; Irwin *et al.*, 1997; U.S. EPA, 2003). In soil extraction experiments, 0.005 g naphthalene was added to the precleaned soil. This amount is hundred times more than the maximum allowable limit. The results of soil extraction experiments demonstrate that although the model component added to the soil was much more than the allowable limit, extracting soil by [bmim][PF₆] was successful and the final concentration of the naphthalene in the soil was below the allowable limit. The results of soil extraction experiments are tabulated in Table 6.1 and Table 6.2.

Table 6.1. The amount of naphthalene extracted from soil by [bmim][PF₆]

Run number	Absorbance (OD)	Amount of naphthalene extracted from soil by [bmim][PF ₆] (g)
1	0.0218	0.004979
2	0.0218	0.004979
3	0.0217	0.004956
4	0.0216	0.004933
5	0.0217	0.004956
6	0.0218	0.004979
7	0.0218	0.004979
8	0.0217	0.004956
9	0.0218	0.004979
10	0.0218	0.004979
11	0.0217	0.004956
12	0.0218	0.004979
13	0.0218	0.004979
14	0.0218	0.004979
15	0.0218	0.004979
16	0.0218	0.004979

The absorbance values of the sample solutions, the amount of naphthalene extracted from soil by [bmim][PF₆] and the amount of naphthalene remained in the soil are given in these tabulations for each experiment separately, shown according to the number of each run. All soil extraction experiments with [bmim][PF₆] were conducted at 50°C and atmospheric pressure. Therefore, the amount of naphthalene extracted from soil is expected to be same in all runs. However, the absorbance values of sample solutions differ slightly causing small differences in the amounts of naphthalene extracted from soil.

Table 6.2. Soil extraction results

Run number	Amount of naphthalene remained in soil (µg naphthalene in 1 g soil)	Results (Limit: 50 µg naphthalene in 1 g soil)
1	20.74	Below the limit
2	20.74	Below the limit
3	43.66	Below the limit
4	66.58	Above the limit
5	43.66	Below the limit
6	20.74	Below the limit
7	20.74	Below the limit
8	43.66	Below the limit
9	20.74	Below the limit
10	20.74	Below the limit
11	43.66	Below the limit
12	20.74	Below the limit
13	20.74	Below the limit
14	20.74	Below the limit
15	20.74	Below the limit
16	20.74	Below the limit

The results of soil extraction experiments indicate that 1 g soil sample containing 0.005 g naphthalene is cleaned by [bmim][PF₆] and the amount of naphthalene remained in the soil is under the maximum allowable concentration limit except for Run 4.

Figure 6.1 and Figure 6.2 demonstrate the amount of naphthalene extracted from soil by [bmim][PF₆] and the amount of naphthalene remained in the soil respectively in soil extraction runs. Although all soil extraction experiments were conducted under the same conditions (50°C and atmospheric pressure) with the same procedure (mixing time, closed containers etc.), there are some differences in the amount of naphthalene extracted from the soil.

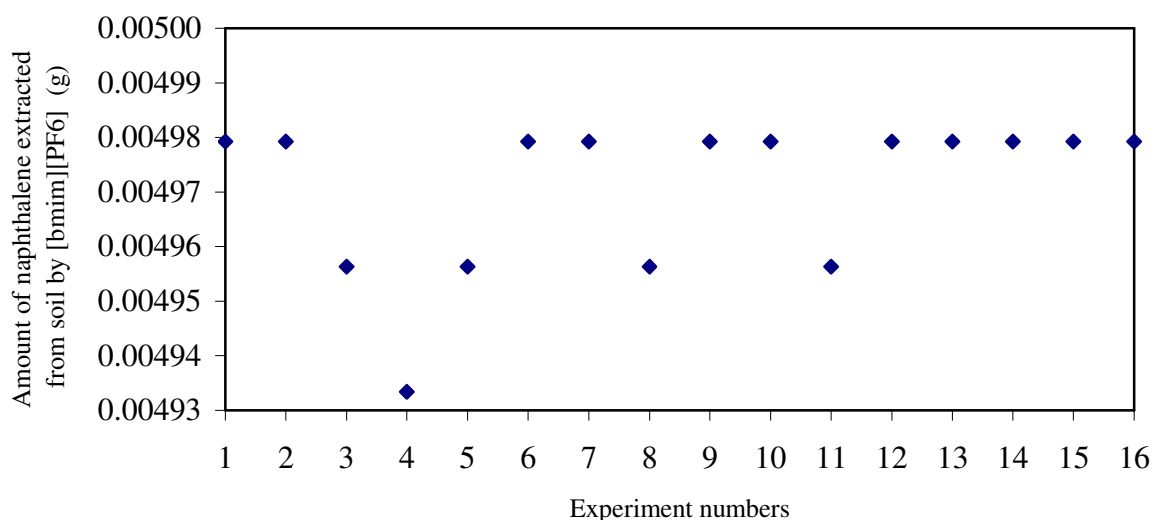


Figure 6.1. Amount of naphthalene extracted from soil vs. experiment numbers

The results suggest that in most of the experiments, 0.004979 g naphthalene was extracted from soil containing 0.005 g naphthalene and the amount of naphthalene remained in the soil was 20.74 µg, below the allowable limit. In four of the experiments, namely in Run 3, 5, 8 and 11, the amount of naphthalene extracted from soil by [bmim][PF₆] was 0.004956 g and the amount of naphthalene remained in the soil was 43.66 µg, again below the allowable limit.

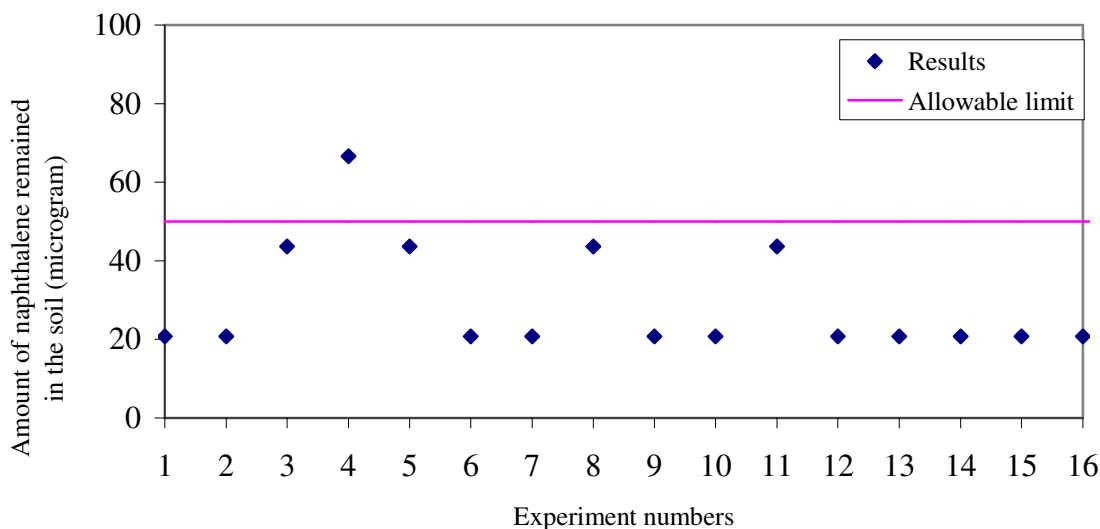


Figure 6.2. Amount of naphthalene remained in the soil vs. experiment numbers

Among the sixteen experiments, only in Run 4, the amount of naphthalene extracted from soil was lower than the other runs. Thus, in this run, the amount of naphthalene remained in the soil was 66.58 μg above the maximum allowable limit. The differences between the amounts of naphthalene removed from the soil by IL may be explained as experimental errors due to mixing or channeling.

