

SULFUR EXTRACTION FROM OIL USING IONIC LIQUIDS

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by

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Abstract

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2017

Organosulfur compounds are amongst the most problematic components present in crude oil which has a direct influence on the performance of the refinery processes as well as during storage, transportation and separation. The presence of sulfur species in fuels are clearly a major issue in air pollution, airborne particulate emissions and endangering health public. The sulfur content of crude oil is an important characteristic which effects the oil price.

Catalytic approaches for sulfur removal, such as hydrodesulfurisation (HDS), are the most commonly applied techniques. Aromatic S-compounds in diesel oil are however, difficult to remove completely by HDS. Therefore, alternative methods to HDS have been studied including oxidation, precipitation, extraction, adsorption, distillation and alkylation.

In the current study, ionic liquids (ILs) have been used for the removal of thiophene (Th), benzothiophene (BT) and dibenzothiophene (DBT) by liquid-liquid extraction and polymerisation. The first stage of the study involved the investigation of the thermodynamics of thiophenic species partitioning into Deep Eutectic Solvents (DESs). It was shown that the extraction process depends on the size of S-compounds and the energy required to make holes in the networks of DESs molecules of suitable dimensions to fit the S-containing molecules. The second stage of the study used a 1:1 mixture of 1-butyl-3-methylimidazolium chloride (Bmim)Cl and FeCl₃ for the extractive electropolymerisation of Th and BT from alkane layers. While the process could be carried out, the kinetics of polymer formation were too slow to make this a viable process.

The final part of the work used a different composition (Bmim)Cl: 2FeCl₃ to chemically remove sulfur containing compounds from alkane based liquids. It was shown that the rate of the chemical polymerisation reaction of Th is around 1000 times faster than electrochemical polymerisation. The technical aspects of the scale up were investigated and it was shown that recycling the catalyst was possible but not simple.

Publications

A) Paper:

Andrew P. Abbott, Azhar Y. M. Al-Murshedi, Odeh A.O. Alshammari, Robert C. Harris, Jalil H. Kareem and Idrees B. Qader, Karl S Ryder, *Fluid-Phase-Equilibria*, 2017, 1-6.

B) Conference:

1- Talk

Jalil H. Kareem, Andrew P. Abbott and Karl S. Ryder, Extraction and electrocatalytic polymerisation of thiophene from oil using ionic liquids, Leicester University for the 21st meeting of the ELECTROCHEM conference series, 17th-19th August 2016, University of Leicester, Leicester.

2- Poster:

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Statement of originality

All the work described in this thesis for the degree of Ph.D entitled “Sulfur Extraction from Oil Using Ionic Liquids” was conducted by the author in the Department of Chemistry at the University of Leicester mainly during the period between January 2014 and April 2017.

The work in this thesis is original unless otherwise acknowledged in the text or by references and none of the work has been submitted for another degree at this or any other university.

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Jalil Hussein Kareem
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Abbreviations

Chemicals

(Bmim)Cl	1-Butyl-3-methylimidazolium chloride
(Bmim)OTf	1-Butyl-3-methylimidazolium trifluoromethanesulfonate
(Emim)NTf ₂	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
ADS	Adsorptive desulfurisation
BDS	Biodesulfurisation
BT	Benzothiophene
BTZ	Benzothiazole
Bu	Butyl
ChCl	Choline chloride
DBT	Dibenzothiophene
dcnm	Dicyano (nitroso) methanide
DEE	Diethyl ether
DES	Deep eutectic solvent
DMSO	Dimethyl sulfoxide
EDS	Extractive desulfurisation
Et	Ethyl
H.C.	Hydrocarbons
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
HDS	Hydrodesulfurisation
IL	Ionic liquid
Me	Methyl
NTf ₂ ⁻	Bis(trifluoromethylsulfonyl)imide
Oc	Octyl
ODS	Oxidative desulfurisation
PBT	Polybenzothiophene
PTh	Polythiophene
Tf ₂ N ⁻	Trifluoromethylsulfonyl imide
Th	Thiophene

ThN	Thianthrene
TOS ⁻	P-toluene sulfonic acid

Units and symbols

Δf	Change of frequency
Δm	Change of mass
Δt	Change of time
$^{\circ}\text{C}$	Degree Celsius
μg	Microgram
μL	Microliter
A	Absorption
A	Ampere
C	Column
cP	Centipoise
E	Potential
g	Gram
g mol^{-1}	Gram per mole
h	Hour
Hz	Hertz
J	Joule
K	Kelvin
k	Rate constant
kJ	Kilojoule
K_p	Partition coefficient
L	Litre
mg/kg	Milligram per kilogram
MHz	Megahertz
min	Minutes
mmol	Millimoles
mol/L	Mole per litre
n	Number of electron
nm	Nanometre

Oxi	Oxidation
ppm	Part per million
Q	Charge
R	Rate of the reaction
Red	Reduction
rpm	Revolutions per minute
V	Volt
V/V	Volume per volume
wt	Weight
wt/wt	Weight per weight
λ	Wavelength
ρ	Density

Techniques and components

CE	Counter electrode
CV	Cyclic voltammetry
EQCM	Electro quartz crystal resonance
FT-IR	Fourier-transform infra-red spectroscopy
GC-FID	Gas chromatography- flame ionisation detector
GC-FPD	Gas chromatography- flame photometric detector
GC-SCD	Gas chromatography- sulfur chemiluminescence detector
NMR	Nuclear magnetic resonance
RE	Reference electrode
UV-Vis spectroscopy	Ultraviolet-visible spectroscopy
WE	Working electrode

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1 Introduction

1.1 Crude oil

Crude oil is a complex mixture of hydrocarbon compounds which are deposited around the world. Mineral oils are viscous, dark greenish-brown fluids due to the variety of compounds present in them. The physical properties including viscosity, volatility and density, vary considerably depending upon the source. The proportion of elements in crude oil generally varies in the following ranges; carbon (83- 87%), hydrogen (10-14%), sulfur (0.02-8%), nitrogen (0.1-2%), oxygen (0.05-1.5%) with small quantities of metallic constituents such as vanadium and nickel which are less than 1000 ppm. Sulfur, oxygen, nitrogen and metals make up most impurities found in crude oil ¹⁻⁴

Crude petroleum oil can be separated into different boiling point fractions as illustrated in **Table 1.1.**⁵

*Table 1.1: Common fractions of crude oil separation.*⁵

Fraction	Boiling point ranges (°C)
Light naphtha oil	-1 to 50
Gasoline fuel oil	20 to 225
Kerosene oil	205 to 260
Diesel fuel oil	160 to 360
Light gas oil	260 to 315
Heavy gas oil	315 to 425
Vacuum gas oil	425 to 600
Lubricating oil	400 to 510
Residuum	> 510

1.2 Types of heteroatom compounds in crude oils

S-, N-, O- and metal-containing compounds can be present in concentrations totalling 15% in some crude oils.⁶ They have negative implications in petroleum refining, and production. For instance, high amounts of O, N and S-containing compounds in asphaltene can foul production by precipitation at various stages.⁷ In addition, sulfur compounds in crude oil produce acid rain upon combustion. Additionally, many components in different fractions include sulfides, polysulfides, thiols and thiophenic

compounds (heterocyclic aromatic sulfur such as benzothiophene, benzonaphthothiophene, dibenzothiophene and thiophene) are carcinogenic.^{2, 8, 9}

Table 1.2: *S-compounds found in refined fuels.*⁹

Sulfur compounds	Corresponding fuels
Mercaptans, RSH; sulphides, R ₂ S, disulphides, RSSR, Thiophene (T) and its alkylated derivatives, benzothiophene.	Gasoline
Mercaptans, RSH; benzothiophene (BT), alkylated benzothiophenes	Jet fuel
Alkylated dibenzothiophenes (DBT); alkylated benzothiophenes.	Diesel fuel
Greater than or equal to three ring polycyclic sulfur compounds, including DBT, phenanthro[4,5-b,c,d] thiophene (PT) and their alkylated derivatives and naphthothiophenes (NT).	Fuel oils (non- road fuel and heavy oils)

The main nitrogen compounds found in crude oil are pyrrolic and pyridinic compounds as shown in **Figure 1.1** which are mostly in asphaltene (these includes azanaphthalene, alkyl pyridine and azaphenanthrene).^{2, 10}

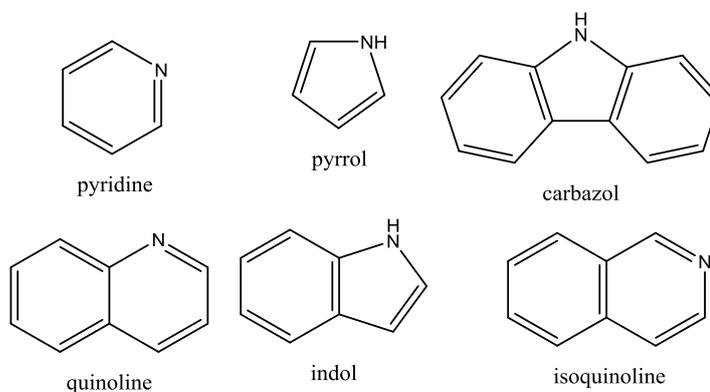


Figure 1.1: *Chemical structure of some heterocyclic nitrogen compounds found in crude oil.*²

Oxygen containing compounds, typically account for 2% of crude oil and occur in two different forms; neutral and acidic as outlined in **Figure 1.2.**^{2, 11}

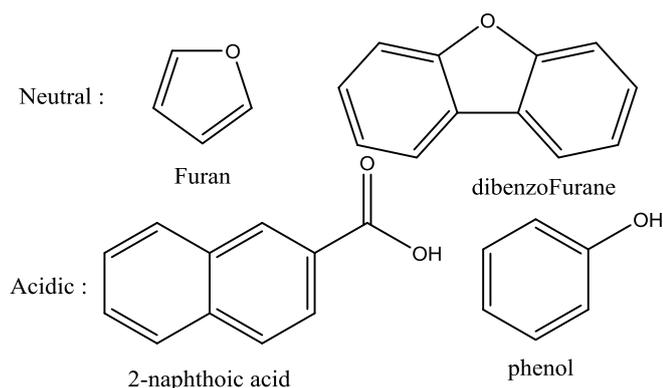


Figure 1.2: Chemical structure of some oxygen containing compounds found in crude oil.¹¹

1.3 Diesel fuel oil

Diesel oil is composed of a very complex mixture of different hydrocarbons boiling at 180- 360 °C including saturated, unsaturated and aromatic compounds in which the carbon number ranges from 8- 24.¹² It is one of the most important sources of energy in the world which is directly derived by atmospheric distillation fractions from crude oils.¹³ It is called multi-purpose petroleum fuel, because of its utilisation as fuel in heavy machinery vehicles, marine vessel bunkering, rail-road locomotives, coaches, aeroplanes, trucks, construction equipment and rough terrain automotive vehicles.¹⁴

1.4 Organosulfur compounds in crude oils

There is no doubt that sulfur compounds are amongst the most problematic components present in crude oil which has a direct influence on the performance of the distillation processes. Many methods were used to remove sulfur compounds in crude oil but none of them are able to eliminate them completely.¹⁵ In fact, sulfur content and the specific gravity of crude oil are the most important characteristics which effect the oil price market.

The organic sulfur content of oil may vary from 0.01- 8 w/w % based on the geographical origin as shown in **Table 1.3**.¹⁶

Table 1.3: Sulfur content in crude oil from different countries.¹⁶

Source	S-content (w/w %)
Australia	0–0.1
Denmark	0.2–0.25
Nigeria	0.04–0.26
Argentina	0.06–0.42
Indonesia	0.01–0.66
Norway	0.03–0.67
United Kingdom	0.05–1.24
Libya	0.01–1.79
Russia	0.08–1.93
Saudi Arabia	0.04–2.92
Iran	0.25–3.23
Iraq	2.26–3.3
Kuwait	0.01–3.48
Mexico	0.9–3.48
Egypt	0.04–4.19
Canada	0.12–4.29
Venezuela	0.44–4.99
USA	0.05–5
Italy	1.98–6.36
Cuba	7.03

In general, there are two groups of S-containing compounds in crude oils; aliphatic (which can be removed by cost-effective procedures like hydrodesulfurisation, HDS) and aromatic (which are recalcitrant). The most common compounds are presented in **Figure 1.3**.^{17, 18}

Aromatic organosulfur compounds mainly include thiophene and its derivatives which are more intractable than mercaptans and sulfides (aliphatic) compounds to desulfurise in crude oils.¹⁹⁻²¹

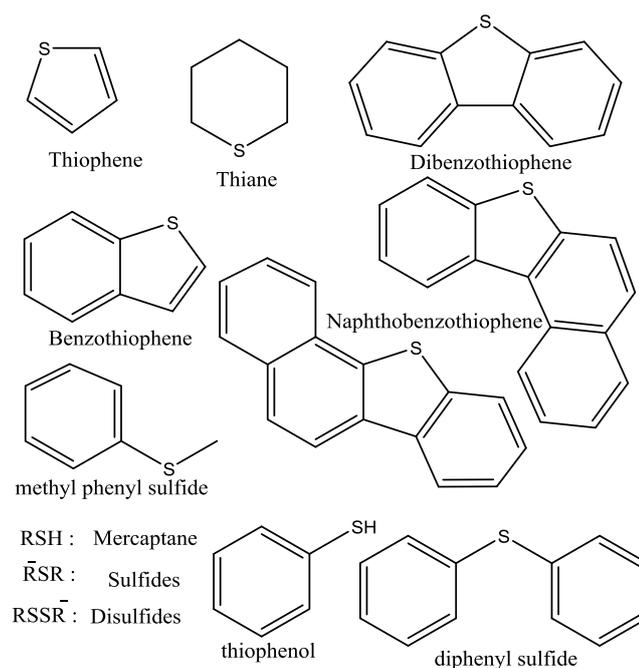


Figure 1.3: Chemical structure of some sulfur containing compounds found in crude oil.¹⁷

1.5 Reactive and non-reactive S-compounds in petroleum and its fractions

Theoretical and practical knowledge of the physicochemical properties and structure of sulfur containing compounds in petroleum oil are needed to improve the kinetics of the HDS process, reduce corrosions of pipelines and refinery equipment and optimise the conditions of the processing.²²

Recently, Lobodin and co-researchers have studied a new method for separation of S-compounds into nonreactive (thiophenic compounds) and reactive (disulfides and sulfides) organosulfur species in crude oil. However, in the analysis of total S-compounds, reactive and non-reactive sulfur classes are not distinguished.²³ Mercaptans, sulfides and disulfides are corrosive and are termed “reactive” S-containing molecules.²³ Analytical approaches to classify the total sulfur compounds in crude oils into fractions which enable easier desulfurisation, were developed in the 1960s.^{24, 25}

Although, refractory thiophenic aromatic compounds are noncorrosive, more specific characterisation is necessary for HDS treatment.²³ Previous studies have assumed that typically 2/3 of nonreactive thiophenic compounds are thiophene.^{26, 27}

1.5.1 Thiophene (Th)

Thiophene (C_4H_4S) is an electron-rich five-membered heteroatomic aromatic colourless liquid at room temperature.²⁸⁻³⁰ It behaves in a similar way to benzene owing to the π -electron cloud on the ring and it is comparable to furan and pyrrole in structure which contain oxygen and nitrogen respectively. Thiophene's structure is similar to that of pyrrole in terms of π -electron density but it is more similar to benzene in terms of its reactivity.^{29, 31}

In general, thiophene is highly flammable, polar, slightly basic, toxic and soluble in ether and alcohol but insoluble in water.²⁹ It is a useful monomer for the production of polythiophene which is frequently used as conductive polymer.³² **Table 1.4** lists some characteristics of thiophene.

The sulfur atom in thiophene is an electron-donating heteroatom which may contribute 2 electrons to the π -electrons system of the ring. Electrophilic reagents can be attached to the 2,5-positions of thiophene, because the resonance stability of intermediates formed in 2- or 5-position. In addition, the activation energy of substitution in the 2- or 5-position is less than in 3,4-substitution due to the delocalising π -electrons in the ring as illustrated in **Figure 1.4**.³³

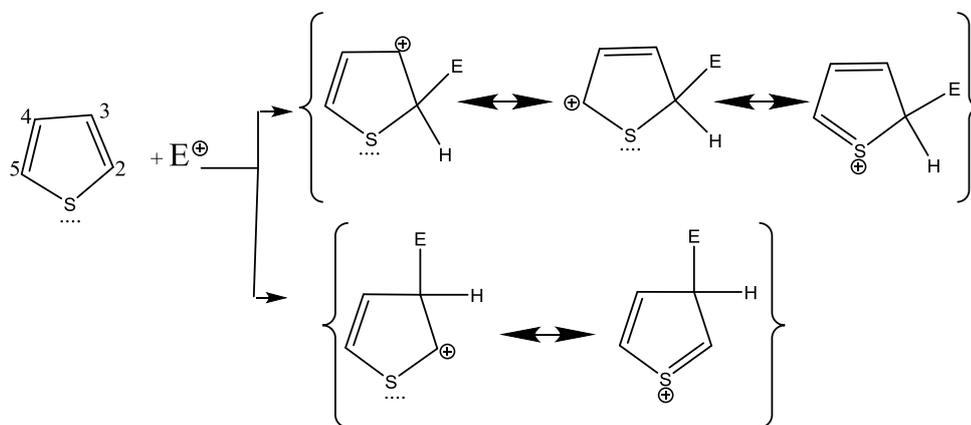
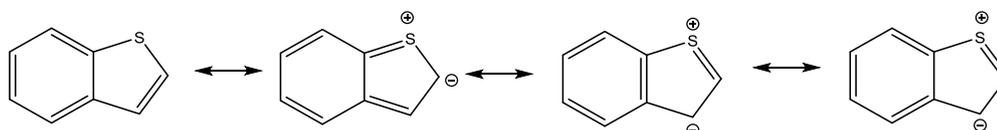


Figure 1.4: Resonance stabilisation of 2- or 5- and 3- position substitution of thiophene attacked by an electrophile.³³

However, owing to the low solubility and stiffness of the conjugated unsubstituted PTh (the rigidity from the conjugated double bond in the main chain) in organic solvents, alkyl thiophenes are preferable to thiophene as monomers used to form polymers.³⁴

1.5.2 Benzothiophene (BT)

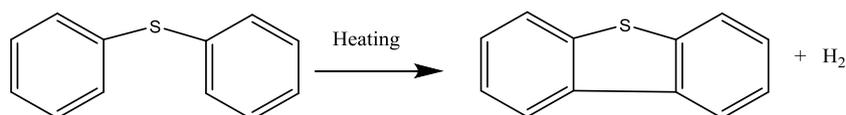
Benzothiophene sometimes named thianaphthene is a colourless to pale yellow solid with an odour similar to naphthalene, it was first isolated in 1902 from coal tar. The predicted resonances consideration is outlined below:³⁵



Therefore, the electrophilic substitution predominantly occurs at the 3-position. **Table 1.4** lists some physical characteristics of BT.