6.2. scCO_2 Extraction of Naphthalene from the IL Extracts

scCO_2 was used to recover the naphthalene dissolved in $[\text{bmim}][\text{PF}_6]$ to be able to recycle the used IL for repetitive extraction jobs. The main processing variables of supercritical extraction experiments were extraction temperature, pressure and the extraction time. The results of scCO_2 extraction experiments to recover naphthalene from $[\text{bmim}][\text{PF}_6]$ are tabulated below. Supercritical extraction conditions, absorbance values of the samples, and the amount of naphthalene remained in IL after scCO_2 extraction are tabulated in Table 6.3.

Table 6.3. The amount of naphthalene remained in [bmim][PF₆] after scCO₂ treatment

Run number	Pressure (bar)	Temperature (°C)	t (h)	Absorbance (OD)	Amount of naphthalene remained in [bmim][PF ₆] after scCO ₂ treatment (g)
1	140	40	4	0.0036	8.08×10^{-4}
2	120	40	4	0.0046	1.04×10^{-3}
3	100	40	4	0.0148	3.37×10^{-3}
4	140	35	4	0.0052	1.17×10^{-3}
5	120	35	4	0.0083	1.88×10^{-3}
6	100	35	4	0.0151	3.44×10^{-3}
7	140	25	4	0.0072	1.63×10^{-3}
8	120	25	4	0.0136	3.10×10^{-3}
9	100	25	4	0.0188	4.29×10^{-3}
10	80	40	4	0.0153	3.49×10^{-3}
11	80	35	4	0.0156	3.56×10^{-3}
12	80	25	4	0.0192	4.38×10^{-3}
13	140	40	6	0.0034	7.62×10^{-4}
14	140	40	2	0.0040	8.99×10^{-4}
15	140	35	2	0.0054	1.22×10^{-3}
16	140	25	2	0.0073	1.66×10^{-3}

After the soil was extracted by [bmim][PF₆], the [bmim][PF₆]-naphthalene extract obtained was further extracted by scCO₂ to remove the naphthalene in the extract. The samples were analyzed by using UV-Vis spectrophotometer to determine the amount of naphthalene remained in [bmim][PF₆] after scCO₂ treatment. Since the amount of naphthalene present in [bmim][PF₆] before the scCO₂ treatment was known, the amount of naphthalene recovered from [bmim][PF₆] by scCO₂ was easily calculated. The results are tabulated in Table 6.4.

Table 6.4. The amount of naphthalene extracted from [bmim][PF₆] by scCO₂

Run number	Pressure (bar)	Temperature (°C)	t (h)	Amount of naphthalene extracted from [bmim][PF ₆] by scCO ₂ (g)
1	140	40	4	0.004172
2	120	40	4	0.003942
3	100	40	4	0.001582
4	140	35	4	0.003759
5	120	35	4	0.003071
6	100	35	4	0.001536
7	140	25	4	0.003346
8	120	25	4	0.001857
9	100	25	4	0.000688
10	80	40	4	0.001490
11	80	35	4	0.001398
12	80	25	4	0.000596
13	140	40	6	0.004217
14	140	40	2	0.004080
15	140	35	2	0.003759
16	140	25	2	0.003324

In the scCO₂ extraction experiments, the effects of temperature and pressure on the recovery of naphthalene from [bmim][PF₆] were investigated. Table 6.4 shows that, as the extraction pressure was increased, the amount of naphthalene recovered from [bmim][PF₆] by scCO₂ also increased. For example, at 40°C, 0.003942 g naphthalene is recovered from IL extract at 120 bar, whereas this amount is 0.004172 g at 140 bar. Furthermore, experimental results suggest that decreasing the temperature reduces the recovery of naphthalene from [bmim][PF₆]. For example, at 140 bar, 0.004172 g naphthalene is recovered from IL extract at 40°C, and the amount of naphthalene recovered is reduced to 0.003759 g when the

temperature is decreased to 35°C. The amount of naphthalene extracted from [bmim][PF₆] by scCO₂ was converted to per cent recovery of the model compound by scCO₂ treatment and presented in Table 6.5.

Table 6.5. Per cent recovery of naphthalene with scCO₂

Pressure (bar)	Temperature (°C)	t (h)	Per cent recovery of naphthalene from [bmim][PF ₆] by scCO ₂
140	40	4	83.8
120	40	4	79.2
100	40	4	31.9
80	40	4	29.9
140	35	4	76.2
120	35	4	62.0
100	35	4	30.8
80	35	4	28.2
140	25	4	67.2
120	25	4	37.5
100	25	4	13.8
80	25	4	12.0

Per cent recovery of naphthalene versus extraction pressure is plotted as a function of temperature in Figure 6.3. At constant temperature, per cent recovery of naphthalene increases as the pressure increases. At constant pressure, as the temperature increases, per cent recovery of naphthalene also increases. The maximum recovery of naphthalene is obtained at maximum pressure and temperature values tried, i.e. at 140 bar and 40°C, where the per cent recovery value reaches to highest value, 83.8. On the other hand, at low end of the pressure and temperature range studied, i.e. at 80 bar and 25°C, the per cent recovery value is extremely low, 12.0. Therefore, the results indicate that both pressure and temperature positively affect the recovery of naphthalene from [bmim][PF₆]. In order to achieve a high recovery,

[bmim][PF₆]-naphthalene solution should be treated by scCO₂ at high pressure and temperature conditions.