1.5.3 Dibenzothiophene (DBT)

Dibenzothiophene is a toxic, colourless crystalline solid which occurs in coal tar fractions in crude oils. It was prepared for the first time in 1870 from diphenyl sulfide ³⁵:

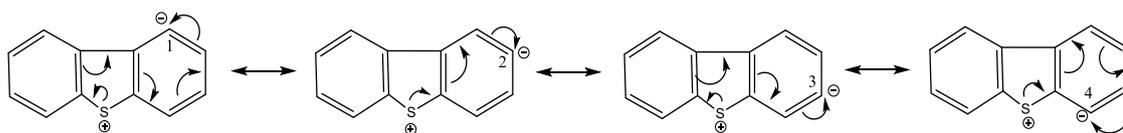


DBT is very soluble in alcohols, benzene and chloroform, while almost insoluble in water (1.47 mg/L). **Table 1.4** shows some physical properties of DBT.

Table 1.4: Some physical properties of Th, BT and DBT.^{31, 35}

Properties	Th	BT	DBT
Chemical formula	C ₄ H ₄ S	C ₈ H ₆ S	C ₁₂ H ₈ S
Molar mass (g mol ⁻¹)	84.14	134.2	184.26
Appearance	Colourless liquid	White solid	Colourless crystal
Density (g ml ⁻¹)	1.059	1.15	1.252
Enthalpy of vaporisation (kJ/mol)	32.483	52.1	78.3
Enthalpy of formation (kJ/mol)	82.13	100.6	120.3
Enthalpy of combustion (kJ/mol)	-2807	-4708.2	-6571
Flash point (°C)	-6.7	101.5	170
Boiling point (°C)	84.16	221- 222	332- 333
Melting point (°C)	-38.3	32- 33	97- 100
Dipole moment (D)	0.53	0.62	0.83

On the basis of the resonance interactions of DBT, the predicted substitution reactions appear either at the 2- or 4-position:³⁵

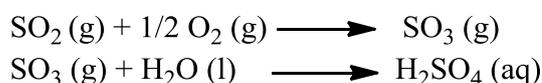


Owing to the lone pair of electrons on the S atom in DBT molecule, it displays Lewis basic properties.³⁶

1.6 Problems arising from sulfur compounds in crude oils

Sulfur removal is essential during refining, because the liquid-phase is very corrosive at high temperature which is a significant issue in combustion engines.³⁷ In addition, sulfur compounds are an issue during the refinery processes as well as during storage, transportation and separation.³⁸⁻⁴⁴

Formation of sulfur species are clearly a major issue in air pollution, airborne particulate emissions and endangering public health. Therefore, the removal of sulfur compounds from diesel down to ultra-low ppm levels is of major importance.⁴⁵ The most important purpose for eliminating sulfur content from oil is to reduce SO₂ emissions producing upon combustion, which cause acid rain.⁴⁶⁻⁵²



Various toxic and irritating fumes result from the decomposition of aromatic S-compounds on heating.⁵³ In addition, thiophenic compounds are notorious as a poison for catalysts which are used to make oil-based products.⁵⁴ Owing to the lower reactivity of sulfur compounds in diesel oil with the removable active catalyst, they are difficult to desulfurise.¹³ Moreover, sulfur compounds tend to deactivate the performance of some catalysts used in refinery processes by blocking catalyst active sites decreasing adsorption and slowing reaction.^{37, 55} The allowable concentration of sulfur in diesel and gasoline fuel in vehicle exhaust emission was lowered to 10 ppm in 2014 (**Table 1.5**).⁵⁶

Table 1.5: Sulfur content in diesel and gasoline fuel according to the European standard requirements.¹²

Standard	The time of standard beginning to work	Sulfur content (ppm)	
		Diesel fuel	Gasoline fuel
Euro 1	1994 (October)	2000	1000

Euro 2	1999 (October)	500	500
Euro 3	2000 (January)	350	150
Euro 4	2005 (January)	50	50
Euro 5	2009 (January)	10	10
Euro 6	2014 (September)	10	10

Figure 1.5 gives the acceptable level of S-compounds in diesel fuel in the USA, EU and Japan in the years between 1990 and 2009.⁵⁷

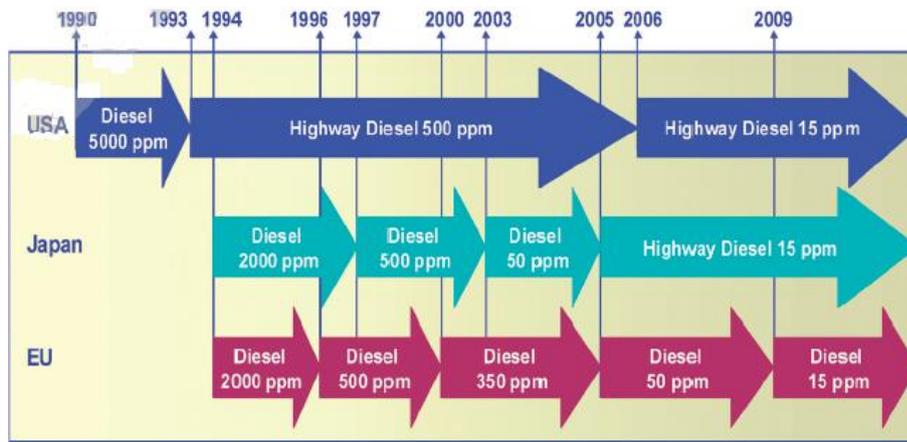


Figure 1.5: The acceptable level of sulfur in highway transportation diesel in a specific period of time.⁵⁷

Additionally, allowable limits for S-specifications in locomotive and marine diesel (LM) and non-road diesel (NR) were lowered to 15 ppm in 2014 (**Figure 1.6**).⁵⁷

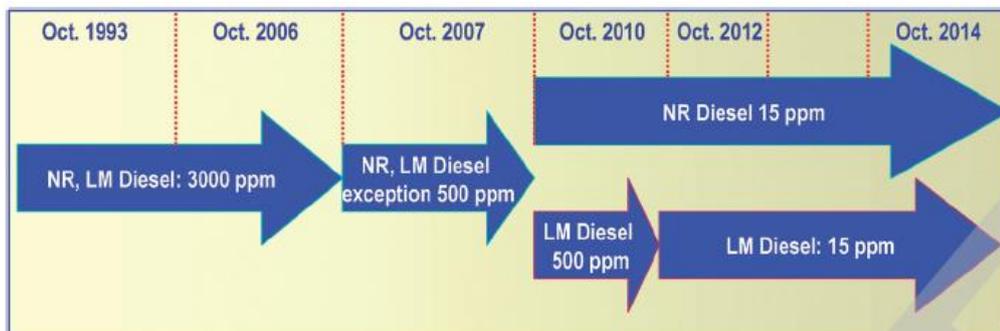


Figure 1.6: Reduction of diesel fuel S-compounds in non-road diesel fuels.⁵⁷

1.7 Methods of desulfurisation

Figure 1.7 shows the classification of desulfurisation into two main categories depending on the kinds of the S-compounds being removed. These are hydrodesulfurisation-based technology and non-hydrodesulfurisation-based technology.

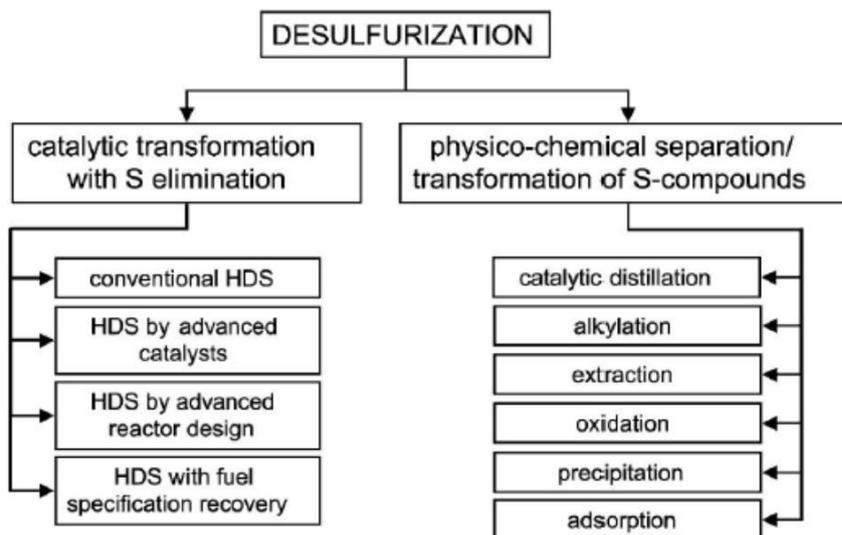


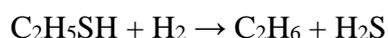
Figure 1.7: Classification of desulfurisation processes in petroleum processes.⁴³

Commercially, catalytic methods such as (HDS) and some chemical processes for sulfur compounds reductions are the most commonly applied techniques, physicochemical methods have also been applied including precipitation, extraction, adsorption, distillation and alkylation processes.⁴³

1.7.1 Hydrodesulfurisation (HDS)

HDS is a catalytic chemical process widely utilised in crude oil refineries for over 75 years.⁵⁸ In the present technology the fuel is heated and mixed with H₂ gas before being fed in to a fixed bed reactor that containing pelleted catalyst known as the “hydrotreater”.⁵⁹

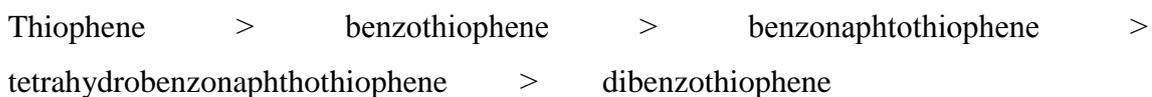
The operational temperature of the hydrotreater is commonly in the range of 300-380 °C and the pressure is above 30 bar.^{18, 60} These catalysts are porous γ -alumina Al₂O₃ loaded with molybdenum sulfide and nickel or cobalt additives. The hydrotreater for diesel converts organosulfur compounds to non-sulfur organics and H₂S gas.⁵⁹ e.g.



1.7.1.1 The reaction of HDS

The HDS process has recently been comprehensively reviewed by Whitehurst and coworkers.^{58, 61} They describe the use of sulfided Ni/Mo/Al₂O₃ or sulfided Co/Mo/Al₂O₃ catalysts in HDS reactions. An idea of the scale of this process is that in the US alone in 2014, 7.5 million tonnes of sulfur were recovered from oil refineries.⁶²

There is a significant difference in the reactivity of sulfur containing compounds toward HDS depending on the total position and substitution around the sulfur atom in the molecule.⁵⁸ Nag et al.⁶³ found that the HDS reaction rates varies in the following order:



In addition, the reactivity of aromatic sulfur compounds depends on the degree of substitution on the aromatic S-ring. For instance, Brien et al.⁵⁸ and Satterfield et al.⁶⁴ have shown the order of reactivity is:



This is because the reactivity of aromatic S-species is based on the overall shape of the molecule, the local environment of the sulfur atom in the compound and the steric hindrance of the methyl groups.

1.7.1.2 Reaction pathways

- Reaction pathway for thiophene (Th)

It has been proposed that thiophene removal by HDS proceeds through two competences pathways as shown in **Figure 1.8**.⁶⁵

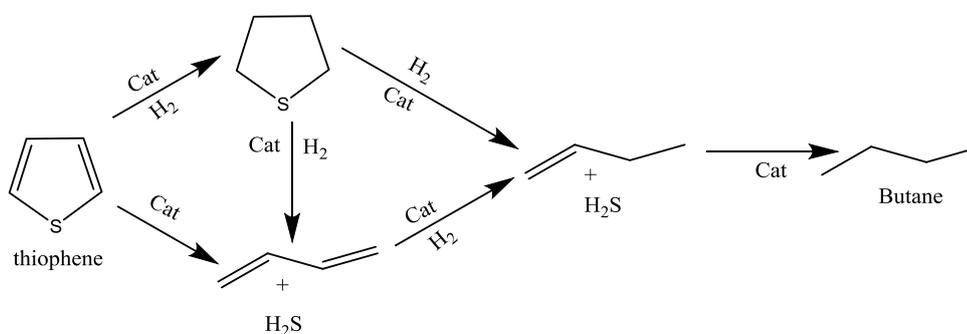


Figure 1.8: General acceptable pathway reactions of thiophene.

The first pathway is known as the hydrogenation pathway resulting in the hydrogenation of thiophene ring. Lipsch and Schuit proposed a second pathway, where H_2 adsorption on the surface of sulfur atom in thiophene ring leads to fission of the C-S bond in the ring.^{58, 66} This is called the hydrogenolysis pathway and leaves butadiene and H_2S .⁵⁸

- Reaction pathway for benzothiophene (BT)

Ethylbenzene is the only HDS product of benzothiophene according to the studies of Kilanowski and Gates as shown in **Figure 1.9**.^{58, 65}

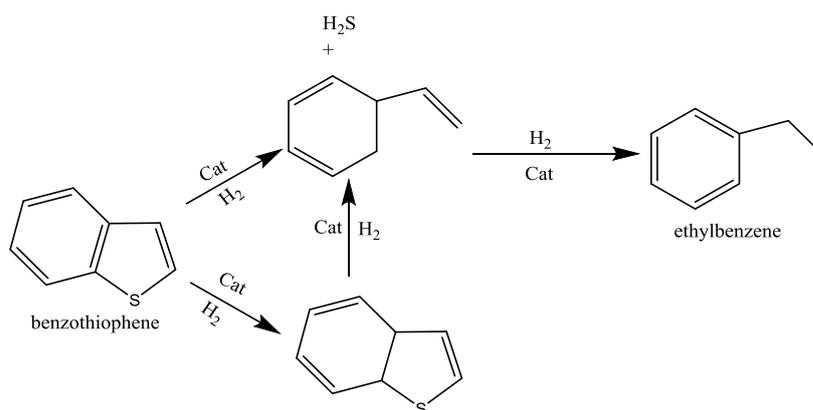


Figure 1.9: The proposed reaction of hydrolysis of benzothiophene in HDS process.

Geneste et al. showed that the only products observed at high pressure are dihydrobenzothiophene and ethylbenzene.⁶⁷ They proposed that ethylbenzene is the only reaction product via a dihydrobenzothiophene intermediate which means that desulfurisation occurs after hydrogenation.

- Reaction pathway for dibenzothiophene (DBT)

Gates and co-workers proposed that HDS of DBT results in biphenyl with a small amount of cyclohexylbenzene.^{58, 68, 69} **Figure 1.10** shows the proposed HDS reaction mechanism of DBT removal studied by Houalla and co-workers.^{58, 70}

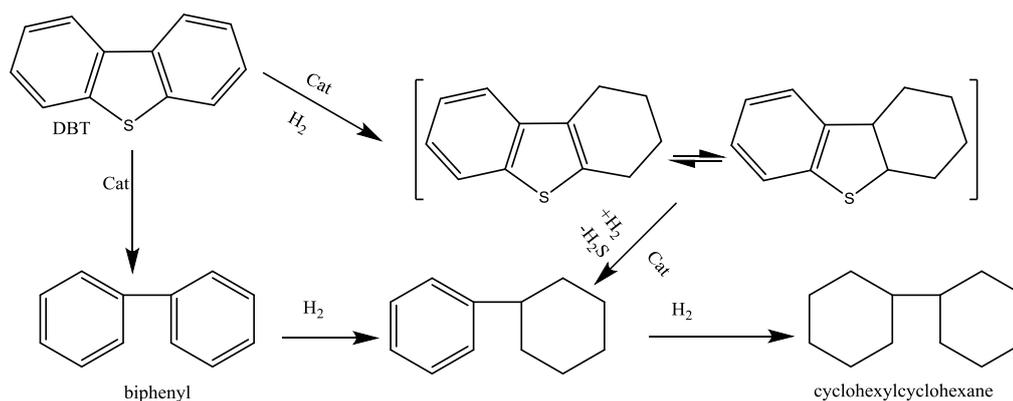


Figure 1.10: Proposed reaction of DBT removal in HDS process.

1.7.2 Non-hydrodesulfurisation (Non-HDS)

Alternative methods to classical HDS processes include oxidation, precipitation, extraction, adsorption, distillation and alkylation.