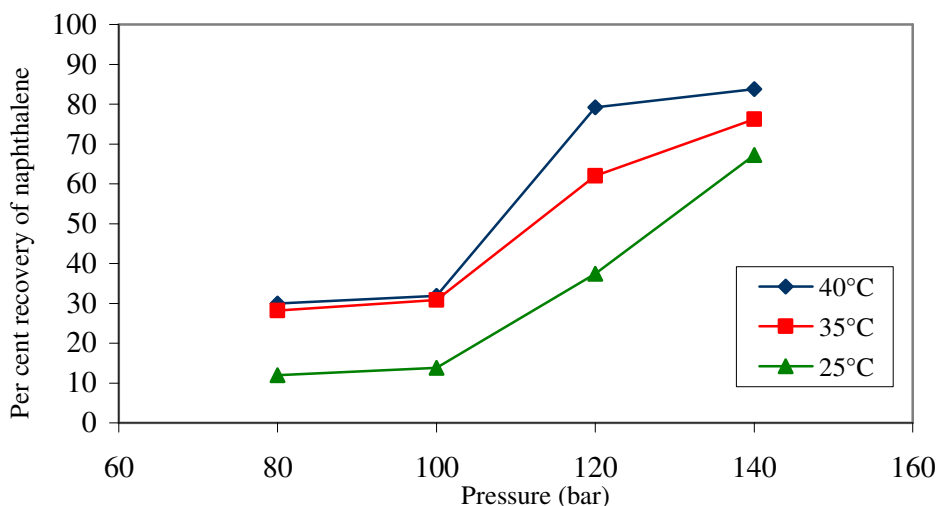


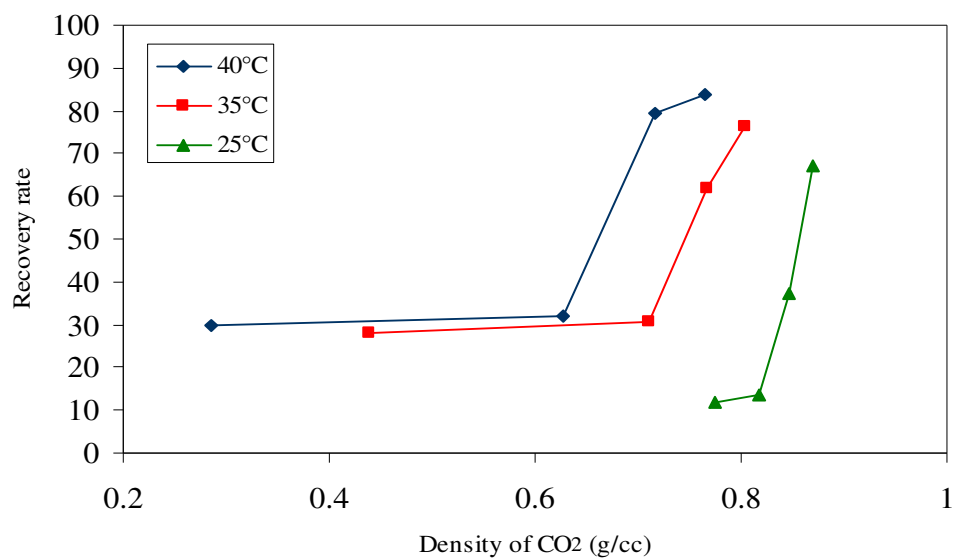
Figure 6.3. Per cent recovery of naphthalene vs. pressure

If the pressure and the temperature parameters are replaced by scCO₂ density as the independent parameter, the relation between recovery and scCO₂ density becomes simpler as demonstrated in Figure 6.4. At low pressures, density decreases dramatically with an increase in temperature; whereas at higher pressures, changes in temperature have much less effect on density. Thus density, not pressure, to a first approximation is proportional to the solvent power of the scCO₂.

The solvent power of scCO₂ increases with density at constant temperature and the solvent power of scCO₂ increases with temperature at constant density. As the solvent power of scCO₂ increases, the recovery of naphthalene from [bmim][PF₆] increases as expected. The relation between density of CO₂ and recovery of naphthalene are given in Table 6.6. The Peng-Robinson equation of state was used to determine the density of CO₂.

Table 6.6. Density of CO₂ and recovery of naphthalene

P (bar)	T (°C)	CO ₂ density (g/cc)	Per cent recovery
140	40	0.76479	83.8
120	40	0.71722	79.2
100	40	0.62710	31.9
80	40	0.28602	29.9
140	35	0.80344	76.2
120	35	0.76755	62.0
100	35	0.71103	30.8
80	35	0.43856	28.2
140	25	0.86974	67.2
120	25	0.84751	37.5
100	25	0.81836	13.8
80	25	0.77518	12.0

Figure 6.4. Recovery of naphthalene vs. density of CO₂

In order to investigate the effect of extraction pressure and temperature on [bmim][PF₆]-naphthalene-scCO₂ system, the solubility relation between the system components must be studied well. In supercritical extraction experiments of this study, there are two basic principles: the solubility of scCO₂ in [bmim][PF₆] and the solubility of naphthalene in scCO₂.

The IL, [bmim][PF₆] is not soluble in scCO₂ however the solubility of scCO₂ in IL is affected by pressure and temperature (Blanchard *et al.*, 2001; Kamps *et al.*, 2003; Lu *et al.*, 2003; Aki *et al.*, 2004; Cadena *et al.*, 2004, Shariati and Peters, 2005). As the pressure increases, the solubility of CO₂ in IL rich phase increases dramatically (Blanchard *et al.*, 2001; Kamps *et al.*, 2003; Shariati and Peters, 2005). A general rule suggests that an increase in temperature results in a decrease in the solubility of gases in liquids. Thus as expected, the solubility of CO₂ in [bmim][PF₆] rich phase decreases with temperature.

If the solubility of naphthalene in scCO₂ at high pressures is examined, it can be seen that the solubility of naphthalene in scCO₂ increases with increasing pressure at constant temperature and increasing temperature at constant pressure (Taylor, 1996). These results are also presented in Section 4.3, Figure 4.1.

If these two discussions above are considered with the results of the supercritical extraction experiments which suggest that both pressure and temperature positively affect the recovery of naphthalene from [bmim][PF₆], it can be concluded that the effect of pressure on the recovery is dominant as compared to the effect of temperature.

Table 6.7. Effect of pressure and temperature on [bmim][PF₆]-naphthalene-scCO₂ system

	Increase in pressure	Increase in temperature
Solubility of scCO ₂ in [bmim][PF ₆]	Increase	Decrease
Solubility of naphthalene in scCO ₂	Increase	Increase
Recovery of naphthalene from [bmim][PF ₆] by scCO ₂	Increase	Increase

In the experiments performed in this thesis, not only the effect of extraction temperature and pressure but also the effect of extraction time on the recovery of the model compound was investigated. At 140 bar and 40°C, scCO₂ extraction was performed at different extraction durations; two, four and six hours. The results of recovery of naphthalene at different extraction durations are given in Table 6.8 and Figure 6.5.

Table 6.8. Effect of extraction time on naphthalene recovery

Run number	Pressure (bar)	Temperature (°C)	t (h)	Absorbance (OD)	Amount of naphthalene extracted from [bmim][PF ₆] with scCO ₂ (g)	Per cent recovery
1	140	40	4	0.0036	0.004172	83.8
4	140	35	4	0.0052	0.003759	76.2
7	140	25	4	0.0072	0.003346	67.2
13	140	40	6	0.0034	0.004217	84.7
14	140	40	2	0.0040	0.004080	81.9
15	140	35	2	0.0054	0.003759	75.5
16	140	25	2	0.0073	0.003324	66.8

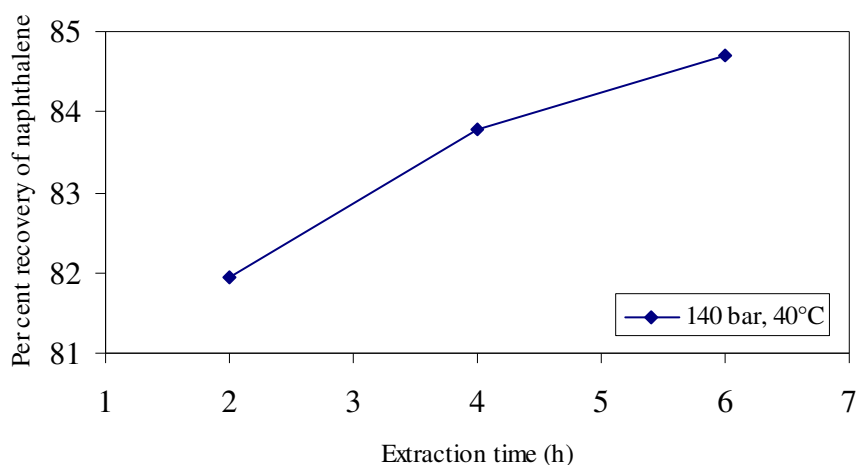


Figure 6.5. Per cent recovery of naphthalene as a function of extraction time

The absorbance of the sample solution treated under scCO₂ for six hours was nearly same with the previous sample solution which was extracted by scCO₂ for four hours. Thus, increasing the extraction duration from four to six hours does not affect the recovery very significantly. However, when the extraction time was reduced from four hours to two hours at 140 bar and 40°C, the absorbance of the sample solution after scCO₂ treatment was reduced and a decrease in recovery of the model compound was observed. Thus, these results show that the amount of naphthalene recovered from [bmim][PF₆] is also positively correlated with extraction duration up to six hours.

6.3. Recycling of [bmim][PF₆]

Recycle of the [bmim][PF₆], is a very important factor in the economic feasibility of this process. Therefore, scCO₂ was used to recover the naphthalene dissolved in [bmim][PF₆]. The IL extract of the doped soil sample treated by scCO₂ was reused in other soil extraction experiments to observe the efficiency of IL recycling. IL extracts cleaned with scCO₂ under different extraction conditions (different temperatures and pressures) were again used to extract the naphthalene from soil and the amount of naphthalene extracted from soil with the recycled [bmim][PF₆] was analyzed by UV-Visible spectrophotometer.

The results of soil extraction performed by recycled IL are given in Table 6.9. The amount of naphthalene extracted from soil using recycled [bmim][PF₆] is less than the amount of naphthalene extracted from soil using fresh IL. Thus, the amount of naphthalene remaining in soil in these experiments were not below the maximum allowable limit. Using recycled [bmim][PF₆] for cleaning of soil is considered to be not successful. Since all the naphthalene is not recovered from [bmim][PF₆] by scCO₂ extraction, it is thought that the solvent power of [bmim][PF₆] is decreased. However, there is a crucial point in recycling of [bmim][PF₆]: In all soil extraction experiments, 1.9 ± 0.1 ml [bmim][PF₆] was used but only 1.5 ml of IL was obtained since some of the [bmim][PF₆] was adsorbed by the soil. After soil extraction, [bmim][PF₆]-naphthalene solution was put into spectrophotometer cell to be analyzed, and then taken into glass bottle for scCO₂ extraction and finally the solution was put into spectrophotometer cell for the final analysis. During the transfer of solution, some portion of

[bmim][PF₆] remained on the cell walls and lost by sticking to glass or quartz material. Thus, the amount of recycled [bmim][PF₆] was not 1.9 ml but it was nearly 1.350 ml. This reduction in the amount of [bmim][PF₆] may be responsible for the low extraction. Two additional experiments were conducted to see whether this opinion is true or not.

Table 6.9. Results of soil extraction by recycled [bmim][PF₆]

Run number	Absorbance (OD)	Amount of naphthalene extracted from soil by recycled [bmim][PF ₆] (g)	Amount of naphthalene remained in soil (µg naphthalene in 1 g soil)	Result (Limit: 50 µg naphthalene in 1 g soil)
1	0.0205	0.004681	318.71	Above the limit
2	0.0186	0.004246	754.20	Above the limit
3	0.0183	0.004177	822.96	Above the limit
4	0.0178	0.004062	937.57	Above the limit
5	0.0149	0.003398	1602.27	Above the limit
6	0.0130	0.002962	2037.76	Above the limit
7	0.0169	0.003856	1143.86	Above the limit
8	0.0132	0.003008	1991.92	Above the limit
9	0.0113	0.002573	2427.42	Above the limit

Two soil extraction experiments were conducted by using fresh [bmim][PF₆] with the same procedure. [bmim][PF₆]-naphthalene solutions were extracted by scCO₂ at 140 bar and 40°C. As in previous cases, at the end of scCO₂ extraction, 1.350 ml [bmim][PF₆] solution was collected in both experiments. The absorbance values, thus the naphthalene concentration of these samples were the same, since they were treated under the same extraction conditions. Equal amounts of these [bmim][PF₆] solutions were combined to make a 1.9 ml solution and this new solution was used as the recycled [bmim][PF₆]. The results of these new recycling experiments are presented in Table 6.10 and 6.11.

Table 6.10. Amount of naphthalene extracted from soil by combined [bmim][PF₆] solutions

Run number	Amount of [bmim][PF ₆] recycled for soil extraction (ml)	Absorbance after soil extraction (OD)	Amount of naphthalene extracted from soil by recycled [bmim][PF ₆] (g)
1	1.350	0.0205	0.004681
Combined (1)	1.900	0.0217	0.004956
2	1.350	0.0186	0.004246
Combined (2)	1.900	0.0216	0.004933

Table 6.11. Results of recycling by combined [bmim][PF₆] solutions

Run number	Amount of naphthalene remained in soil (µg naphthalene in 1 g soil)	Result (Limit: 50 µg naphthalene in 1 g soil)
1	318.71	Above the limit
Combined (1)	43.66	Below the limit
2	754.20	Above the limit
Combined (2)	66.58	Above the limit

The results demonstrate that in Run 1, using 1.350 ml recycled [bmim][PF₆] was not sufficient to extract naphthalene from soil and the amount of naphthalene remained in the soil was above the maximum allowable limit. However, after combining two scCO₂ treated [bmim][PF₆] and obtaining the original IL amount, the soil was cleaned and the amount of naphthalene remained in the soil was below the limit. The same procedure was repeated for Run 2. When 1.350 ml [bmim][PF₆] was used as recycle, the amount of naphthalene remained in the soil was above the allowable limit. Then, 1.9 ml IL was used and the amount of naphthalene remained in the soil was reduced to 66.58 µg. Although, this value is still above the allowable limit, a significant decrease is observed. Thus, probably some pretreatment of

the used IL, such as vacuum drying may be necessary and helpful to revive its solvent power. However, this was not tried.

In this process, some portion of IL was adsorbed by the soil and a very small portion of it was lost during experiment. Therefore, it is suggested that some make-up IL may be required in the process for multiple uses of the IL solvent. However, it is quite well known that in such large scale operations the per cent losses are much lower as compared to the laboratory scale operations.

6.4. Reproducibility Experiments

In this study, three types of experiments were performed: soil extraction using fresh IL, scCO₂ extraction of the IL extract and soil extraction using recycled IL. In the original experimental program, sixteen experiments were conducted for soil and scCO₂ extractions whereas nine experiments were conducted for soil extraction using recycled IL.

Since all soil extraction experiments were performed under the same conditions without changing any of the processing parameters, the reproducibility of soil extraction results were already checked. Furthermore, when a problem occurred during soil extraction such as stopping of draining due to a blockage in the needle, soil extraction experiments were repeated.

In order to check the reproducibility of scCO₂ extraction results Run 1, 2, 4, 5 and 9 were performed again. These runs are chosen due to their different operating conditions. For example, Run 1 represents the experiment performed at highest pressure and temperature. Table 6.12 presents the results of supercritical extraction experiments. Replicate runs are symbolized with R. Since the concentration values are calculated using absorbance values, a small change in the absorbance value of the sample may significantly influence the results.

Table 6.12. Results of reproducibility experiments

Run Number	Amount of naphthalene recovered from [bmim][PF ₆] by scCO ₂ (g)	Per cent difference
1	0.004172	0.53
1R	0.004194	
2	0.003942	0
2R	0.003942	
4	0.003759	0
4R	0.003759	
5	0.003071	2.18
5R	0.003138	
9	0.000688	2.91
9R	0.000708	

6.5. Air and Water Stability of [bmim][PF₆]

ILs containing PF₆⁻ have been reported to decompose in the presence of water, giving off HF. The degree to which this hydration proceeds is a problem depends on the application. For this kind of application, ILs must be handled under dry atmosphere as much as possible. Moreover, as discussed earlier, the effect of water impurity in IL is significant in IL-scCO₂ systems. The solubility of CO₂ in IL is low in wet IL samples, whereas higher solubility of CO₂ is observed in dry IL samples (Blanchard *et al.*, 2001). The effect of water impurity may be explained by CO₂-phobic nature of water since the mutual solubilities of water and CO₂ are very low (King *et al.*, 1992).