1.7.2.1 *Adsorptive desulfurisation methods*

Adsorption of sulfur compounds from oils on to an adsorbent, ADS, might be reactive or direct and the type of adsorbent has a pronounced effect on the adsorptive efficiency.^{60, 71, 72} Activated carbon, zeolites, alumina, silica gel and zirconia are various types of adsorbents that have been investigated due to the large density of active sites, high surface area and benign porosity; activated carbon is the mostly studied.^{71, 73, 74}

ADS does, however, have some disadvantages, for example, an important prerequisite is that it should not adsorb olefins and hydrocarbons, but should be specific towards adsorbing sulfur compounds. Other challenges of the ADS process are the difficulty of regeneration of adsorbents entirely after adsorption and poor efficiencies of many adsorbents which means a large amount of adsorbent is need to adsorb a small amount of S-compounds.⁷¹

1.7.2.2 *Biodesulfurisation (BDS)*

Some microorganisms are naturally able to metabolise organosulfur compounds from fuel which enables BDS to be carried out. Consequently, they are able to remove sulfur atoms from organic compounds by oxidative C-C and C-S bond cleavage or reductive C-S bond cleavage.⁷¹ In general, BDS occurs in two ways; the Kodama pathway, where a C-C bond is broken and a water soluble compound is metabolised (usually a carboxylic acid) or the 4s pathway in which the C-S bond is cleaved producing HSO_2^- and a substituted binaphthalene.^{71, 75, 76} However, due to the sensitivity of living microbes in nature, healthy

storage, carriage, treatment, storage of microorganisms in the refinery environment is problematic.^{71,77}

1.7.2.3 Oxidative desulfurisation (ODS)

ODS is accomplished by oxidation of sulfides into sulfoxides or sulfones, then, depending on their increased polarity, sulfoxides and sulfones are separated from fuel oils using solvent extraction. The solvent is then recycled by distillation.^{78,79} NO₂ has been used as an oxidant followed by extraction with alcohols, but it was unwanted owing to the solvent contaminations by residue and waste formation.⁷¹

Organic and inorganic acids have been utilised in ODS systems as catalysts including formic, performic and acetic acids in addition to the use of hydrogen peroxide (H₂O₂) as shown in **Figure 1.11**.

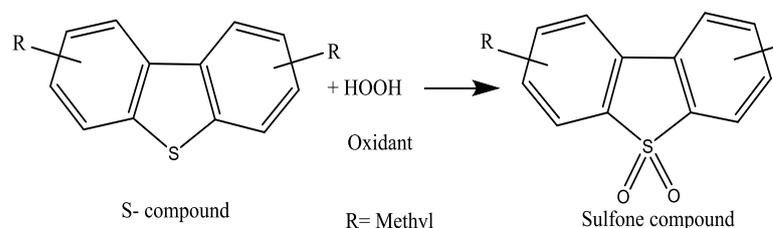


Figure 1.11: General oxidation desulfurisation (ODS) reaction.

Recently, several kinds of ionic liquids have also been used as alternative solvents to conventional volatile solvents in this system. However, poor choice of the liquid can cause removal of olefins and aromatic compounds from the oil resulting in undesirable side reactions and a reduction in the quality of the fuel oils. Therefore, selectivity of the extractive solvent and oxidant is an important prerequisite for ODS process.^{71,80}

1.7.2.4 Extractive desulfurisation (EDS)

Principally, EDS depends upon the different partitioning of sulfur compounds between the organic phase and the extractant phase. Extractive desulfurisation (EDS) does have some advantages in that it is simple and can be carried out at moderate conditions (low pressure and temperature), without using a catalyst or hydrogen gas. Secondly, EDS does not make any change to the structure of the chemical compounds in the fuel oils and S-compounds can be re-employed as raw materials as showed in **Figure 1.12**.⁷¹

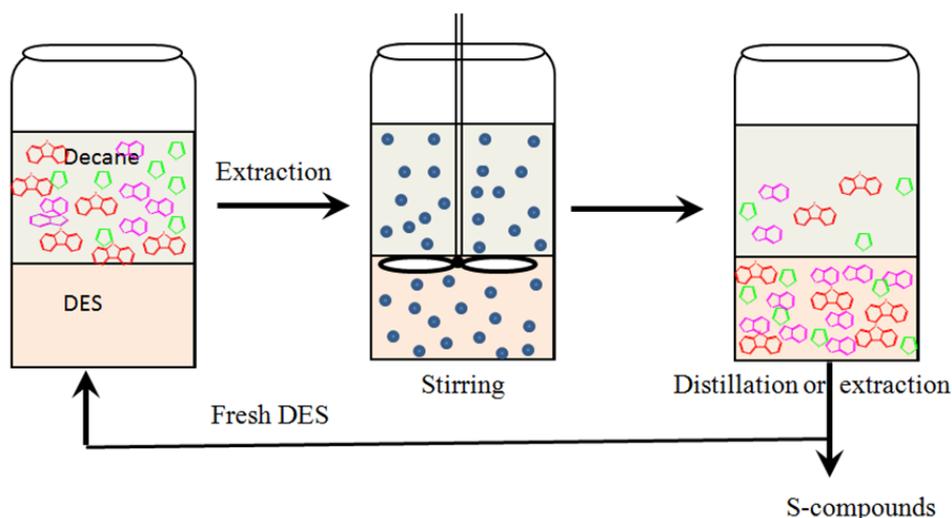


Figure 1.12: Extractive desulfurisation.

The selectivity of an extractive solvent is an important factor in EDS design as it controls efficiency, reusability and recyclability.⁷¹ The difficulty with the technique is regenerating the extractive solvent. In the current study the aim will be to convert the thiophene or thiophene derivative into a solid polymer which will simplify the separation methodology. This could be done either chemically or electrochemically.

1.8 Electrochemical synthesis of polythiophene

Polythiophene has been used in a wide variety of applications such as chemical sensors, transistors, solar cells and light emitted diode, it has become one of the most widely used conductive polymers as shown in **Figure 1.13**.⁸¹ In addition to their conductivity, electroactivity and stability, PTh has found applications in different areas such as nanoswitches, artificial muscles and noses, nanoelectronic devices, recording materials, drug release devices, all organic electrochemical transistors, light emitting diodes, smart windows, antistatic coatings, recording materials, solar cells, nonlinear optical devices, transistors, photoresists, optical valves and modulators, imaging materials, sensors and biosensors, antistatic coatings, energy storage, rechargeable batteries, electrodes, electrochromic windows, electromagnetic materials, microwave absorbing materials, electronic interconnect polymers and new types of memory devices.⁸²⁻⁸⁵

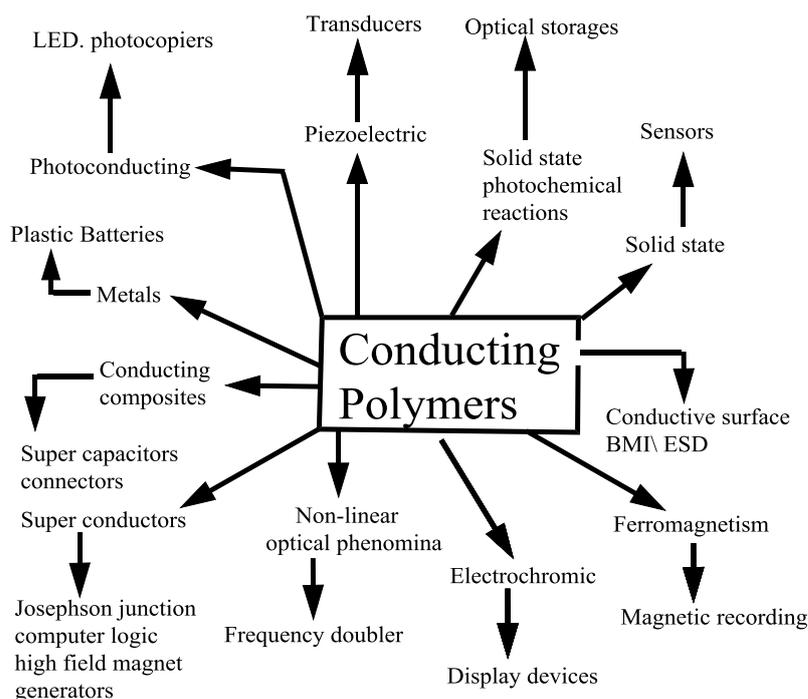


Figure 1.13: Technological uses of conductive polymers.⁸⁶

These types of conductive polymers are useful as semiconductors coatings, as ion gate membranes or for organic reactions as electrode materials.⁸⁷

Polythiophene has good environmental stability and electronic conductivity compared to other conjugated polymers.⁸⁸ Since the reactivity of α -positions in thiophene to electropolymerise is more than in β -positions, polymerisation mainly occurs through the α,α -positions. Mislinkage through the β -position result in defects in the polymer chain reducing the conjugation length and raising the oxidation potential of the polymer.⁸⁸ Thus, 3-linkages have a deleterious influence on the conductivity of the polymer.⁸⁸

When the monomer is oxidised at the electrode surface to a radical cation, electron transfer is faster than the diffusion of monomer. Then two radical cations dimerise in the α -positions resulting in the formation of a bond of an unstable di-cation dimer which then convert to an aromatic dimer by losing two protons. The oxidation potential of the dimer is lower than the monomer oxidation, so the dimer can be easily oxidised to form a stable radical cation dimer. Then it becomes a trimer, oligomer and finally the propagation goes on through the same sequence of oxidation, coupling, deprotonation until the final long chain polymer is obtained.^{89, 90}

The lower the basicity of the anion and higher the acidity of the cation, the larger the conductivity of the polymers. Also by increasing the electrolyte concentration, the conductivity of the polymer rises.^{89, 90} The electron transfer from the bulk solution to the working electrode surface is faster than monomer diffusion, therefore, a high concentration of radical cations remains close to the surface electrode at the applied potential.^{89, 91} During electropolymerisation of thiophene, the pH of the solution decreases as a consequence of reduction of protons.⁹¹

Waltman and Bargon reported that thiophene substituting in the α -position, do not allow electropolymerisation, perhaps due to the blockage of the reactive 2-positions.⁹¹ Oligomeric radical cations on the electrode surface become bigger in chain length as the reactions of electropolymerisation proceed with other monomer radical cations coupling and they become less reactive but more easier to electrooxidise.⁹¹ Krische and Zagorska studied over-oxidation in polythiophene and found that at an oxidation potential of about 1.9 - 2.0 V, polythiophene is susceptible to overoxidation resulting in the destruction of the electroactivity and preventing polymerisation.^{92, 93} The effect of all of the process parameters including sweep rate, electrode material, concentration of monomer, temperature, supporting electrolyte and solvent on the properties of polythiophene have been studied.⁹⁴ If the concentration of thiophene in a solution is high, then the oxidation potential shifts to more negative values and a decrease of the oxidative current occurs due to thiophene absorption on the electrode surface.⁸⁷

Despite the issues with low solubility and fusibility of unsubstituted conjugated polythiophene in many organic solvents caused by backbone rigidity, a large number of studies have been devoted to the polymerisation of Th probably as a consequence of its ease of structural regeneration, its predominating electrochemical behaviour and its high stability in both undoped and doped states.^{88, 89}

The mechanism of polythiophene formation is quite complex, however, a broadly accepted mechanism is illustrated in **Figure 1.14**. The first step of the mechanism involves oxidation of the monomer to form a radical cation. In the second step, the radical combines with another radical cation to form bithiophene (dimer) resulting in the loss of two protons and re-aromatisation.

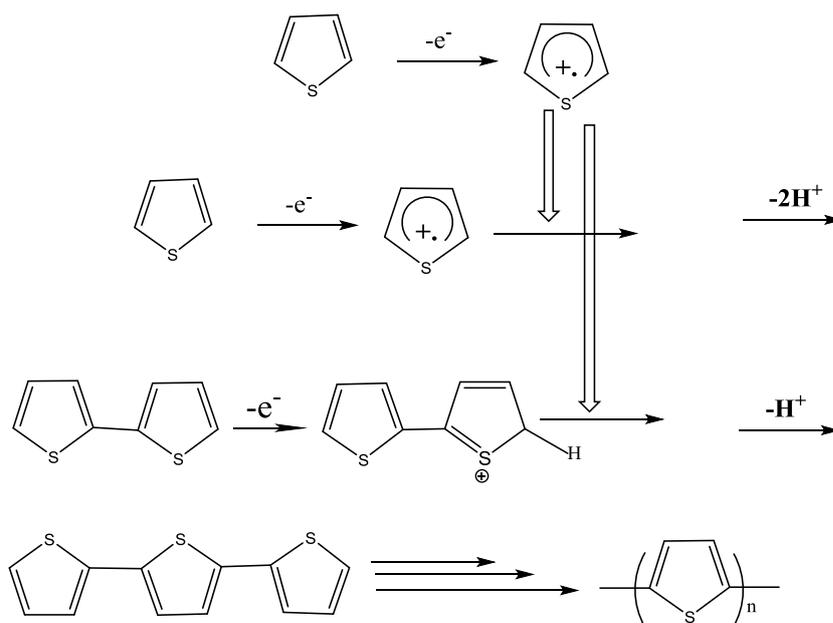
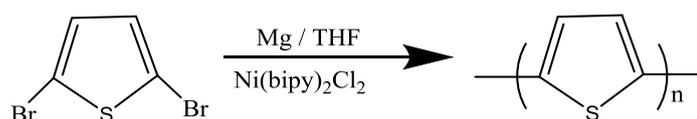


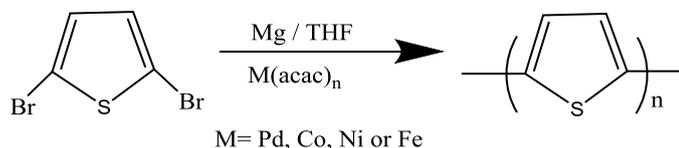
Figure 1.14: The proposed mechanism of Th oxidative electropolymerisation.⁹⁵⁻⁹⁷

1.8.1 Chemical synthesis of PTh

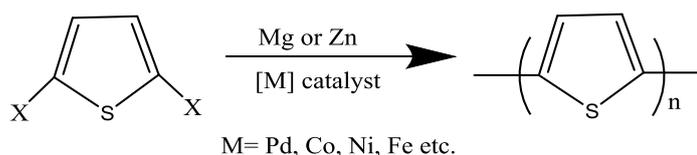
Shirakawa and coworkers chemically prepared a semi-conducting conjugated polyacetylene in the late 1970s which set the scene for preparing other conjugated polymers.⁹⁸ Yamamoto et al.,⁹⁹ prepared thiophene-based conjugated polymer by a chemical route as shown below:



In addition, Lin and Dubek prepared the same unsubstituted conjugated polymer in a similar route as follows:¹⁰⁰



Moreover, based on the dehalogenations, PTh has been prepared by other researchers^{101, 102}.



All methods are classified as organometallic polycondensation from 2,5-dihalothiophene and after elimination of salt, two monomers are condensed in the presence of a metal (Mg or Zn).

1.9 Ionic liquids (ILs)

Ionic liquids can be defined as liquids which consist of ions and have, by definition, melting points below 100 °C. They are composed of discrete organic cations and anions.^{103, 104} In addition, they normally can be composed of quaternary ammonium, pyridinium, pyrrolidinium or other heterocyclic cations and some are even derivatives of natural products.¹⁰⁵ Moreover, their physicochemical properties depend upon the choice of anions. Some commonly used cations are shown in **Figure 1.15**.¹⁰⁶

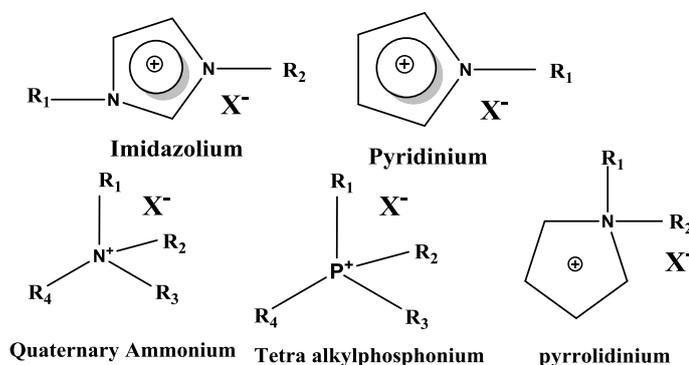


Figure 1.15: Structure of common ionic liquids types.¹⁰⁶

Ionic liquids have been classified in many ways, e.g. protic and aprotic ionic liquids; simple and complex anions; and some of these classes are shown in **Figure 1.16**.^{107, 108}

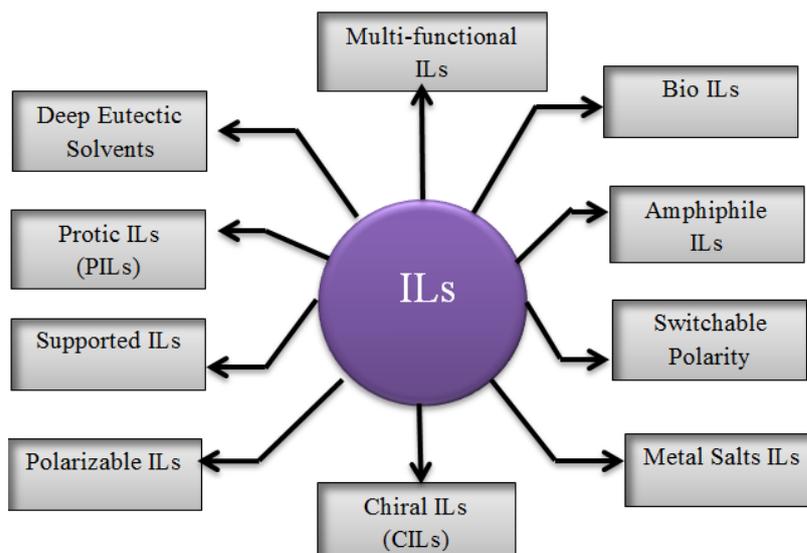


Figure 1.16: Classification of ionic liquids.¹⁰⁸

ILs based on imidazolium cation are one of the most widely studied. ILs have been used in many fields such as electrochemistry, synthesis, industrial applications, energy, extraction processes and catalysis.^{109, 110} Many ionic liquids have a large liquids range, negligible vapour pressure, and a high chemical/thermal stability.⁷¹ Recently, researchers have used ILs for extractive desulfurisation (EDS) in place of molecular solvents.⁷¹ The results are summarised in **Table 1.8**.

ILs are also suitable for electropolymerisation processes. As Roncali reported that owing to the high potential requirement to oxidise thiophene ring ($\sim 1.4 - 2.3V$), the solvent should have a perfect electrochemical stability to prevent decomposition of the medium and good conductivity of the electrolyte (a high dielectric constant).⁸⁹ A review of electropolymerisation in ILs has recently been presented by Pringle.^{111, 112}

1.10 Deep eutectic solvents (DESs)

Deep eutectic solvents (DESs) are composed of a mixture of Brønsted or Lewis acids such as quaternary ammonium chlorides and hydrogen bond donors such as alcohols or amides or metal halide salts. With moderate heating, they form a liquid phase due to complexing of a quaternary ammonium halide with a metal salts such as zinc, iron, aluminium or tin chloride or with hydrogen bond donors (HBD) such as urea, glycerol or

oxalic acid. Since they are generally non-toxic, inexpensive and often biodegradable, they have been used for a variety of applications.¹¹³⁻¹¹⁷

Although many characteristics and physical properties of ionic liquids and DESs are similar, they are frequently different in chemical properties and application areas. This means that they are two different solvents. Generally, the general formula of DESs can be classified into four types as shown in **Table 1.6**.¹⁰⁴

Table 1.6 : General formula of DESs types.¹⁰⁴

Type	General formula	Terms
Type 1	$\text{Cat}^+\text{X}^- \text{zMCl}_x$	M= Zn, Sn, Fe, Al, Ga, In
Type 2	$\text{Cat}^+\text{X}^- \text{zMCl}_x \cdot y\text{H}_2\text{O}$	M= Cr, Co, Cu, Ni, Fe
Type 3	$\text{Cat}^+\text{X}^- \text{zRZ}$	Z= CONH ₂ , COOH, OH
Type 4	$\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1}^+ \cdot \text{RZ} + \text{MCl}_{x+1}$	M= Zn, Al and Z= CONH ₂ , OH

Type 3 are the most commonly used in eutectic mixtures particularly with cholinium cations [(2-hydroxyethyl)-trimethylammonium HOC₂H₄N⁺(CH₃)₃].^{113, 118} **Figure 1.17** shows some typical structures of hydrogen-bond donors and accepters (halide salts) utilized for synthesising type 3 DESs.¹¹³

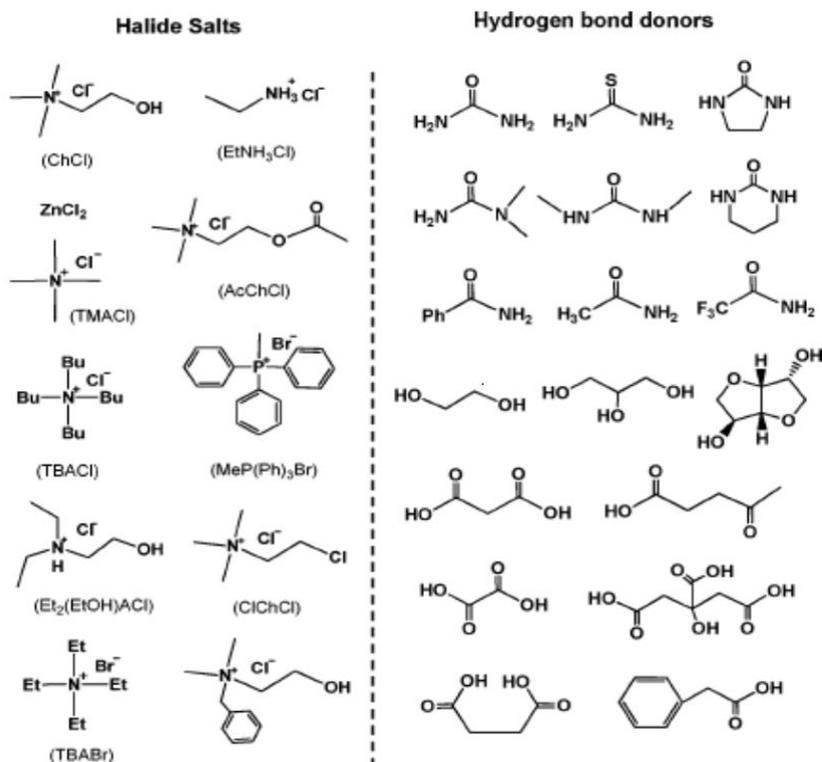


Figure 1.17: Structures of some HBDs and halide salts.¹¹³

1.11 Using ILs as extractants in fossil fuel desulfurisation

Ionic liquids have been studied for sulfur extraction from oil as they are nearly insoluble in fuel oil, stable over a wide range of temperature, they are non-volatile, non-toxic and non-flammable.¹¹⁹ The main practical difficulties are their cost and toxicity. **Table 1.8** presents most of the methods used in the desulfurisation of diesel fraction, which has been studied for the past two decades.

The mechanism by which thiophene is extracted into ILs has also been studied. Owing to the π - π interaction between unsaturated bonds of a cyclic sulfur-containing compounds and the imidazolium ring of ILs, the extraction ability is relatively higher and probably relevant to the liquid clathrate formation.¹¹⁹⁻¹²² In addition, complex formation between π -electrons of unsaturated bonds of aromatic thiophenic species and the charged imidazolium based ILs increases as the size of imidazolium cation increase and decrease interactions between anions and cations via alkyl groups (such as methyl, ethyl, butyl and octyl), because these groups are electron donating groups.^{119, 123}

It was found that the dipole moments of Th (0.53), BT (0.62) and DBT (0.83) are almost parallel to the electron density around the sulfur.¹²⁴ In addition, Nie and coworkers outlined that sulfuric compounds with higher electron π density are extracted favourably than those S-compounds with less electron density.¹¹⁹ The consequence of such information is that the electron density on sulfur atoms of the thiophenic compounds which are 5.758, 5.739 and 5.696 for DBT, BT and Th respectively has a pronounced effect on the interaction between ILs and sulfur compounds.^{122, 125, 126}

Most of the studies below have not used real fuel oils as test phases due to their complexity, so model compounds have been used to represent diesel fuel. Due to its physicochemical properties n-decane is commonly used experimentally as model diesel fuel. **Table 1.7** displays a comparison of some properties of n-decane with typical diesel.

Table 1.7: Properties of diesel fuel and decane.^{59, 127}

Properties	Diesel	Decane
Molecular formula	C ₈ -C ₂₅	C ₁₀
Molecular weight	~200 g/mol	142.28 g/mol
Cetane number	40-55	77
Boiling point	160-360 °C	173.8-174.4 °C
Density at 25 °C	0.8475 g/mL	0.73 g/mL

In a similar fashion, most studies have also chosen a subset of sulfur containing compound, typically Th, BT and DBT.

Table 1.8: Extraction studies of ILs.

Lead author (Year)	Cation, anion and oxidant or catalyst	Extracted S-compound(s)
Bösmann (2001) ¹²⁸	Imidazolium, (AlCl ₃ , Cl ⁻)	DBT, 4,6-DMDBT
W. H. Lo (2003) ¹²⁹	Imidazolium, (PF ₆ ⁻ , BF ₄ ⁻ , CH ₃ CO ₂ ⁻ , H ₂ O ₂)	DBT
J. Eßer (2004) ⁴⁸ *	Imidazolium, (Cl ⁻ /AlCl ₃ , BF ₄ ⁻ , PF ₆ ⁻ , OcSO ₄ ⁻ , EtSO ₄ ⁻ , Me ₂ PO ₄ ⁻)	DBT, 4-MDBT, 4,6-DMDBT
S. Zhang (2004) ^{130*}	Imidazolium, ammonium (Cl ⁻ , BF ₄ ⁻ , PF ₆ ⁻ , AlCl ₃)	Th, 3-MTh, DBT, 4,6-DMDBT
J. Planeta (2006) ^{131*}	Imidazolium, (CO ₂ , Tf ₂ N ⁻)	Th, BT, DBT, 4,6-DMDBT, BTZ, ThN
D. Zhao (2007) ¹³²	Pyrrolidinium, (BF ₄ ⁻ , H ₂ O ₂)	DBT
L. Lu (2007) ¹³³	Imidazolium, (BF ₄ ⁻ , H ₂ O ₂)	DBT
L. He (2008) ¹³⁴	Imidazolium, (BF ₄ ⁻ , PMo ₁₂ O ₄₀ ³⁻ , H ₂ O ₂)	BT, DBT, 4,6-DMDBT
C. Xuemei (2008) ¹³⁵	Imidazolium, pyridinium, (BF ₄ ⁻)	Multi S-compounds
W. Zhu (2008) ¹³⁶	Imidazolium, (BF ₄ ⁻ , PF ₆ ⁻ , MoO ₄ ²⁻ , F ₃ CCO ₂ ⁻)	BT, DBT, 4,6-DMDBT
Y. Mochizuki (2008) ¹³⁷	Imidazolium, (MeSO ₄ ⁻ , EtSO ₄ ⁻)	DBT
R. Schmidt (2008) ^{138*}	Imidazolium, (Cl ⁻ /AlCl ₃)	DBT
D. Liu (2008) ¹³⁹	Imidazolium, pyridinium, ammonium, (BF ₄ ⁻ , PF ₆ ⁻ , HSO ₄ ⁻ , TOS ⁻)	DBT
C. C. Cheng (2008) ¹⁴⁰	Imidazolium, (MeSO ₄ ⁻ , H ₂ O ₂ , F ₃ CCO ₂ ⁻)	Th, BT, DBT
H. Gao (2008) ¹⁴¹	Pyridinium, (BF ₄ ⁻)	Th, BT, DBT
D. Xu (2009) ¹⁴²	Imidazolium, (BF ₄ ⁻ , H ₂ O ₂ , V ₂ O ₅)	DBT, BT, 4,6-DMDBT
J. Zhang (2009) ¹⁴³	Imidazolium, (Cl ⁻ /FeCl ₃ , H ₂ O ₂)	BT, DBT, 4,6-DMDBT
H. Li (2009) ⁴⁹	Imidazolium, (PF ₆ ⁻ , W ₁₀ O ₃₂ ⁴⁻ , H ₂ O ₂)	BT, DBT, 4,6-DMDBT
Z. Di-shun (2009) ¹⁴⁴	Pyrrolidinium, (H ₂ PO ₄ ⁻ , H ₂ O ₂)	DBT
H. Gao (2009) ¹⁴⁵	Pyridinium, (BF ₄ ⁻)	Th, BT, DBT, 4,6-DMDBT

H. Gao (2009) ¹⁴⁶	Imidazolium, (Cl ⁻ /FeCl ₃ , BF ₄ ⁻ , PF ₆ ⁻)	DBT, BT, 4,6-DMDBT
H. Li (2009) ¹⁴⁷	Imidazolium, (PF ₆ ⁻ , BF ₄ ⁻ , PW ₁₂ O ₄₀ ³⁻)	DBT, BT, 4,6-DMDBT
J. Wang (2009) ^{148*}	Pyrrolidinium (H ₂ O ₂ , BF ₄ ⁻)	DBT
F. Li (2009) ¹⁴⁹	Ammonium, (CH ₃ CO ₂ ⁻ , H ₂ O ₂ , Cl ⁻ /Zn ²⁺)	DBT
A. Seeberger (2010) ¹⁵⁰	Imidazolium, (H ₂ O ₂ , Et ₂ PO ₄ ⁻)	DBT, 4-MDBT, 4,6-DMDBT
H. Gao (2010) ¹⁵¹	Imidazolium, pyridinium, (HSO ₄ ⁻)	Th, BT, DBT, 4,6-DMDBT
M. Francisco (2010) ^{152*}	Pyridinium, (NTf ₂ ⁻)	Th
D. Zhao (2010) ¹⁵³	Pyridinium, (HSO ₄ ⁻ , SCN ⁻ , H ₂ PO ₄ ⁻ , HCO ₂ ⁻ , H ₂ O ₂)	DBT
C. Asum (2010) ^{154*}	Imidazolium, sulfonium, thiophenium, (N(CN) ₂ ⁻)	Th, DBT
P. S. Kulkarni (2010) ¹⁵⁵	Imidazolium, pyridinium, (BF ₄ ⁻ , PF ₆ ⁻ , NTf ₂ ⁻)	DBT, 4-MDBT, 4,6-DMDBT
J. Gui (2010) ¹⁵⁶	Imidazolium, (HSO ₄ ⁻ , Cl ⁻ , H ₂ PO ₄ ⁻ , H ₂ O ₂)	DBT, 4,6-DMDBT
W. Zhang (2010) ¹⁵⁷	Imidazolium, (HSO ₄ ⁻ , H ₂ O ₂)	DBT
C. Yansheng (2011) ¹⁵⁸	Imidazolium, pyridinium, (PF ₆ ⁻ , NTf ₂ ⁻ , HSO ₄ ⁻ , H ₂ O ₂)	DBT
W. Zhu (2011) ¹⁵⁹	Imidazolium, (MoO ₄ ²⁻ , PMo ₁₂ O ₄₀ ³⁻ , H ₂ O ₂)	DBT, 4,6-DMDBT
G. Yu (2011) ^{160*}	Imidazolium, (CH ₃ CO ₂ ⁻ , N(CN) ₂ ⁻)	Th, DBT
K. K. Kro'lil (2011) ^{161*}	Imidazolium, ammonium, (SCN ⁻ , MeSO ₄ ⁻ , Me ₂ PO ₄ ⁻)	Th
A. R. Hansmeier (2011) ^{162*}	Imidazolium, pyridinium, (SCN ⁻ , N(CN) ₂ ⁻)	Th, BT, DBT
J. Zhang (2011) ¹⁶³	Imidazolium, (Br ⁻ , PMo ₁₂ O ₄₀ ³⁻ /Al ³⁺ , Si ⁴⁺ , Ti ⁴⁺)	DBT
X. Chen (2012) ¹⁶⁴	Imidazolium, (Cl ⁻ /Fe ²⁺ , Zn ²⁺ , Cu ²⁺ , Mg ²⁺ , Sn ²⁺ , H ₂ O ₂)	DBT
C. D. Wilfred (2012) ¹⁶⁵	Imidazolium, (BF ₄ ⁻ , PF ₆ ⁻ , PF ₃ ⁻ , OTf ⁻ , NTf ₂ ⁻ , TOS ⁻ , SCN ⁻ , N(CN) ₂ ⁻)	DBT
H. Zhang (2012) ¹⁶⁶	Ammonium, (Cl ⁻ /PMo ₁₂ O ₄₀ ³⁻ , H ₂ O ₂)	3-MT, DBT, BT
Z. Li (2012) ¹⁶⁷	Amine propionate (CO ₂ Et)	DBT
W. Zhu (2012) ¹⁶⁸	Ammonium, (Cl ⁻ /Fe ³⁺ , Cr ³⁺ , Co ²⁺ , Cu ²⁺ , Sn ²⁺ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT

C. Zhang (2012) ¹⁶⁹	Pyridinium, (HSO ₄ ⁻ , H ₂ O ₂ , HCO ₂ ⁻)	BT, 4,6-DMDBT
H. Gao (2012) ¹⁷⁰	Pyridinium, (BF ₄ ⁻)	Th, DBT, BT, 4,6-DMDBT
D. Liu (2012) ¹⁷¹	Imidazolium, (HSO ₄ ⁻ , H ₂ O ₂)	Multi S-compounds
Y. Nie (2013) ¹⁷²	Pyridinium, (Cl ⁻ /Fe ³⁺ , H ₂ O ₂)	DBT
G. O. Yahaya (2013) ¹⁷³	Pyridinium, (MeSO ₄ ⁻)	Th, DBT
W. Zhu (2013) ¹⁷⁴	Pyridinium, (Cl ⁻ /FeCl ₃)	DBT, BT, 4,6-DMDBT
G. N. Yun (2013) ¹⁷⁵	Ammonium, (Cl ⁻ /PW ₁₂ O ₄₀ ³⁻ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT, DBTS
W. Zhu (2013) ¹⁷⁶	Ammonium, (Cl ⁻ /PMO ₁₂ O ₄₀ ³⁻ , PW ₁₂ O ₄₀ ³⁻ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT
M. Zhang (2013) ¹⁷⁷	Imidazolium, (PF ₆ ⁻ , BF ₄ ⁻ , PW ₁₂ O ₄₀ ³⁻ , H ₂ O ₂ , CeO ₂)	DBT, BT, 4,6-DMDBT
L. Ban (2013) ¹⁷⁸	Imidazolium, (Cl ⁻ /FeCl ₃)	DBT, BT, 4,6-DMDBT
H. Lu (2013) ¹⁷⁹	Imidazolium, (PF ₆ ⁻ , BF ₄ ⁻ , NiMo ₆ O ₂₄ H ₆ ⁴⁺ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT, 5-MBT, 4-MDBT
Q. Wang (2013) ^{180*}	Pyridinium, (N(CN) ₂ ⁻)	Th, DBT, BT, 4,6-DMDBT
S. A. Dharaskar (2013) ¹⁸¹	Imidazolium, ammonium, (Cl ⁻ /Fe ³⁺ , Al ³⁺ , Co ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺)	DBT
Y. Dong (2013) ¹⁸²	Imidazolium, pyridinium, (Cl ⁻ /FeCl ₃ , H ₂ O ₂)	DBT, BT
S. A. Dharaskar (2013) ¹⁸³	Imidazolium, (Br ⁻ , Cl ⁻ /AlCl ₃ , PF ₆ ⁻ , BF ₄ ⁻ , OcSO ₄ ⁻)	DBT
C. Asumana (2013) ^{184*}	Imidazolium, (N(CN) ₂ ⁻)	Multi S-compounds
J. Xiong (2013) ¹⁸⁵	Imidazolium, (Cl ⁻ /FeCl ₃ , PF ₆ ⁻ , BF ₄ ⁻ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT
W. Xiang (2013) ¹⁸⁶	Imidazolium, ammonium, (Cl ⁻ /FeCl ₃ , PF ₆ ⁻ , BF ₄ ⁻ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT
H. Lu (2014) ¹⁸⁷	Imidazolium, (PF ₆ ⁻ , Mo ₇ O ₂₄ ⁶⁻ , H ₂ O ₂)	BT, DBT, 3-MBT, 4,6-DMDBT
C. Shu (2014) ¹⁸⁸	Pyrrolidinium (Cl ⁻ , H ₂ O ₂ , Ni ²⁺)	BT, DBT, 3-MBT, 4,6-DMDBT
B. Cabo (2014) ^{189*}	Imidazolium, pyridinium, (NTf ₂ ⁻ , /Al ³⁺ , Cr ³⁺ , Ti ⁴⁺)	Th, DBT
X. Chen (2014) ^{190*}	Imidazolium, (Cl ⁻ /Zn ²⁺ , HSO ₄ ⁻)	Th, DBT
H. Lu (2014) ¹⁹¹	Pyridinium, (Cl ⁻ /HCO ₂ ⁻ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT

W. Jiang (2014) ¹⁹²	Pyridinium, (Cl ⁻ /FeCl ₃ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT
B. Shao (2014) ¹⁹³	Imidazolium, (Me ₂ PO ₄ ⁻ , Et ₂ PO ₄ ⁻ , Bu ₂ PO ₄ ⁻ , Mo ₇ O ₂₄ ⁶⁻ , H ₂ O ₂)	4,6-DMDBT
W. Jiang (2014) ¹⁹⁴	Imidazolium, ammonium, (BF ₄ ⁻ , Cl ⁻ /Fe ³⁺ , Sn ²⁺ , Zn ²⁺ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT
Z. S. Gano (2014) ¹⁹⁵	Phosphonium, ammonium, (Br ⁻ , Cl ⁻ /Fe ³⁺ , Zn ²⁺)	DBT, Th
Z. S. Gano (2015) ¹⁹⁶	Phosphonium, (Br ⁻ , Sn ²⁺)	DBT, Th
G. C. Laredo (2015) ¹⁹⁷	Imidazolium, ammonium, (Cl ⁻ , Br ⁻ , CH ₃ OCO ₂ ⁻ , CH ₃ CO ₂ ⁻ , CH ₃ (CH ₂) ₂ O ₂ ⁻ , HCO ₃ ⁻)	BT
X. Chem (2015) ¹⁹⁸	Pyrrolidinium (Cl ⁻ /ZnCl ₂ , H ₂ O ₂)	DBT
X. Chem (2015) ¹⁹⁹	Imidazolium, (Cl ⁻ /Fe ³⁺ , Zn ²⁺ , TOS, H ₂ O ₂ , H ₂ PO ₄ ⁻)	Multi S-compounds
D. Zheng (2015) ²⁰⁰	Imidazolium, (PF ₆ ⁻ , BF ₄ ⁻ , Cl ⁻ /Ti ⁴⁺)	DBT, BT, 4,6-DMDBT
H. Gao (2015) ²⁰¹	Pyridinium, (NTf ₂ ⁻ , SCN ⁻ , N(CN) ₂ ⁻)	DBT, BT, 4,6-DMDBT
J. J. Ibrahim (2015) ^{202*}	Pyrrolidinium, imidazolium, (dcnm)	Th, DBT
T. Ren (2015) ³⁶	Imidazolium, (HSO ₄ ⁻ , BF ₄ ⁻ , Cl ⁻ , Br ⁻ , OH ⁻ , /Fe ³⁺ , Co ²⁺ , Zn ²⁺ , Mn ²⁺ , Cu ²⁺ , Mo ²⁺)	Th, DBT, BT, 2-MTh
W. Zhu (2015) ²⁰³	Ammonium, (Cl ⁻ , CH ₃ CO ₂ ⁻ , C ₂ H ₅ CO ₂ ⁻ , C ₃ H ₇ CO ₂ ⁻ , HCO ₂ ⁻ , C ₄ H ₉ CO ₂ ⁻)	DBT, BT, 4,6-DMDBT
H. Lu (2015) ²⁰⁴	Ammonium, (Cl ⁻ , C ₂ O ₄ ²⁻)	DBT
S. Xun (2015) ²⁰⁵	Imidazolium, (PF ₆ ⁻ , BF ₄ ⁻ , Cl ⁻ , FeCl ₃ , Ti ⁴⁺ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT
S. A. Dharaskar (2015) ^{206*}	Imidazolium, ammonium, (Cl ⁻ , FeCl ₃ , H ₂ O ₂)	Th, DBT, BT, 3-MTh, 4,6-DMDBT, 4-MDBT
O. U. Ahmed (2015) ²⁰⁷	Phosphonium, (Cl ⁻ , Br ⁻ , N(CN) ₂ ⁻ , NTf ₂ ⁻)	Th, DBT
X. Shi (2015) ²⁰⁸	Imidazolium, (Cl ⁻ /PW ₁₂ O ₄₀ ³⁻ , Si ⁴⁺ , H ₂ O ₂)	BT, DBT
Z. Li (2015) ²⁰⁹	Ammonium, (CH ₃ CO ₂ ⁻ , C ₂ H ₅ CO ₂ ⁻ , C ₃ H ₇ CO ₂ ⁻ , HCO ₂ ⁻)	Th, BT
J. Yin (2015) ²¹⁰	Ammonium, (Cl ⁻ , Me-Ph-SO ₃ H, H ₂ O ₂)	BT
M. Li (2016) ²¹¹	Imidazolium, (SCN ⁻ , NTf ₂ ⁻ , CH ₃ CO ₂ ⁻ , H ₂ O ₂)	DBT, BT, 4,6-DMDBT

D. Jha (2016) ²¹²	Phosphonium, (Cl ⁻)	DBT
Y. Nie (2016) ²¹³	Pyridinium, (Cl ⁻ /Zn ²⁺ , H ₂ O ₂)	DBT, BT, Th
S. Xun (2016) ²¹⁴	Imidazolium, (Cl ⁻ , SiW ₁₂ O ₄₀ ⁴⁻ , H ₂ O ₂)	4,6-DMDBT, BT, 4-MTh, DBT
J. Yuan (2016) ²¹⁵	Imidazolium, (Cl ⁻ , SiW ₁₂ O ₄₀ ⁴⁻ , H ₂ O ₂)	4,6-DMDBT, BT, DBT
C. Li (2016) ²¹⁶	Ammonium, (Cl ⁻ / Fe ³⁺ , Co ²⁺ , Zn ²⁺ , Cu ²⁺)	DBT
J. Li (2016) ^{217*}	Ammonium, (Br ⁻ , CH ₃ CO ₂ ⁻ , C ₂ H ₅ CO ₂ ⁻ , ⁻ OOCCO ₂ ⁻ , ⁻ OOC(CH ₂) ₄ CO ₂ ⁻ , HCO ₂ ⁻ , ⁻ OOCCH ₂ CO ₂ ⁻)	DBT, BT, Th
M. Safa (2016) ²¹⁸	Imidazolium, pyridinium, (NO ₃ ⁻)	DBT
X. Wang (2016) ²¹⁹	Ammonium, (Cl ⁻ , HCO ₂ ⁻ , CH ₃ CO ₂ ⁻ , CH ₃ CH ₂ CO ₂ ⁻ , CH ₃ (CH ₂) ₂ O ₂ ⁻ , CH ₃ (CH ₂) ₃ CO ₂ ⁻)	4,6-DMDBT, BT, DBT, 1-dodecanethiol

*: Extraction from both gasoline and diesel fuels.

1.12 Research objectives

The effective desulfurisation of fuel oil needs to:

- 1- have a minimal effect on the price of the fuel.
- 2- reduce the amount of pollutants in air.
- 3- employ the minimum energy during the desulfurisation process.¹⁸

The need to remove thiophenic compounds in diesel fuel has led to intense research into a variety of methods due to these species accounting for more than 80 % in the total sulfur contents in diesel fuel.¹⁵⁸ Therefore, in this work, much attention has been paid on the removal of Th, BT and DBT from diesel fuel. It has been shown by numerous groups that ILs and DESs can be efficient for removal of thiophene from model fuel oils but most of the systems studied are impractical and do not fulfil the above criteria. This work mainly concentrates on the use of some DESs as alternative solvents for the removal of thiophenic species from diesel fuel using choline and methyl-imidazolium based ionic liquids and DESs.

The first part of the project determines the extraction efficiency, namely the partition coefficient of Th, BT and DBT from decane (a model oil analogue) into a variety of DESs. The aim of this part of the study is to determine the thermodynamics of extraction to understand the conditions under which thiophenic species is extracted. The amount extracted from the oil phase was analysed by UV-visible spectroscopy and GC-FID. The

physical properties of the different DESs studied were used to deduce what factors control phase formation.

Electrochemical oxidation of thiophene for polymerisation would in principle allow extraction and separation through solid phase formation. This also has the advantage that it drives extraction of thiophene from the oil phase by shifting the equilibrium.



An electrocatalytic method was attempted using ferric chlorides as both a chemical and electro-catalyst. A variety of different ionic liquids are tested to determine the phase behaviour of the catalyst and ensure optimum turnover. The electrochemistry of Th, BT and DBT were investigated and different electrode configurations were tested to develop an electrocatalytic method of regenerating ferric chloride.

The final part of the thesis was carried out on the applications of the methods on commercial diesel and designing a schematic diagram for extractive polymerisation of thiophene from diesel to test the efficacy of the extraction and polymerisation methodology.

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Chapter two: Experimental

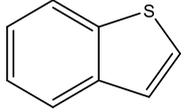
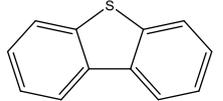
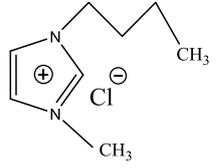
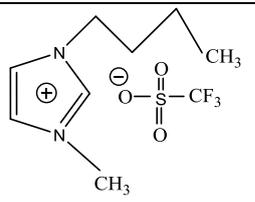
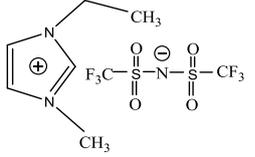
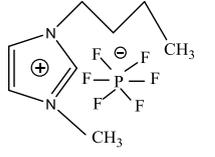
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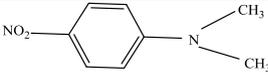
2 Experimental

2.1 Chemicals and reagents

All materials and reagents employed in this work are shown in **Table 2.1** and **Table 2.2** with respective purities and suppliers. All substances and solvents have been employed as received. **Table 2.1** shows the solvents and chemical materials used in this study.

Table 2.1: List of used solvents and reagents in this work.

Materials and solvents	Origin	Formula	Purity
Methanol	Sigma-Aldrich	CH ₃ OH	99 %
Ethanol	Sigma-Aldrich	CH ₃ CH ₂ OH	99 %
Diethyl ether	Sigma-Aldrich	CH ₃ CH ₂ OCH ₂ CH ₃	99 %
n-Decane	Sigma-Aldrich	CH ₃ -(CH ₂) ₈ -CH ₃	≥99 %
Thiophene	Sigma-Aldrich		≥99 %
Benzothiophene	Alfa Aeser		98+ %
Dibenzothiophene	Sigma-Aldrich		98 %
1-Butyl-3-methylimidazolium chloride	Sigma-Aldrich		95 %
Iron(III) chloride anhydrous	Sigma-Aldrich	FeCl ₃	97 %
Copper(II) chloride anhydrous	Acros	CuCl ₂	99 %
Iron(II) chloride anhydrous	Alfa Aeser	FeCl ₂	99.5 %
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	Sigma-Aldrich		≥98 %
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Sigma-Aldrich		97 %
1-Butyl-3-methylimidazolium hexafluorophosphate	Sigma-Aldrich		98 %
Dimethyl sulfoxide	Alfa Aeser	CH ₃ SOCH ₃	99+ %

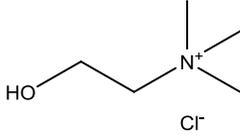
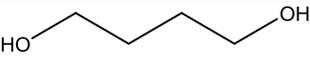
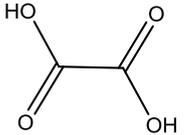
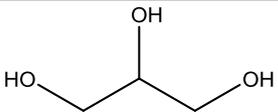
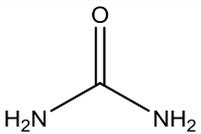
Cyclohexane	Sigma-Aldrich		99+ %
Propan-1-ol	Sigma-Aldrich	CH ₃ CH ₂ CH ₂ OH	98 %
4-Nitro aniline	Sigma-Aldrich		99 %
N,N-dimethyl-4-nitro aniline	Alfa Aeser		97 %

Deuterated benzene (C₆D₆) was used as a solvent for NMR spectroscopy to determine the compositions of the extractant and raffinate phases.

2.1.1 DESS and IL mixture preparation method

The DESs used choline salts as the hydrogen-bond acceptor (HBAs) and a range of hydrogen-bond donors (HBDs). Ethaline (ethylene glycol, choline chloride, 2:1), Reline (urea, choline chloride, 2:1), Glyceline (glycerol, choline chloride, 2:1), Butaline (1,4-butandiol, choline chloride, 3:1), Pentaline (1,5-pentandiol, choline chloride, 3.5:1), and Oxaline (anhydrous oxalic acid, choline chloride, 1:1) were utilized as DESs for extraction process. **Table 2.2** shows the materials utilised in the preparation of the Deep Eutectic Solvents (DESs).

Table 2.2: List of HBA and HBDs and their specification.

Name	Origin	Formula	Purity
Choline chloride	Sigma-Aldrich		≥98 %
Ethylene glycol	Sigma-Aldrich		≥99 %
1,5-Pentan-diol	Sigma-Aldrich		96 %
1,4-Butan-diol	Sigma-Aldrich		99 %
Oxalic acid dihydrate	Fisher		≥99 %
Glycerol	Fisher		98 %
Urea	Sigma-Aldrich		99.9 %

The deep eutectic solvents and imidazolium ionic liquid mixtures were synthesised using similar approaches described by literature methods.¹⁻⁵ The hydrogen bond donor (HBD) and salt are mixed with respect to specified HBD: salt molar ratio at a particular mixing speed and temperature until a clear homogeneous liquid phase was produced. Ethaline was prepared by mixing choline chloride with ethylene glycol in a 1:2 molar ratio. Then, the mixture was stirred in a flask and placed on a hot plate magnetic stirrer at 80 °C and 500 rpm for at least 3 hours until a colourless homogeneous liquid was formed. The same procedure was employed to synthesise Glyceline, but for preparation of Oxaline, oxalic acid dihydrate has been used as HBD in a molar ratio of 1:1 with the salt.

With respect to preparation of Butaline and Pentaline, they were produced in the same way as Ethaline except the molar ratio which was 1:3 and 3.5:1 respectively. For Reline, a 1:2 molar ratio of quaternary ammonium salts and urea were mixed together, stirred and placed in an oven until 24 hours at 50°C until a homogeneous, clear colourless liquid was formed.

(Bmim)FeCl₄ eutectic mixture has been made according to the literature procedure.⁶⁻⁹

In the extraction experiments thiophenic species were put into decane and a mass weight of this solution was stirred with that of each of the DESs addition, the extracted amount of thiophenic compounds was calculated as follows:

$$\text{Sulfur species \%} = \frac{C_o - C_e}{C_o} \times 100 \quad (2.1)$$

where, C_o is the initial concentration of thiophene and its analogues in model fuel, and C_e is the concentration of remaining S-containing compounds in the oil phase after the reaction began for a certain amount of time.

2.1.2 Some physical properties of (Bmim)Cl/FeCl₃

Density of 1:1 and 2:1 of FeCl₃: (Bmim)Cl was measured at four different temperatures as shown in **Figure 2.1**.

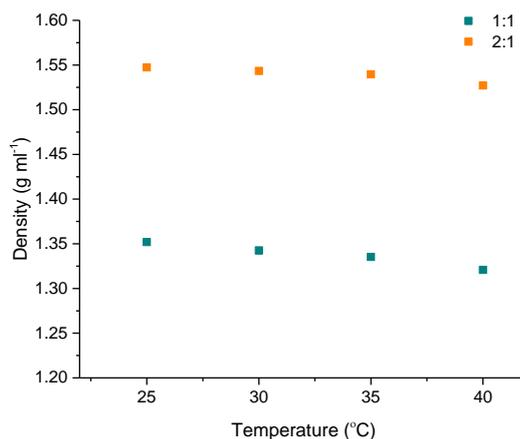


Figure 2.1: Density of $(Bmim)FeCl_4$ as a function of temperature.

The density of the same molar ratio of $FeCl_2/(Bmim)Cl$ was measured, however due to the high viscosity of the mixture, it was not clear that their densities were 1.367 (1:1) and 1.2093 $g\ cm^{-3}$ (2:1). In addition to the density, the dynamic viscosity has been measured (from measuring oscillating frequency of polished gold crystal exposed to the liquid) of $Fe(III)$ -containing imidazolium cation in the molar proportion of 1:1 and 2:1 using QCM technique which was 47.44 and 59.5 cP respectively.

2.2 Instrumentation

2.2.1 GC-FID

The technique used to measure the concentration of sulfur containing compounds in oil was gas chromatography (GC) coupled to either flame ionisation detector (FID) (as seen in **Figure 2.2**) or mass spectroscopy (MS).

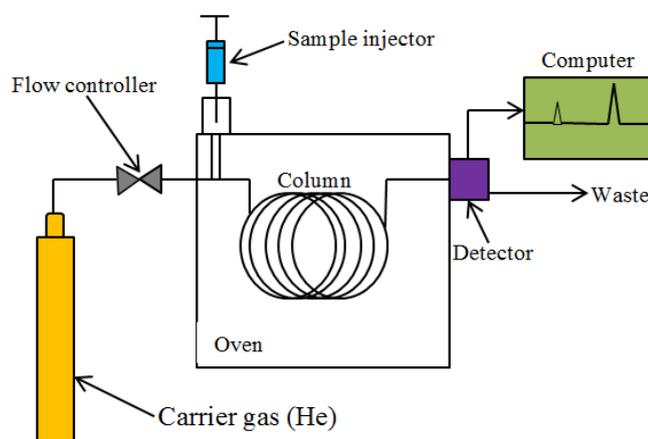


Figure 2.2: Schematic diagram of the GC-FID apparatus.