Measurements show that most widely studied IL; [bmim][PF₆] absorbs water when left open to the atmosphere. After the effect of water impurity was noticed, researchers have started to dry and degas all ILs under vacuum at room temperature for several days prior to use for highly precise experiments (Blanchard *et al.*, 2001; Kamps *et al.*, 2003; Lu *et al.*, 2003;

Aki *et al.*, 2004; Cadena *et al.*, 2004, Shariati and Peters, 2005). After ILs are dried and degassed, the water contents are calculated by the Karl Fischer analysis before solubility data are taken. Almost all studies mentioned here and in the literature survey earlier, investigate the solubility of CO₂ in [bmim][PF₆]. Therefore, water is a significant impurity which can influence the correctness of solubility data. However, in this present study, solubility data were not taken, and the effect of water impurity was neglected and [bmim][PF₆] was used as it is received without any further purification.

Although [bmim][PF₆] was not dried and degassed, its contact time with air was kept at minimum to prevent cross contamination. In soil extraction experiments, [bmim][PF₆] was taken from its original bottle and poured on the soil quickly. During mixing of soil and [bmim][PF₆], solid-liquid extraction set-up was open to atmosphere, thus [bmim][PF₆] was contacted with air for two minutes. When it was draining from the injector, the top part was kept closed with a parafilm layer. The draining time for [bmim][PF₆]-naphthalene solution was approximately twenty minutes where air contamination may still exist. In spectrophotometric analysis, quartz cells were also closed with parafilm layer. In supercritical extraction experiments, the air inside the cell was removed as explained in Section 5.3.4. The [bmim][PF₆] was always tightly closed and stored at room temperature.

6.6. A Process Suggested for the Cleaning of Soils Using IL and scCO₂

This study is expected to be the first one in the literature which investigates soil-model compound-IL-scCO₂ system and suggests a process based on this system. A process for the cleaning of contaminated soils, containing a continuous supercritical recovery step, is suggested based on the principles set and the experimental results obtained in this study.

A process flowsheet for the remediation of contaminated soils using IL and scCO₂ is suggested. This process contains two different extraction systems: soil extraction and supercritical extraction. The contaminated soil and IL, i.e. extraction solvent, are mixed in a mixing tank for a certain time as the process feeds. During mixing, IL dissolves the contaminants present in the soil and the draining extract is fed to the IL draining tanks. The

soil is recovered and drained IL extract containing the IL and the contaminant solution is collected into an extract collector. In order to recycle the IL, IL-contaminant solution is pumped to the scCO₂ extraction column. Since scCO₂ is soluble in IL, but IL is insoluble in scCO₂, the extraction is performed without cross contamination. The scCO₂ extracts soil contaminants from IL, therefore IL is cleaned. Cleaned IL is recycled to the soil extraction system again for reuse. Due to the reason that some portion of the IL is lost during the process by absorption of the soil, a make-up IL stream is required.

In commercial SCFE plants, recycle of CO₂ is a must for economic feasibility of the process, as well as for environmental concerns. Cyclone separator is responsible to separate the contaminants dissolved in CO₂ from the gas stream. Cleaned CO₂ is also recycled to the scCO₂ extraction column.

One of the main goals in this process is to return the treated soil to the environment after total remediation. For this purpose the small amount of the IL extract remaining on the soil after the initial draining should also be recovered. Thus a secondary solvent, which we call the IL extract recovery solvent, should be used to remove the remaining IL and the contaminants it has already extracted from the soil. Therefore, after this secondary solvent is added to the soil, mixed and drained, the recovered liquid containing the IL used, the contaminants extracted by the IL and also the secondary solvent are treated to recover the secondary solvent (acetone in our experiments). In our experiments this recovery operation was done using heat (75°C) to evaporate the acetone since the IL used is claimed not to have any vapor pressure. The secondary solvent thus evaporated is then condensed and then recycled for further use. The remaining IL extract is further mixed with the IL extract already collected from the first draining and further processed with scCO₂, to strip it from its contaminant contents. In the cases where the IL used is hydrophilic, the secondary solvent used, i.e. the IL extraction solvent, may be water. In such a case depending upon the vapor pressure of the IL some vacuum may be applied during the vaporization operation to lower the temperature.

In this new process, the contaminants are separated from the soil and the cleaned soil is recovered. The recovery steps of the extraction solvents, IL and scCO₂, are designed for the

economic feasibility of the process. This new suggested process for the cleaning of the contaminated soils using ILs and continuous scCO_2 stripping is depicted in Figure 6.6.

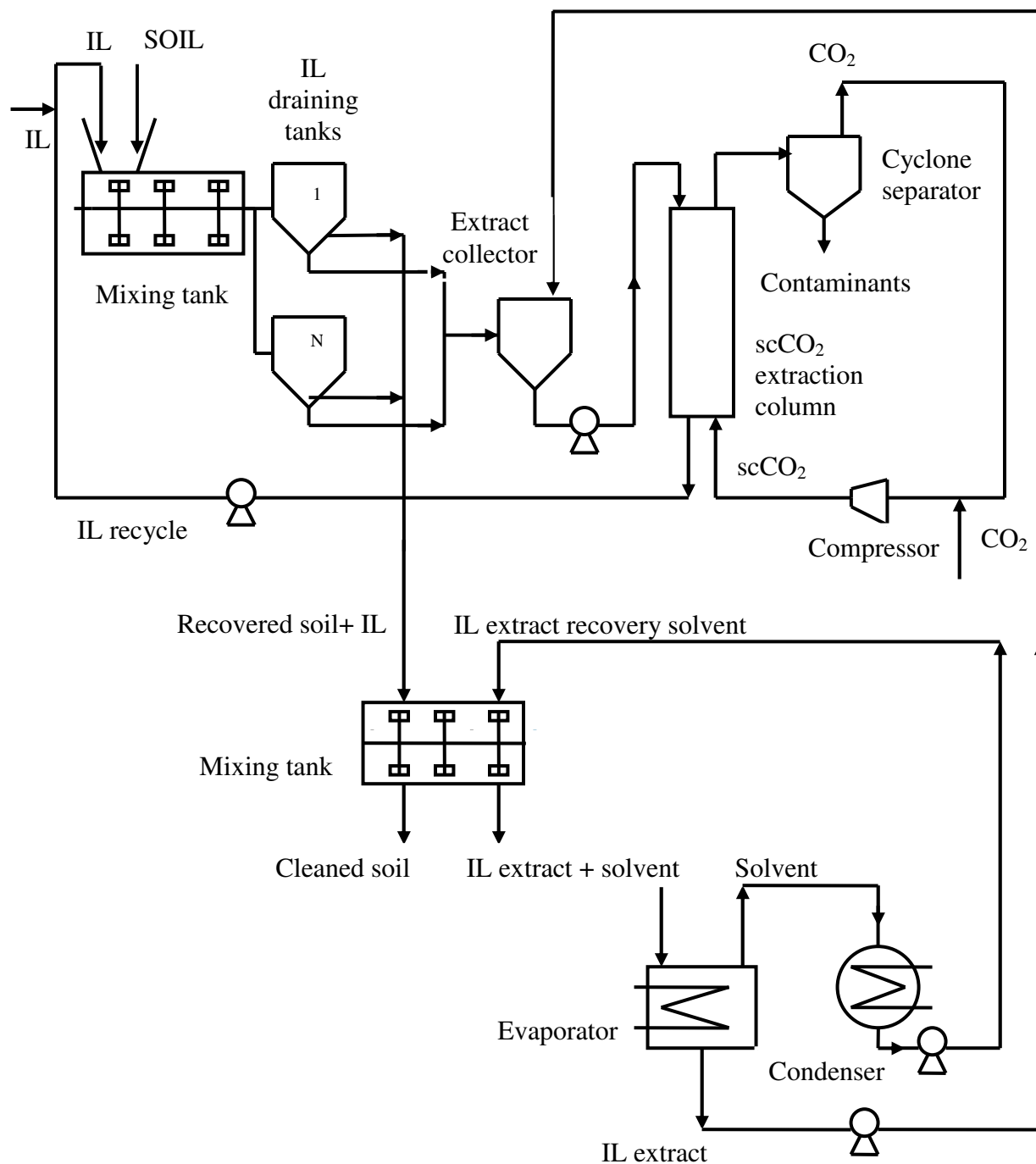


Figure 6.6. A process suggested for cleaning of soils using IL and scCO_2

The results of experimental studies show that it is better to work at high pressures and higher temperatures in the scCO₂ extraction part. However, working under high pressures requires highly cost equipment. Using IL instead of a volatile organic solvent also makes the process expensive. However, as explained before, ILs have numerous advantages such as their high ability to dissolve various kinds of contaminants and negligible vapor pressure. For example, it is difficult to extract organometallic compounds from the soil by organic solvents whereas TSILs are appropriate for these compounds. Since properties of ILs can be designed for specific applications, different ILs can be suggested according to the type of soil contaminant. These different ILs may be used in series or jointly as a mixture (cocktail), depending on the processing economics that will emerge.