Analysis of thiophene and its analogs was conducted in a fused silica capillary column (PE Elite-5, 29.45 m long, 0.25 mm in diameter) connected to gas chromatograph (Perkin Elmer Autosystem XL) using the Totalchrom software. The operational temperature of the FID was 320 °C, and that of the injector was 310 °C. For the first three minutes, the temperature of column was set at 50 °C, increased to 300 °C at a rate of 15 °C/min, kept at 300 C for 2 min. Helium (He) was the carrier gas at a flow rate of 1ml/min. The quantities of S-compounds in a model fuel were determined from peak areas corresponding to these sulfur species on the gas chromatography. According to the GC setup, the retention time chromatograms for Th, BT and DBT were around 3.14, 9.88 and 14.7 minutes respectively which is in agreement with the results arising from the Lobodin co-workers.¹⁰

2.2.2 UV-Vis spectrophotometry

A Shimadzu model UV-1601 spectrophotometer was used for all UV-Vis absorption measurements. The amount of thiophene, benzothiophene and dibenzothiophene extracted by the DESs and iron based ILs was determined by measuring the absorbance spectrum of organic phase to determine the remaining amount in it.

Calibration curves for Th, BT and DBT were constructed in the range of 0.005- 0.15, 0.005- 0.03 and 0.001- 0.016 mmol L⁻¹ respectively and the sample concentrations were diluted to sure that they were always in these ranges.

2.2.3 Cyclic voltammetry (CV)

All electrochemical experiments were recorded employing three electrodes (Pt working electrode (WE), a Ag wire pseudo-reference electrode (RE) and Pt mesh counter electrode (CE). CVs were carried out at a polished 0.5 mm diameter ($1.963 \times 10^{-3} \text{ cm}^2$) Pt disc working electrode immersed in DESs and eutectic (Bmim)Cl mixture as a function of sweep rate (see **Figure 2.3**).

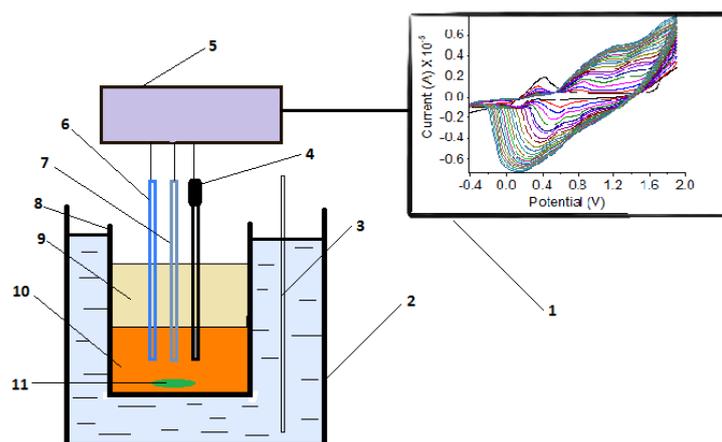


Figure 2.3: Schematic of the electrochemical desulfurisation experimental set up : 1- voltammogram, 2- thermostat water bath, 3- thermometer, 4- CE, 5- potentiostat, 6- RE, 7- WE, 8- electrolysis cell, 9- raw oil, 10- IL-mixture, 11 magnetic stirrer.

Before each experiment, the WE was cleaned and washed with deionised water, polished with alumina paste and after sonicating in deionised water for 5 min, it was dried with N_2 gas. The WE acts as a substrate for electro-deposition of polythiophene. Since the polymeric film was deposited by an oxidative process, an inert electrode (Pt) was utilised so as not to oxidise concurrently with the aromatic thiophene monomer.¹¹

2.2.4 EQCM

The Quartz Crystal Microbalance (QCM) is a frequency control technique, which depends on the piezoelectric characterisation of the AT-cut α -quartz crystal. This tool, involves an oscillator circuit and a crystal, where the piezoelectric crystal composes of two metal electrodes placed on opposite sides of a thin crystal wafer disc.¹²

The mechanical vibrations of the quartz crystal are attributed to resonators, which are characterised by resonant frequency and amplitude responses. Mechanical oscillations are generated within the crystal lattice due to the fact that an alternating potential is applied, leading to a shear distortion of the crystal due to its piezoelectric properties. The cut of the quartz shape and thickness-shear mode are sensitive for deposition of mass, which impact on the crystal's fundamental vibrational frequency.¹²

Electrochemical quartz crystal microbalance (EQCM) is an apparatus uses to measure the change in resonance frequency of the crystal during an electrochemical reaction. A part of device consisting of a quartz crystal resonator, which is used to measure the current

efficiency (mass-to-charge ratio).¹³ A redox reaction that brings about a phase change process causes a mass change to occur on the surface of electrode due to the solid phase dissolution or deposition. EQCM is a technique able to measure these mass changes using piezoelectric nature of quartz to monitor mass variation at the surface of the electrode. The measurement was carried out on a platinum thin film electrode deposited on electroactive 10 MHz AT-cut quartz crystal with an area of 0.23 cm² that provides piezoelectrical and electrochemical activities (**Figure 2.4**).



Figure 2.4: Platinum coated quartz crystal.

The resonance frequency is shifted due to the deposited mass on the crystal surface. Experimentally, any change in crystal frequency (Δf) is on account of the mass changes (Δm) on it and this change can be calculated using the Sauerbrey equation (2.2):¹⁴

$$\Delta f = -\frac{2f_0^2}{\rho v A} \Delta m \quad (2.2)$$

where, ρ is a quartz density (2.65 g cm⁻³); v is a wave velocity of quartz crystal (3.34x10⁵ cm s⁻¹); Δm is a change of polymer mass, A is the area of crystal electrode and f_0 is the fundamental frequency. In addition, this equation could only be used accurately when the deposited resonator is rigid.

2.2.5 ¹H NMR

Proton nuclear magnetic resonance ¹H NMR spectroscopy is a powerful analytical technique utilised to determine the molecular structure of organic compounds by measuring the absorption of electromagnetic radiation in the radiofrequency region of nearly 4 to 900 MHz.¹⁵ If an external magnetic field is applied on a compound, all electrically charged nuclei spin. Then an energy transfer is occurred between the low energy to a higher energy level and the resonant frequency of the energy transitions is dependent on the effective magnetic field at the nuclei.

The NMR spectra were measured on Bruker DPX 400 (^1H , 400 MHz). All chemical shifts (δ) of the NMR are quoted in ppm comparative to the residual non-deuterated solvent peaks and coupling constants (J) are quoted to the nearest 0.1 Hz.

^1H NMR study of recyclable DESs was undertaken using the solvent C_6D_6 . Each chemical shift (ppm) in ^1H NMR data is referred to the residual protic solvent peak and coupling constant is expressed in hertz (Hz).

2.2.6 FT-IR

The Fourier-transform infra-red (FTIR) spectrometer is an analytical technique used to achieve an absorption or emission infrared spectrum of solids, liquids or gases (It means qualitative analysis). This device, provides determined information depending on the chemical composition of the different functional groups structure.¹⁵ Absorption peaks in an infrared absorption spectrum make up from vibration of molecules. Then, a net change in the dipole moment could be created through molecular motions after molecules absorption of energy.¹⁶

The FT-IR which was used in this project was a Perkin Elmer Spectrum One with universal attenuated total reflectance (ATR). ATR is a technique used in combination with IR spectrometer which enables samples to be examined promptly in the solid or liquid state without further preparation.¹⁶ (ATR is an accessory of FT-IR spectrometer to achieve surface properties of thin film or solid samples (such as PTh) rather than their bulk characteristics) or with KBr disc for ionic liquids (Bmim)OTf and (Emim)NTf₂. All FTIR spectra were recorded from 4000 to 650 cm^{-1} .

2.2.7 Raman spectroscopy

Polythiophene was also identified by Raman spectroscopy in which the spectrum of the obtained polymer was recorded using a HORIBA Jobin Yvon Raman Spectrometer coupled with an Olympus microscope to monitor sample with different Leitz lenses (10x, 50x and 100x). The laser power was adjusted using a set of neutral filters. Additionally, the surface of polymer with an area of 0.3- 0.5 mm^2 was excited by a weak single frequency green laser beam (532 nm) with a power of (3.5- 35 mW) for a specific period of 10 - 100 s.

2.2.8 3D-Microscopy

3D images were obtained using a Zeta optical profiler. In addition, it was used to clearly find out the morphology of the obtaining conjugated neutral polymer.

2.3 Physical Property Measurements

2.3.1 Conductivity

The conductivity of iron-based imidazolium chloride in this study was measured with Jenway 4510 conductivity meter. Firstly, the probe of conductivity meter should be immersed in a liquid and left till the liquid temperature reached equilibrium. At least three measurements were recorded for each temperature.

2.3.2 Surface tension

The surface tension of DESs was measured with a Krüss Tensiometer K9 model K9MK1. A water jacket is surrounded a glass dish which contains a liquid extractant. A thermostat connected to the water jacket controlled the temperature of the sample. A Pt–Ir alloy plate (Krüss, part number PL21) was employed to record surface tension. Directly from the screen, the surface tension was read wherein the Pt plate was immersed to the surface layer of an extractant.

2.3.3 Viscosity

The viscosity of the DESs was measured using a rotational viscometer (Brookfield DV-II+ Pro) and QCM for viscosity of (Bmim)FeCl₄ mixtures which fitted with a thermostatic jacket. For rotating viscometer the spindle was rotated in each DES between 5 and 200 rpm to ensure the appropriate torque and the derived dynamic viscosities have been converted to kinematic viscosity using their densities at the same temperature to be used for measuring viscosity index. The viscosity of the used DESs was measured at three different temperatures (25, 35 and 45 °C).

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Chapter three: Partition coefficient determination

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3 Thiophenic compounds extraction from oil

3.1 Introduction

Separation of a solute from a liquid phase can occur through;

- evaporation (for a volatile solute)
- precipitation for solutes with low solubility
- adsorption on a solid substrate
- or liquid-liquid extraction with an immiscible solvent.

The first two options are not suitable for the extraction of sulfur containing compounds from oil and this thesis will focus on liquid-liquid extraction. For the extraction of solutes from oil, a polar solvent is required but water an unsuitable choice because as it impedes combustion in fuels and causes corrosion in lubricants. Ionic liquids have the advantage that they can be made immiscible with hydrocarbons but they can also show significant solubility for heterocyclic compounds.

The aim of this chapter is to extract thiophenic compounds (Th, BT and DBT) from diesel and determine their partition coefficient (K_p) using type 3 DESs. Initially n-decane will be used as a model hydrocarbon to simplify the chemistry. While a few studies have used DESs to extract thiophenic compounds, nothing is known about the thermodynamics of extraction and therefore it is impossible to predict which DESs are optimal for the extraction process. This study will use classical equilibrium thermodynamics to determine the effect of the hydrogen bond donor on the extraction efficiency.

The first task for the extraction was to develop an analytical method that was capable of accurately determining the amount of thiophenic species in the oil phase following extraction. Two techniques were chosen from the literature. These were gas chromatography-pulsed flame ionization detection (GC-FID) and UV-Vis spectroscopy.

Compared to other methods, GC-FID showed high sensitivity, good reliability and widely dynamic range compared to other techniques.¹ GC-FID chromatograms provide a distribution modality of hydrocarbons in crude oils and gives a fingerprints of the major oil components.² In the FID detector, the gas sample is passed into a hydrogen flame for combustion. The hydrocarbon concentration in the sample gas will affect the rate of

ionisation which in turn is directly proportional to the current. An electrical signal is produced when the ions are collected and this is used as a measure of the analyte concentration.

3.2 Extraction of organosulfur species by Type 3 DESs

Initial studies were carried out using both GC-FID and UV-vis spectroscopy. Six calibration curves were made using thiophene (Th), benzothiophene (BT) and dibenzothiophene (DBT) separately in decane in different concentrations and the results are shown in **Figure 3.1** for Th and in the appendix (**Chapter six**) for BT and DBT. These are similar to the results of Albro et al.³ and Shearer et al.⁴

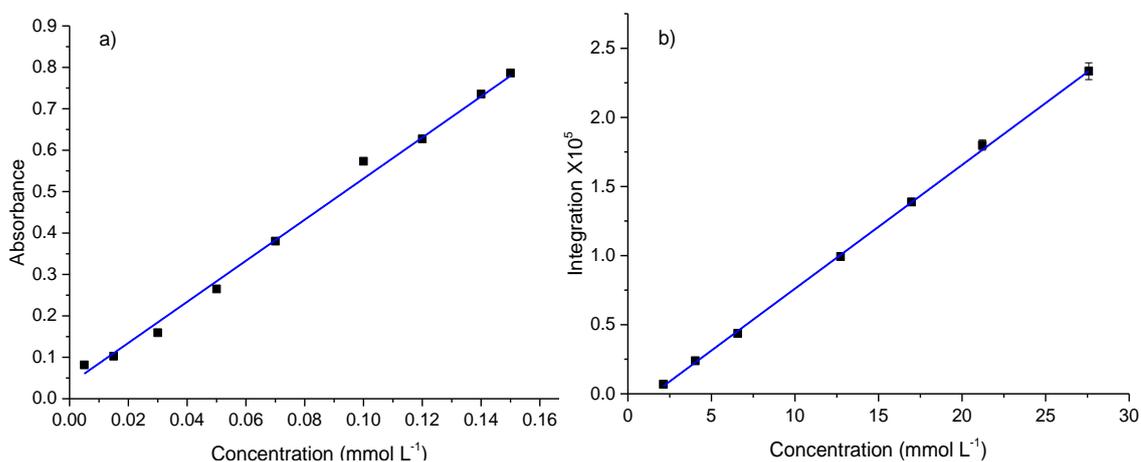


Figure 3.1: Calibration curves using standard known Th concentrations in decane which are plotted against a) absorbance peaks in UV-Vis spectroscopy, b) the GC area absorbance in GC-FID.

It can be seen that good linear correlation was achieved for both analytical techniques, with an R^2 value of more than 0.99 for UV-Vis spectroscopy and for GC-FID. Because of the smallest uncertainty of the error bars of the measured values, the error bars for most of the data are within the size of the plot symbols showing that replicate results are accurate. UV-Vis absorption is more useful at lower concentrations, because of the high extinction coefficient of S-compounds whereas GC-FID enables concentrations which are two orders of magnitude higher to be determined. The reproducibility of replicate measurements can again be seen from the small error bars on the curve. Thiophene,

benzothiophene and dibenzothiophene eluted at about 3.14, 9.88 and 14.7 minutes respectively on GC-FID and all absorbed at around 231 nm on UV-Vis spectroscopy in decane.

3.2.1 Optimisation of the Th extraction and (K_p) determination

A partition-coefficient (K_p) or sometimes called distribution-coefficient (K_D) is defined as the ratio of concentrations of a compound (S- compound) in a mixture of two immiscible phases at equilibrium.⁵ It is an important parameter for an extractive desulfurisation process, and the higher the partition coefficient is, the better the desulfurization performance of an extractant.^{5, 6} Numerous studies in the literature have been carried out on the determination of K_p for the extraction between aromatic sulfur compounds with ionic liquids.⁶⁻⁸

In this work, the corresponding partition coefficient of organosulfur species between oil and DES, was derived and defined according to the following equation.^{5, 9}

$$K_p = \frac{[\text{sulfur species}]_{in\ DES}}{[\text{sulfur species}]_{in\ fuel}} \quad (3.1)$$

The first aim was to investigate the sulfur partition coefficients for sulfur compounds Th, BT and DBT into a series of choline chloride based DESs namely, Pentaline, Butaline, Ethaline, Glyceline, Oxaline and Reline, from diesel model which were determined experimentally at different temperature over a wide range of sulfur content. These were chosen due to their wide spread of physical properties, their low cost and immiscibility with decane.

Furthermore, to optimise the performance of DESs in extractive desulfurisation (EDS) the partition coefficient of sulfur compounds (especially thiophene) between decane and DESs was measured as a function of;

- viscosity,
- polarity,
- mass ratio of DES-decane,
- initial S contents,
- temperature,
- time and
- stirring speed.

In addition, the regeneration of the DESs following multiple extractions was determined.

3.2.1.1 Effect of temperature

EDS has been studied by a number of groups but the thermodynamics of extraction have not been studied and the determination of the optimal temperature for extraction is inconclusive. Caero and co-workers¹⁰ showed that the desulfurisation of aromatic S-containing compounds from an organic layer could be performed at a reaction temperature of about 70 °C.¹⁰ A similar approach was used by Lu et al.,¹¹ who investigated the same process at 70 °C, and found that organosulfur species removal could be as high as 84 %. It was also reported by Shiraishi et al.,¹² that the rate of removing and oxidising aromatic sulfur compounds using H₂O₂ accelerates as the temperature of reaction increases. Additionally, Huang et al.,¹³ outlined that the feasibility of increasing temperature to 80 °C is to accelerate the desulfurisation reaction. However, Li and co-workers investigated EDS using DESs and showed that higher temperatures had little effect on the partition coefficient.¹⁴

In the current study the effect of temperature on the extraction of thiophene into DESs was carried out. A maximum temperature of 45 °C was used, because Th is highly volatile (b.p. = 84 °C). The decane and DES phases were contacted for 120 min using an overhead stirrer with a constant stirring rate of 500 rpm and 0.8 decane: 1 DES mass ratio. It is impractical to have this mass ratio in an operational extraction system but it was chosen as suitable way of carrying out the experiment in the laboratory.

Figure 3.2 shows the effect of temperature (25, 35 and 45 °C) on the removal of Th from decane into six DESs. An initial concentration of Th in decane of 17.47mM, (0.2 wt %) was chosen as it is a typical loading found in many crude oils. Firstly, it is reassuring to see that both analytical techniques gave very similar extraction efficiency data confirming the accuracy of the analytical techniques. It can be seen that increasing the temperature from 25 to 45 °C does not have a significant effect on the extraction efficiency of Th except in Butaline which gradually increases extraction percentage from 27 % to 37 %. This confirms the results by Li who used other DESs. (Note this study was carried out before the paper by Li was published).