7. CONCLUSIONS AND RECOMMENDATIONS

The feasibility of using an IL-scCO₂ system for the separation of harmful contaminants from contaminated soils was studied in this work. As the IL, [bmim][PF₆] was used and CO₂ was chosen as the SCF. Model component naphthalene was used to simulate the soil contaminant, since it is a member of one of the important soil pollutant groups, PAHs. Naphthalene is soluble in [bmim][PF₆] and the behavior of naphthalene in scCO₂ is well documented in literature. The amounts of soil contaminant extracted from soil by IL, per cent recovery of the contaminant from IL by scCO₂ and dependence of these values upon the processing variables such as extraction pressure, temperature, and extraction time were studied. Furthermore, recycled [bmim][PF₆] was reused to extract the model compound from soil and thus, the efficiency of the recycling process was investigated.

7.1. Conclusions

In this study, contaminated soil was remediated with [bmim][PF₆], which is a potential replacement for hazardous volatile organic solvents conventionally used because of its non-volatility and excellent dissolution properties. The soil extraction experiments were all conducted under same conditions i.e., at 50°C and atmospheric pressure. The amounts of naphthalene extracted from soil by [bmim][PF₆] were determined by spectrometric analysis. After extracting the doped soil using IL, the amount of naphthalene remaining in the soil was found to be below the maximum allowable limit given in the literature sources in all tests. Therefore, it is concluded that soil was successfully cleaned using IL.

The model component dissolved in [bmim][PF₆] was recovered with another environmentally benign solvent, scCO₂, in order to recycle the IL. Supercritical extraction experiments were conducted at different conditions of 80, 100, 120, 140 bar and 25, 35, and 40°C to observe the influence of supercritical extraction pressure and temperature on the recovery of the model compound from IL.

The maximum recovery of naphthalene from the IL extract was obtained at maximum pressure and temperature. At 140 bar and 40°C, per cent recovery value reached to its highest value of 83.8, whereas at the low end of the pressure and temperature range studied, i.e. at 80 bar and 25°C, the per cent recovery value was extremely low, 12.0. Therefore, it is concluded that both pressure and temperature positively affect the recovery of naphthalene from [bmim][PF₆].

In order to achieve a high recovery, [bmim][PF₆]-naphthalene solution should be treated by scCO₂ under high pressure and temperature. To understand which parameter has the higher influence on the per cent recovery of the model component from IL, the solubility of scCO₂ in [bmim][PF₆] and the solubility of naphthalene in scCO₂ were investigated in detail. The solubility of scCO₂ in [bmim][PF₆] increases with pressure and decreases with temperature. On the other hand, both pressure and temperature have a positive effect on the solubility of naphthalene in scCO₂. Since the experimental results of this work show that both pressure and temperature positively affect the recovery of naphthalene from [bmim][PF₆], it is concluded that the pressure effect is dominant as compared to the temperature effect.

The supercritical extraction duration was increased to six hours and decreased to two hours to observe the effect of extraction time on the recovery of the model compound from [bmim][PF₆]. When the extraction duration was increased from four hours to six hours, the per cent recovery of the model compound from IL extract by scCO₂ was increased from 83.8 to 84.7 at 140 bar and 40°C. On the other hand, decreasing the extraction duration from four hours to two hours reduced the per cent recovery value of naphthalene from 83.8 to 82 at 140 bar and 40°C. Although, per cent recovery of naphthalene was not very significantly affected, a positive correlation was observed between the extraction time and recovery of naphthalene.

Recycle of the extraction solvents is a must from both the economical and environmental aspects of the processes therefore, recycle of the extraction solvent, [bmim][PF₆] was also studied in this work. To observe the efficiency of IL recycling, extraction solvent treated with scCO₂ was used again to extract other contaminated soils. Since the amount of recycled IL was less than the original IL used in the soil extraction runs due to the lost occurred during

experimentation, recycled [bmim][PF₆] was not capable of cleaning the contaminated soil successfully. Thus, two scCO₂ treated [bmim][PF₆] were combined in order to obtain the original IL amount and recycled for soil extraction runs. The soil was cleaned successfully and the amount of the model compound remained in the soil was below the allowable limit. Finally, it is concluded that the reduction in the amount of [bmim][PF₆] is responsible for the low extraction rate.

The aim of this research was to utilize the ability of ILs to dissolve organic contaminants at near ambient conditions from soil and the ability of scCO₂ to recover the organic contaminants from the IL extract in order to design a process for the cleaning of contaminated soils. A new process for this purpose was suggested for cleaning of the contaminated soils using ILs and scCO₂ and discussed in detail in Section 6.6.

With this new process, various advantages of two environmentally benign solvents, IL and scCO₂ are combined: Many variations in compositions and large numbers of possible variations in cation and anion conformation allow fine tuning of the IL properties for specific applications. The solvent properties of ILs can be designed according to the soil contaminant type. This advantage gives an opportunity for the design of different soil remediation treatments depending on the contaminants. For example, TSILs are synthesized to extract metal ions and organometallic compounds. If a soil is contaminated with these materials, such as metal ions, a TSIL can be used as the extraction solvent. Another alternative may be using a mixture of different ILs to remediate soils containing various types of contaminants. However, the overall effect of such a mixture (cocktail) may be less than the sum of the effects of individual IL's. A remediation process using IL creates a contaminant dependent soil cleaning technology and choice of IL depends on the chemistry of the soil and its contaminants.

7.2. Recommendations

In this work, the main aim was to suggest a process for the cleaning of contaminated soils using IL and scCO₂. Soil-naphthalene-[bmim][PF₆]-scCO₂ system was used as the model system for soil-contaminant-IL-SCF system. Although the remediation of the soil, which was

contaminated with naphthalene, using [bmim][PF₆] and cleaning of [bmim][PF₆] using scCO₂ extraction technique were achieved successfully, still some improvements may be done in further work.

This study may be extended using model compounds other than naphthalene to represent other types of soil contaminants, and by using other appropriate ILs for extraction. However, in extending the process to other contaminants and ILs, the choice of the SCF to be used should also be considered. In making these choices it should be noted that the model compound must be soluble both in the IL and the SCF and the affinity of the model component must be higher for the SCF phase than the IL phase. This condition should be satisfied to recover the model compound from the IL by SCF phase.

The soil may be doped with more than one type of model compound and different ILs may be used in series to extract these model compounds from the soil. Moreover, instead of using ILs in series, a cocktail of ILs may be prepared to clean contaminated soils with multiple hazardous chemicals. In this way, the overall effect of such a mixture (cocktail) may be compared with the sum of effects of individual IL's.