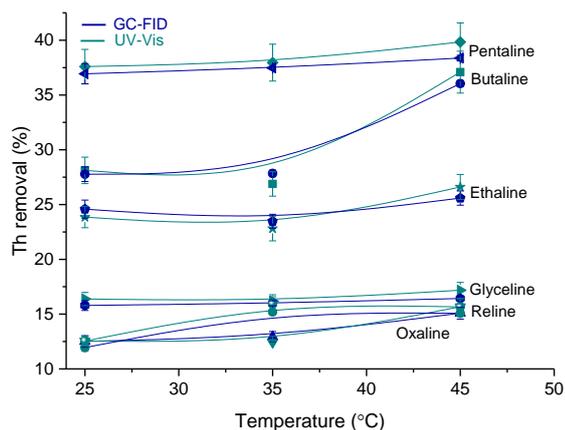


Figure 3.2: Th extraction by DESs at three different temperatures, the mass ratio of fuel: DES was 0.8:1, speed mixing at 500 (rpm), stirring for 2 hours.

Two reasons for the small effect of temperature on the extraction efficiency in DESs could be the high viscosity and the high polarity. A variety of studies^{15,16,17} in DESs and ILs suggested that viscosity may be an issue in desulfurisation. Viscosity should have less of an effect on Th removal using Pentaline, Butaline and Ethaline as these are the least viscous DESs in this study. **Table 3.1**, shows the viscosities of the DESs at the three different temperatures used. The viscosity of Ethaline is lower than Pentaline and Butaline at 25 °C, but the K_P followed the order of Pentaline > Butaline > Ethaline.

Table 3.1: Viscosities of the used DESs in the extraction desulfurisation of Th at different temperatures.

Temperature (°C)	Viscosity (cP)					
	Pentaline	Butaline	Ethaline	Glyceline	Oxaline	Reline
25	110 ± 0.4	94 ± 0.8	40 ± 0.04	296 ± 1.6	767 ± 3.9	849 ± 0.2
35	78 ± 1.1	65 ± 0.1	30 ± 0.3	182 ± 1.2	242 ± 0.6	374 ± 0.7
45	57 ± 0.05	50 ± 0.7	23 ± 1.05	105 ± 0.2	138 ± 0.3	225 ± 1

Furthermore, the changes in viscosity with temperature are all relatively similar i.e. they all roughly decrease by half when the temperature is raised from 25 to 45 °C. This does not however follow the trend in extraction efficiency with temperature as the extraction is significantly increased in Butaline at 45 °C compared to the other two liquids.

It can therefore be concluded that viscosity probably has some effect on extraction efficiency but it is not the only factor. It is most likely that it affects the rate at which equilibrium is established. When the viscosity of the extracting phase (DES) is low, inter-phase mass transfer is facilitated. In the DESs with low viscosity, the polarisability of the DES or its ability to form strong hydrogen bond networks¹⁸ with thiophenic species may increase their solubility in DESs.

There are numerous methods of determining solvent polarity (π^*), acidity (α) and basicity (β), but one of the most commonly used, particularly with DESs is the Kamlet-Taft solvent parameters using solvatochromism.^{19, 20} Reichardt's Dye 30 is solvatochromic substance that can be defined as a chemical substance that can change its colour due to the solvent polarity and its shift absorption strongly depends on the absorption and emission of solvent polarity. The so-called π^* scale was developed by measuring the absorption of the solvent induced shift of several indicators using UV-Vis spectrometer and is one of the most popular scales employed to date. The energy of the $\pi \rightarrow \pi^*$ transitions are affected by the electronic polarisability of the solvating medium. The π^* scale is normalised to produce a scale from 0.00 for cyclohexane to 1.00 for dimethyl sulfoxide. The use of other indicator molecules with hydrogen bond donating and accepting abilities enables similar normalised scales to be developed for the hydrogen bonding ability of the solvent.

These scales rely on linear solvation energy relationship (LSER) which has the generalised form

$$XYZ = XYZ_0 + s\pi^* + b\beta + a\alpha \quad (3.2)$$

where XYZ and XYZ_0 are solvent-dependent properties for a given solvent and a standard reference solvent respectively. XYZ could represent reaction rates, equilibrium constants or a position/intensity of spectral absorption. The α term is a measure of the hydrogen bond donor properties β is the hydrogen bond acceptor property and π^* is the polarisability/ dipolarity parameter. The terms s , a and b are constants obtained from experiment.

The π^* , α and β parameters were obtained using the same technique as that used by R. Harris for the same liquids.²⁰ The data for the DESs used above are shown in **Table 3.2**. Note that no parameters could be determined for Oxaline which did not form a complex with Reichardt's Dye 30.

The solvatochromic parameters (α , β and π^*) were calculated for each of the DESs used in this study. This was done by measuring the UV-Vis spectra of 3 indicator dyes in each DES of interest. The total concentration of dye in the DES was kept low (~1-2 mM) to avoid any solute-solute interactions being observed. It was previously shown that the single set probe approach was suitable for measuring these parameters in DES and so this technique was employed in this work.²¹ To calculate π^* , the following formula was used with the data obtained from the indicator molecule 4-nitroaniline:

$$\pi^* = (V_{\text{solvent}} - V_{\text{cyclohexane}}) / (V_{\text{dmsO}} - V_{\text{cyclohexane}}) \quad (3.3)$$

α values were calculated using Reichardt's dye ET30 and π^* values

$$\alpha = (\text{ET}(30) - 14.6(\pi^* - 0.23) - 30.31) / 16.5 \quad (3.4)$$

β values were calculated from the data obtained for 4-nitroaniline and N, N-dimethyl-4-nitroaniline

$$\beta = 0.9 (\Delta v_{\text{cyclohexane}} - \Delta v_{\text{solvent}}) / (\Delta v_{\text{cyclohexane}} - \Delta v_{\text{propan-1-ol}}) \quad (3.5)$$

The results for Ethaline, Glyceline and Reline are in good agreement with those obtained by Harris.²⁰ It can be seen that the polarity of all of the DESs is high. The polarisability parameter is comparable to that for DMSO (1.0) and is comparable to a wide range of imidazolium based ionic liquids.²² The hydrogen bond donor properties are also high and comparable with molecular solvents such as methanol (0.93) and water (1.17). The α values are considerably higher than imidazolium based ionic liquids which is not surprising given the relatively acidic protons on both choline and the HBDs of the DESs. The β parameters are also relatively high which again is not surprising given the relatively basic nitrogen and oxygen functionalities in the HBDs.

Table 3.2: Polarity (π^*), HBD (α) ability and HBA (β) ability of used DESs.

DESs	π^*	α	β
Pentaline	0.959 ± 0.03	0.893 ± 0.02	0.61 ± 0.03
Butaline	0.929 ± 0.02	0.957 ± 0.02	0.42 ± 0.003
Ethaline	0.955 ± 0.001	1.022 ± 0.02	0.33 ± 0.007
Glyceline	0.964 ± 0.04	1.042 ± 0.06	0.32 ± 0.01
Reline	0.975 ± 0.02	1.05 ± 0.02	0.30 ± 0.01

The results from **Table 3.2** show that the polarity parameters are all very similar and are therefore unlikely to have a significant effect upon the extraction efficiency. Thiophenic species are polarisable molecules with hydrogen bond acceptor ability through the relatively basic sulfur moiety. It would therefore be expected that the solvent with the highest polarisability and hydrogen bond donor capacity would be the best solvent. This is however not the case. It can therefore be concluded that DESs are in general good solvents for thiophene but the high viscosity of some of the fluids makes extraction slow.

3.2.1.2 Effect of time

The extraction of Th into DESs is probably a slow process and so it was decided to see whether the system had actually reached equilibrium after the two hours allowed for each experiment above. Analogous experiments in DESs found that extraction was slow.¹¹ Zhu and coworkers showed the sulfur removal from fuel increased from 40% after 1 hour to and 90% after 3 hours.²³

Figure 3.3 shows the change of thiophene concentration (Th in n-decane) after extraction with DESs for 60, 120 and 180 min at 25 °C with a mass ratio of 0.8 decane: 1 DES. It can be seen that there is only a relatively small change in extraction efficiency with time suggesting that the above results are relatively close to being at equilibrium.

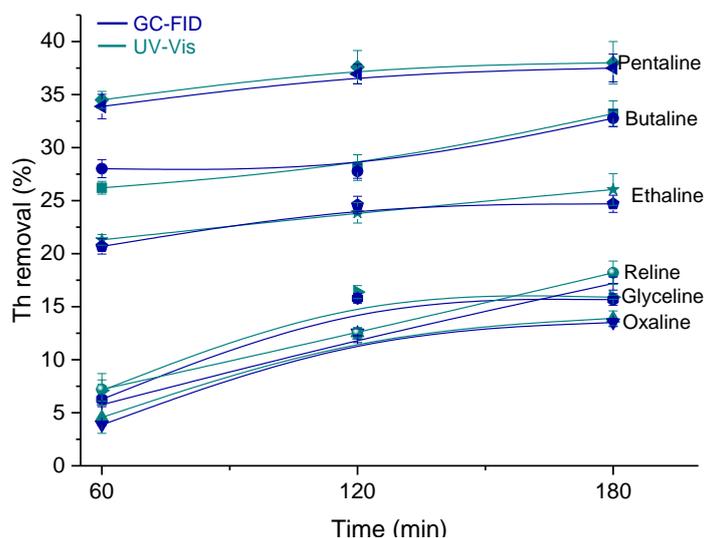


Figure 3.3: *Th extraction by DESs as a function of time, the mass ratio was 0.8 decane: 1DES, at 25 °C and 500 rpm speed stirring.*

3.2.1.3 Effect of mixing speed

Stirring the liquid-liquid system maybe affects the mass transport to the interface and should aid the extraction process. This should enable the system to reach equilibrium faster. Therefore, to study the effect of mixing rate on the extraction efficiency of Th, DESs were stirred at three different mixing rates as shown in **Figure 3.4**.

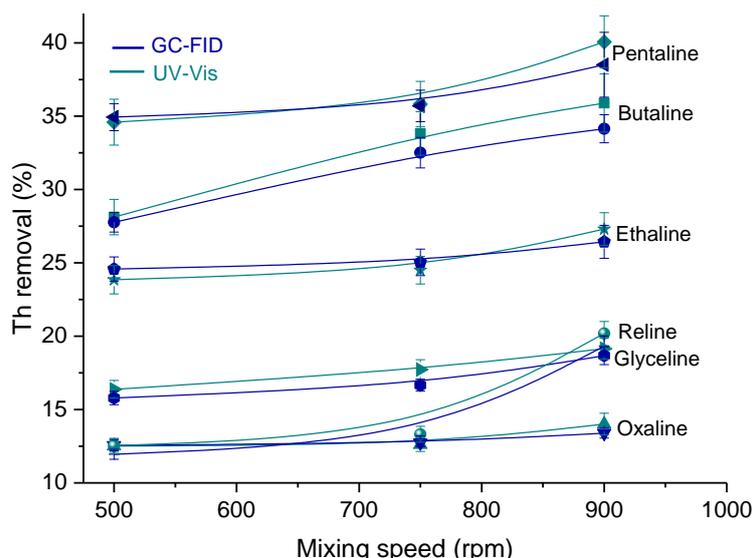


Figure 3.4: Th removal as a function to mixing rate at 25 °C, the mass ratio was 0.8 fuel: 1 DES

As can be seen in the **Figure 3.4**, at three stirring rates, there is only a slight increase in extraction efficiency when the stirring rate exceeded 900 rpm. The only system that showed a significant increase in extraction was Reline which is probably because it is more viscous than most of the other DESs used.

3.2.1.4 Effect of phase ratio

As for every industrial process, minimising the volume of solvent extractant is important.¹⁴ However, very low solvent utilisation is probably not possible in this case, and so, an optimisation is required. As shown in **Figure 3.5**, the effect of the fuel: DES ratio was studied using the same thiophene mass ratio as used in the literature.^{8, 9, 24}

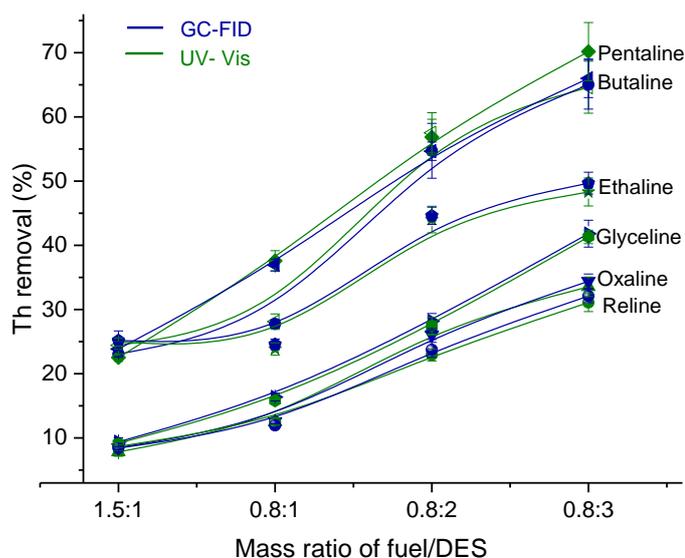


Figure 3.5: Extraction of Th by DESs at 25 °C, 500 rpm mixing speed, at different mass ratios during 2 hrs stirring

As expected, with increasing DES, the Th extraction efficiency increases. At low DES ratios all three glycolic systems showed similar extraction efficiencies but as the amount of DES was increased, the thiophene extraction also increased. This shows that the above results are limited by the solubility of Th in the DES. Surprisingly although Th is polarisable and capable of H-bonding it partitions preferentially into the non-polarisable decane rather than the DES.

3.2.1.5 Multiple extraction

In order to increase thiophene removal, multiple extractions were performed with fresh batches of DESs for the desulfurisation of thiophene. Each extraction was carried out at 25 °C, fuel with a 0.8:1 fuel: DES mass ratio, 500 rpm stirring speed for 90 min each. The results are presented in **Figure 3.6**.

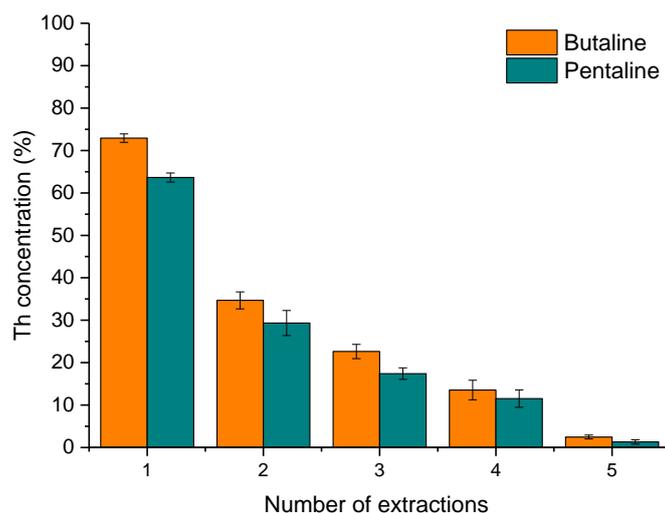


Figure 3.6: Multiple extraction times of thiophene in n-C₁₀.

It is worth noting that, after five cycles, the S-content unmistakably reduced to 1.3% and 2.4% by Pentaline and Butaline respectively. While this is a functional method of reducing Th content, it is in no way a practical alternative for fuel desulfurisation.

3.2.1.6 Recycling of used DESs

Regeneration of used DESs after extractive desulfurisation is obviously vital. **Figure 3.7** shows the extractive desulfurisation efficiency of thiophene into two DESs.

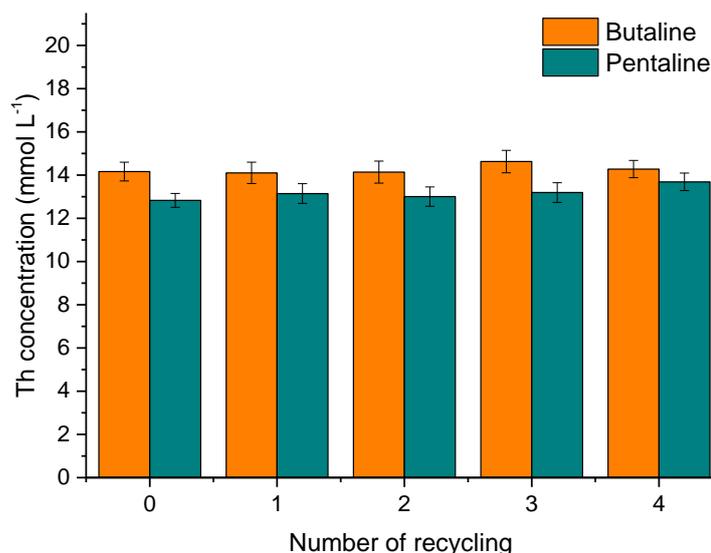


Figure 3.7: Extraction performance with recycled Butaline and Pentaline, conditions; 0.8:1 mass ratio of fuel oil and extractant, 500 rpm, 60 min stirring at 25 °C.

After each extraction, the DES was recycled and reused up to 4 times. It can be seen that the liquid can be recycled without significant decrease in the extraction efficiency.

Regeneration of the used Pentaline and Butaline was performed by diethyl ether (DEE) using rotary evaporator and after regeneration, the composition of the DES remained unchangeable. Moreover, the feasibility of using DEE is that it is immiscible in DESs, because of the hydrophobic and the ability of it to re-extract thiophene in the used extractant. It could be seen from above figure that Pentaline and Butaline over four times were employed repeatedly without any conspicuous loss of extraction potential and DESs can be characterised as a benign re-usability.

To characterise the stabilities of recycled DESs and to determine the identification peaks required to perform compositional analysis for DESs, ^1H NMR was used as seen in **Figure 3.8**.