As the IL, [bmim][PF₆] was used in this study. This IL is the most widely studied one in the literature and its high pressure phase behavior with scCO₂ is also well-known. However, different types of ILs may be used with varying solvent power and physical properties. For example, IL used in this study, [bmim][PF₆] is not miscible with water. During soil extraction experiments, some portion of the IL was adsorbed by the soil and a volatile organic solvent; acetone was used to recover it. If a hydrophilic IL was chosen for the process, remaining IL would be easily recovered by water without any need for an organic solvent.

Most imidazolium salts are hydrophilic and if they are used in open vessels, hydration certainly occurs. Despite its wide spread usage, [bmim][PF₆] decomposes in the presence of water, giving off HF. In this study, [bmim][PF₆] was used as it is received without any further purification, drying and degassing. The effect of water impurity on the solvent power of IL, if any, was neglected. For further studies, IL may be dried and degassed, and the results of using

purified IL may be compared with the results of this present study. Although, it is extremely difficult, an inert atmosphere may be provided for the whole processes including soil extraction, scCO₂ extraction and UV-Vis analysis.

APPENDIX A: [bmim][PF₆]

Physical and chemical properties:

Chemical name: 1-butyl-3-methylimidazolium hexafluorophosphate

Chemical formula: C₈H₁₅F₆N₂P

Molecular weight: 284.18 g/gmol

Melting point: 6.5°C

Decomposition temperature: > 300°C

Density: 1.37 g/cm³ at 20°C

Viscosity: 281.00 mm²/s at 20°C

Conductivity: 1.8 mS/cm at 22°C

Ph value: 5 at 20°C

Boiling point: not available

Ignition temperature: not available

Flash point: not available

Use of substance: solvent, chemical for synthesis

Form: liquid to viscous

Color: yellowish

Odor: pleasant

Handling and storage: tightly closed, at 15°C to 25°C

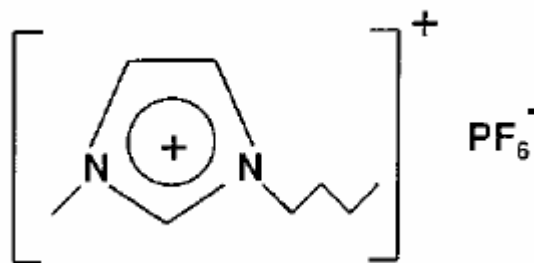


Figure A.1. Structure of [bmim][PF₆]

Stability and reactivity:

Strong heating must be avoided, strong oxidizing agents must be avoided.

Hazard identification:

Irritation to eyes and skin, substance is not yet fully tested; the test results available so far do not permit a complete evaluation.

First aid measures:

After inhalation: breathe some fresh air.

After skin contact: wash off with plenty of water, remove contaminated clothing.

After eye contact: rinse out with plenty of water with eyelid held wide open.

After swallowing: immediately drink plenty of water.

Fire fighting measures:

Suitable extinguishing media : CO₂, foam, powder

Development of hazardous combustible gases or vapours (phosphorus oxides, nitrogen oxides, hydrogen fluoride etc.) possible in the event of a fire.

Exposure controls:

Respiratory protection is required when vapours are generated, eye protection is required, nitrile rubber gloves are required in full contact for hand protection.

Toxicological information:

Quantitative data on toxicity of this product are not available.

APPENDIX B: CALIBRATION CHART

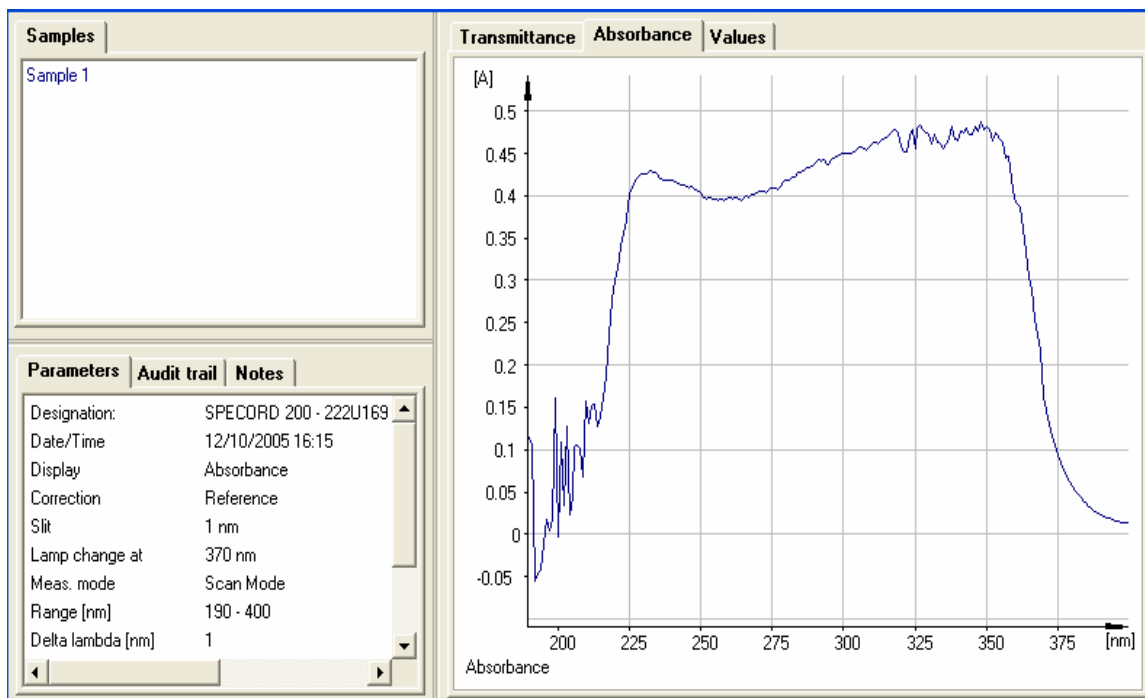


Figure B.1. Wavelength scan for [bmim][PF₆]-naphthalene

Table B.1. Concentration-absorbance data

Concentration (g naphthalene / ml IL)	Absorbance (OD)
0	0
0.001	0.0042
0.002	0.0096
0.003	0.0132
0.004	0.0164
0.005	0.0225

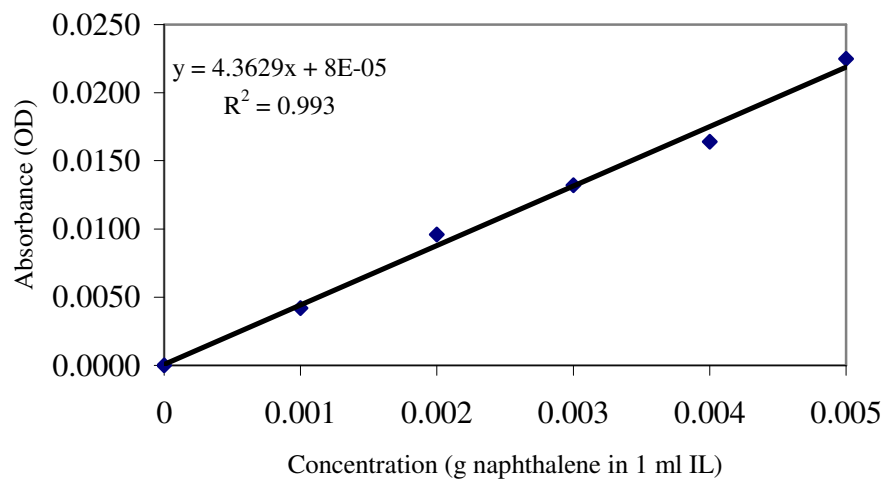


Figure B.2. Calibration chart

The following equation was used to convert OD values of samples to concentration values:

$$\text{Concentration} = (\text{Absorbance} - 7.61905 \cdot 10^{-5}) / 4.36286 \quad (\text{B.1})$$

APPENDIX C: PARTICLE SIZE DISTRIBUTION OF THE SOIL

Table C.1. Soil particle size distribution data

Size of particles (mm)	Weight fraction
>0.800	13.64
0.400<<0.800	27.59
0.180<<0.400	29.46
<0.180	29.31

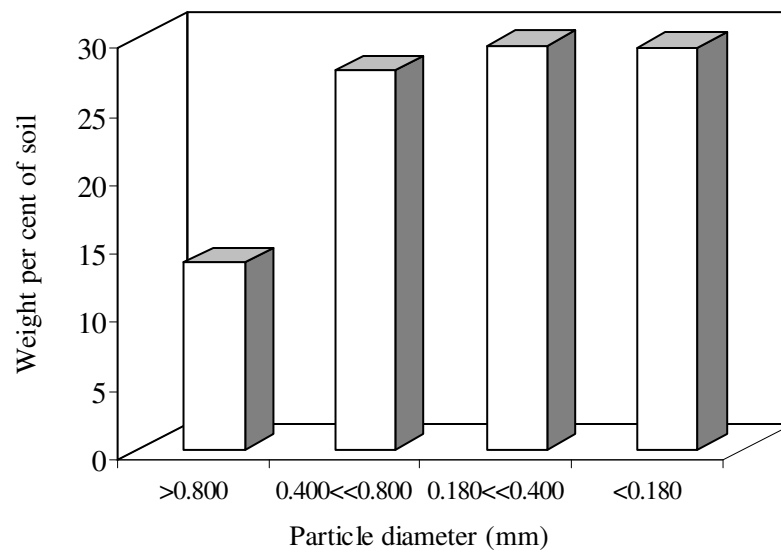


Figure C.1. Particle size distribution of the soil

APPENDIX D: X-RAY DIFFRACTION ANALYSIS OF THE SOIL

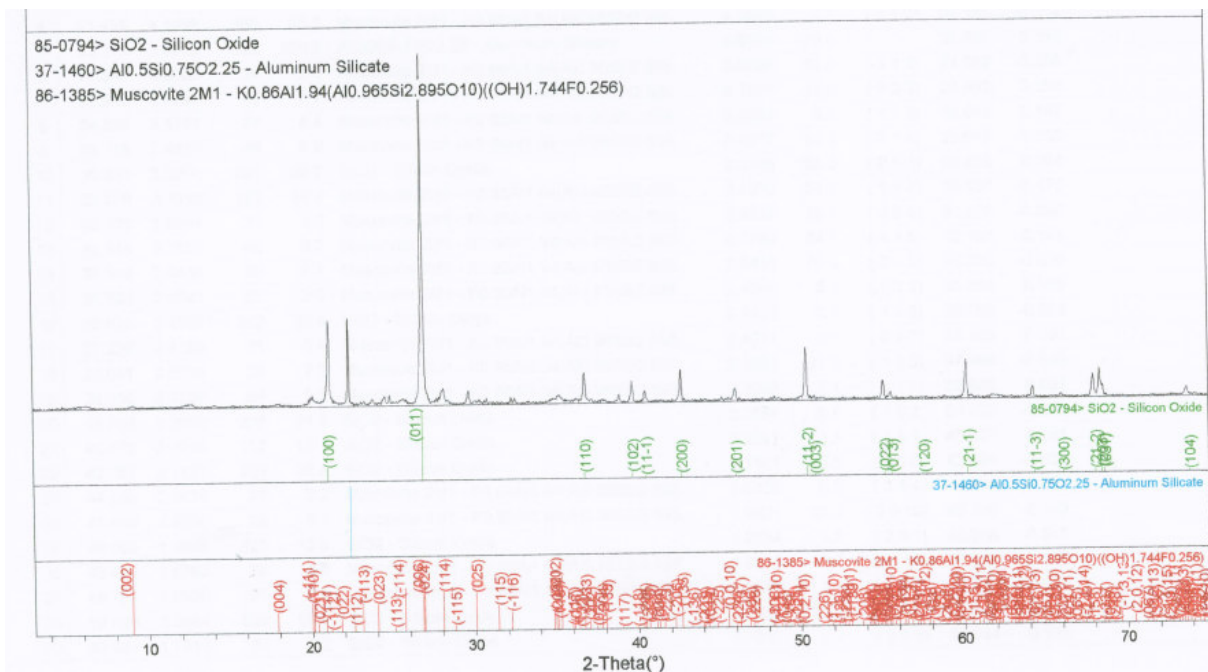


Figure D.1. X-ray diffraction result of precleaned soil

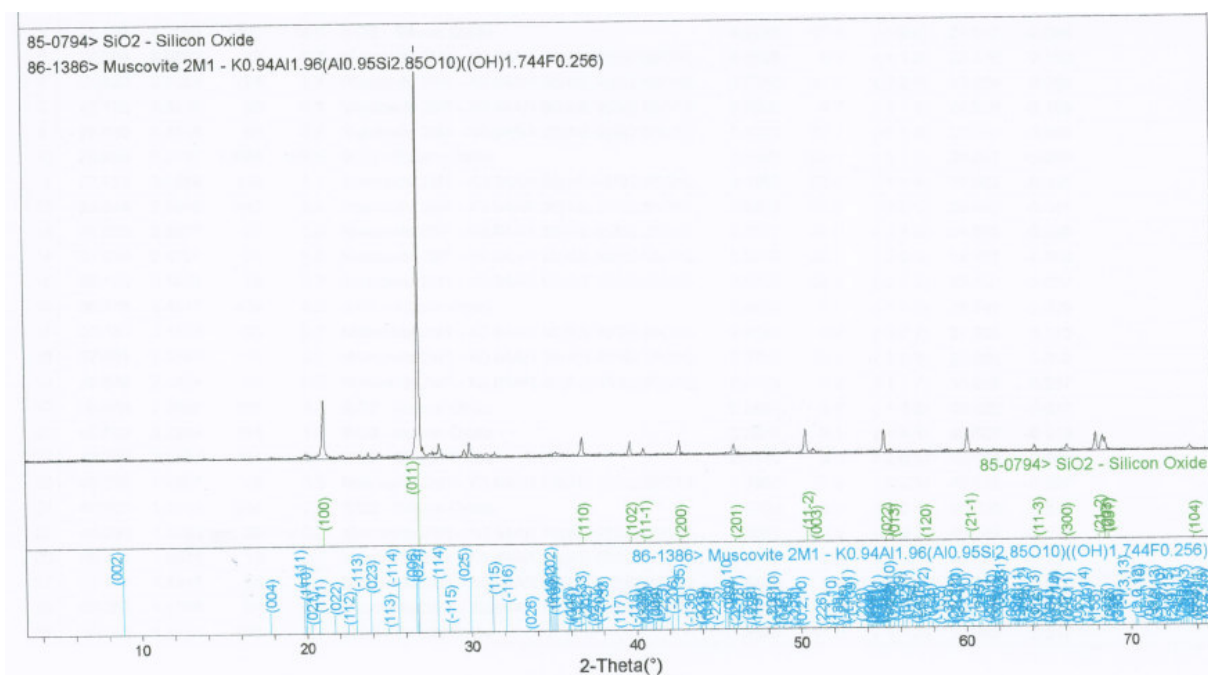


Figure D.2. X-ray diffraction result of soil extracted by [bmim][PF₆] and acetone

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