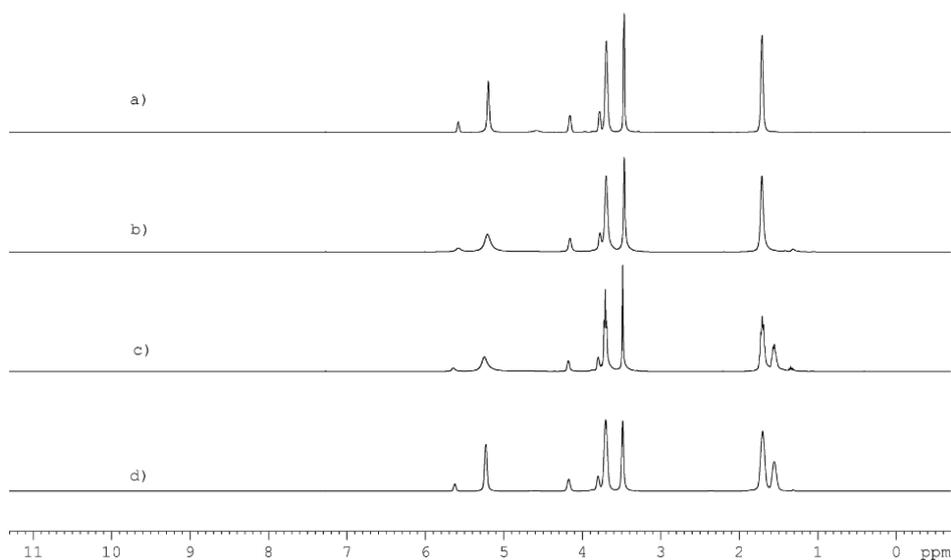


Figure 3.8: Structural comparison of recycled and pure DESs, a) pure Butaline, b) recycled Butaline, c) pure Pentaline, d) recycled Pentaline.

The ^1H NMR spectra show that the structures of Pentaline and Butaline does not change after recycling and does not contain any detectable impurities. It is evident that in whole thiophene removal process, the composition of DESs is stable not only from ^1H NMR characterisation, but also from extraction efficiency aspect. It was used to validate that the purity of DESs was retained after recycling.

3.2.1.7 Repeated use of DESs

For extraction desulfurisation of thiophene in diesel fuel, repeated use of Pentaline and Butaline was done to see if they have become saturated. From **Figure 3.9**, the extraction capabilities of the DESs are dropped with repeated use. After five times of repeating use, the extraction efficiency almost was lost, because of the saturation of extractants by Th. So, it stops absorbing Th.

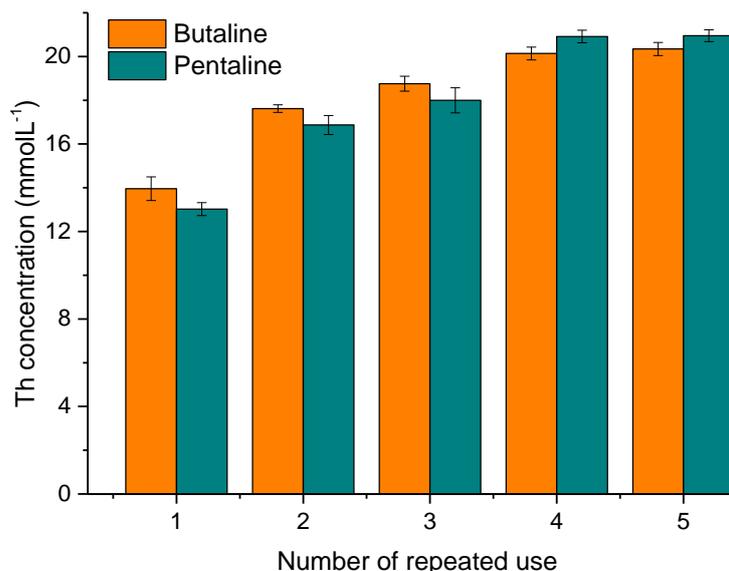


Figure 3.9 : The influence of repeated use of DESs in extraction of thiophene in decane, condition: 500 rpm, 1hour stirring, 25 °C, 0.8:1 molar ratio of decane/DES.

The optimum operating conditions of thiophene desulfurisation by DESs were summarised as follows: extractant temperature: 35 °C, reaction time: 1 hrs, mass ratio of DES: oil fuel: 1:2, stirring rate: 750 rpm.

3.2.2 Thermodynamics of Th extraction

Analysis of **Figure 3.2** shows that the transfer of thiophene from decane to the DES increases with temperature which shows that the phase transition must be endothermic (ΔH is positive). Given that for most of the processes the partition of thiophene has an equilibrium constant of less than 1 the Gibbs' Energy of transfer must be positive.

Since thiophene is polarisable and has the capacity to accept a hydrogen bond it would be logical that it would partition into the DES rather than the non-polar alkane layer. The observation that it does not suggests that it is thermodynamically unfavourable to dissolve Th in the DES. Energy is recovered when the DES interacts with Th, however energy is also required to form a void for the Th to fit into. It could therefore be argued that liquids with a lower energy for void formation should be better for dissolving Th.

It has previously been shown that the surface tension can be used to measure the energy required to make a cavity in the liquid.^{25, 26} **Figure 3.10** shows the surface tension as a function of temperature for the 6 extractants used above which were measured using a Krüss Tensiometer.

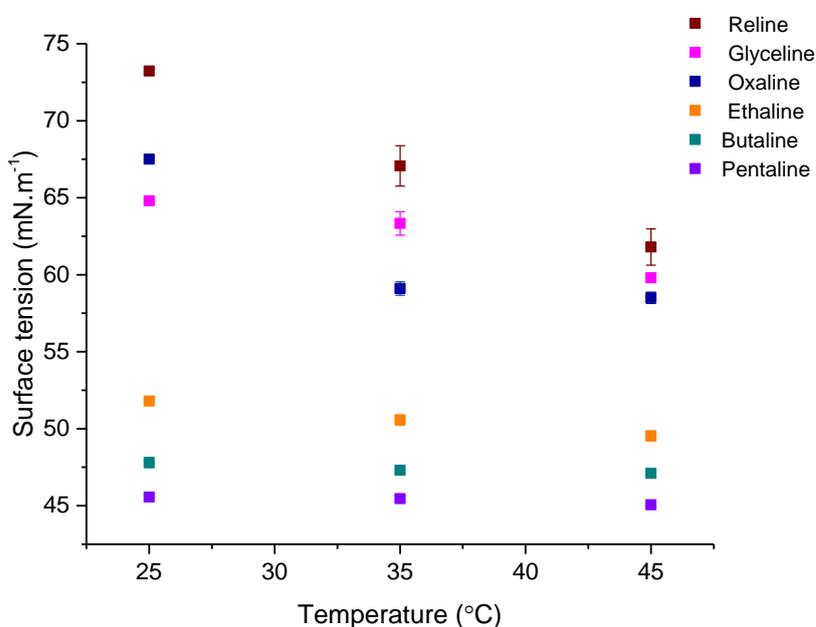


Figure 3.10: Surface tensions of the DESs used above as a function of temperature.

Figure 3.10 shows that Pentaline, Butaline and Ethaline have lower surface tensions than the other liquids which correlates with the extraction efficiency shown in **Figure 3.2**. Toh et al., revealed that low surface tension allows extractant to form emulsion owing to the mechanical excitation, hence growing interfacial area and capability of extraction.²⁷ A low surface tension decreases the cohesive forces at the interface, hence increasing liquid solubilisation.²⁸ The average void radius $\sqrt{\langle r \rangle}$ can be related to the surface tension (γ) by the equation **3.6**.^{29, 30}

$$4\pi \langle r^2 \rangle = \frac{3.5kT}{\gamma} \quad (3.6)$$

where k is the Boltzmann constant and T the absolute temperature.

The probability of the finding a hole that is bigger than ion ($P(r > R_{+/-})$) (equation 3.7) can be related to the size of ions and voids.²⁹

$$P = 0.602a^{7/2} \left[-\frac{r^5 e^{-ar^2}}{2a} + 2.5 \left\{ \left[-\frac{r^3 e^{-ar^2}}{2a} + \frac{1.5 \left(\frac{r e^{-ar^2}}{2a} + \frac{0.443 \operatorname{erf} \sqrt{ar}}{r^{3/2}} \right)}{a} \right] / a \right\} \right] \quad (3.7)$$

The average void radius in the liquid can be calculated using equation 3.6 and the data in **Figure 3.10**:

Table 3.3: Average void radius of DESs extractants as a function of temperature.

Temperature (°C) ± 0.4	Void radius (Å)					
	Pentaline	Butaline	Ethaline	Oxaline	Reline	Glyceline
25	1.56 ± 0.004	1.52 ± 0.005	1.46 ± 0.003	1.28 ± 0.001	1.23 ± 0.002	1.31 ± 0.001
35	1.59 ± 0.005	1.56 ± 0.004	1.50 ± 0.005	1.39 ± 0.005	1.31 ± 0.01	1.34 ± 0.01
45	1.62 ± 0.003	1.58 ± 0.003	1.54 ± 0.005	1.42 ± 0.004	1.38 ± 0.01	1.40 ± 0.003

Comparing the data in **Figure 3.10** and **Table 3.3** it can be concluded that the energy required to make a void in the liquid is the controlling factor limiting the partition of Th into the DES. The thermodynamics of Th partition can be determined knowing the partition coefficient as a function of temperature. These parameters were determined at 298 and 308 K using the Gibbs and Van't Hoff equations.³¹⁻³³

$$\Delta G = -RT \ln K_p \quad (3.8)$$

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3.9)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (3.10)$$

where, R is the universal gas constant, T is the absolute temperature, K_p is the value of partition coefficient at equilibrium defined as:

$$K_p = \frac{(\text{molality of Th})_{\text{in DES}}}{(\text{molality of Th})_{\text{in decane}}} \quad (3.11)$$

A solution of Th was prepared in decane (0.124 mmol in 2 g decane) and then extracted at two different temperatures (25 and 35 °C) with 2 g of DES, at a stirring rate of 700 rpm for 60 min. The decane layer was analysed by GC and the data are shown in **Table 3.4**.

Table 3.4: Partition coefficients and Gibbs energy change for Th partition from decane to DESs.

DES(s)	K_p at		ΔG (kJ mol ⁻¹) at		ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹) at 298 (K)
	298 (K)	308(K)	298(K)	308 (K)		
Pentaline	0.46 ±0.02	0.52 ± 0.007	+1.9 ± 0.1	+1.7 ± 0.04	+9 ± 2.1	+23.8 ± 7.4
Butaline	0.39 ± 0.007	0.45 ± 0.03	+2.3 ± 0.04	+2.1 ± 0.15	+10.4 ± 3.2	+27.13 ± 5.1
Ethaline	0.3 ± 0.002	0.35 ± 0.001	+3 ± 0.02	+2.6 ± 0.04	+13.2 ± 0.5	+34 ± 1.7
Oxaline	0.1 ± 0.007	0.16 ± 0.01	+5.6 ± 0.16	+4.8 ± 0.2	+31.2 ± 0.9	+85.9 ± 3.4
Glyceline	0.09 ± 0.01	0.14 ± 0.004	+6 ± 0.3	+5 ± 0.07	+35 ± 5.9	+97.4 ± 7.3
Reline	0.06 ± 0.002	0.14 ± 0.01	+7.2 ± 0.08	+5.04 ± 0.2	+70.8 ± 3.2	+213.46 ± 11.1

The data in **Table 3.4** confirm that the transfer of Th from the alkane layer to the DES is controlled by the enthalpy of solvation. ΔG is positive but small showing that the process is nonspontaneous so the equilibrium lies largely towards the thiophene being in oil phase. As the temperature increases, ΔG decreases i.e. the thiophene partitions into the DES. It can be seen that the entropy of partition in to the DESs is positive which would also seem logical as the thiophene is disrupting the structure of the ordered DES which confirms that it is the formation of voids that limits partition. This is the first time that this important conclusion has been proposed about DESs and ILs in general.

Figure 3.11 shows a plot of thiophene enthalpy of phase transfer (**Table 3.4**) as a function of surface tension (**Figure 3.10**) at 25 °C and a good correlation between the two parameters can be seen. The surface tension is a measure of the inter-molecular/ionic forces in the liquid and are an indicator of the energy required to form a void in the liquid.

This correlation suggests that the enthalpy of transfer for Th is governed by the ability to form a hole of sufficient dimensions for the solute to fit in.

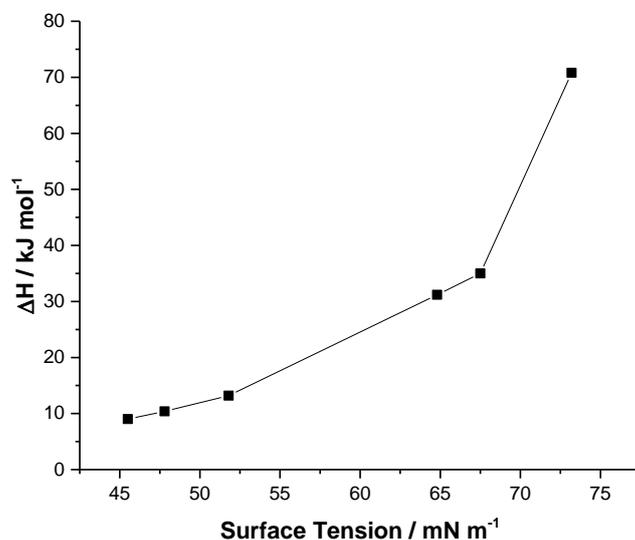


Figure 3.11: Plot of measured surface tension of different DESs vs the calculated ΔH of transference of Th from decane to DESs at 25 °C.

3.2.3 K_P determination of BT and DBT extraction

If the conclusion of the previous section is correct then extracting molecules of similar polarity but different sizes should be more difficult as the molecules get larger. In this experiments, bigger molecules of S-compounds (BT, DBT) were used for their extraction from decane into DESs to determine the influence of the solute size on the extraction efficiency.

Nie and coworkers reported that S-removal efficiency depends on the molecular structure of sulfur compounds, the size and the structure of both cations and anions of the ILs.³⁴ The results of Chen et al. showed that DBT extraction ability is better than Th removal by ILs due to the π -electron density on the molecule.³⁵ Similarly, Otsuki et al. reported that the differences in S-removal by ILs was probably due to the variation of aromatic π -electron densities of sulfur atom in aromatic S-species.^{36,37} In contrast to Chen's research,

Yu and co-workers proposed that increased intermolecular forces meant that Th removal was easier than DBT extraction.³⁸

In a first set of experiments, the desulfurisation of decane containing separately 17.47 mmol L⁻¹ BT and DBT (similar to the Th concentration) was investigated. Rather than testing all the DESs used above, two DESs (Pentaline and Glyceline) were studied using the same conditions (see **Figure 3.2**), i.e. 0.8 fuel- 1 DES mass ratio, time of stirring: 2hrs, speed rate: 500 rpm at 35 °C.

Figure 3.12, shows that the extraction efficiency of thiophenic compounds in Pentaline was in the order Th > BT > DBT. Glyceline showed the same order although with a lower extraction efficiency which is what would be expected given the size of the extracts and the sizes of the holes. The average radius in all cases is significantly smaller than that needed to accommodate the solute. The solutes are all non-spherical but approximations of their radii in the plane of the molecule are; Th = 5.2 Å, BT = 6.9 Å, DBT = 8.0 Å. It is clear that their dimensions are considerably larger than the hole radii listed in **Table 3.3** so a significantly larger hole will need to be made to accept the solute.

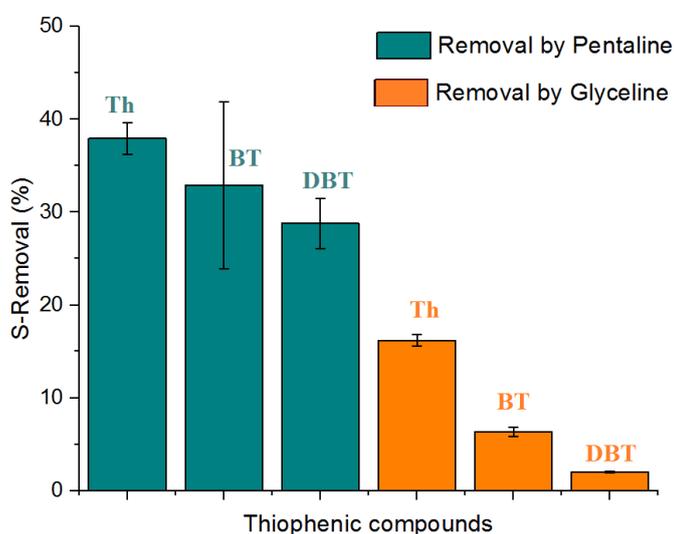


Figure 3.12: Extraction of BT and DBT by DESs measured by GC-FID.

It can therefore be concluded that with thiophenic compounds the over-riding factors which control the partitioning of species between an oil and a DES are the size of the solute and the surface tension of the liquid.

The thermodynamics of BT and DBT extraction by these two DESs can be determined knowing the partition coefficient. The temperature effect on the BT and DBT removal could be evaluated in terms of their thermodynamic values calculated from the equations 3.8, 3.9, 3.10 and 3.11 (see Table 3.5).

Table 3.5: Partition coefficients and Gibbs energy changes for BT and DBT partitions from decane to two DESs.

DES		Pentaline			Glyceline		
S- compound		Th	BT	DBT	Th	BT	DBT
K_P at 298 (K)		0.46 ± 0.02	0.49 ± 0.01	0.31 ± 0.05	0.09 ± 0.01	0.07 ± 0.05	0.042 ± 0.02
K_P at 308 (K)		0.52 ± 0.007	0.55 ± 0.03	0.32 ± 0.1	0.14 ± 0.004	0.11 ± 0.014	0.05 ± 0.01
ΔG (kJ mol ⁻¹)	298 (K)	+1.9 ± 0.1	+1.8 ± 0.05	+2.9 ± 0.4	+6 ± 0.3	+6.5 ± 1.2	+7.8 ± 0.8
	308 (K)	+1.7 ± 0.04	+1.5 ± 0.1	+2.9 ± 0.7	+5 ± 0.07	+5.6 ± 0.3	+7.6 ± 0.4
ΔH (kJ mol ⁻¹)		+9 ± 2.1	+10 ± 2	+2.2 ± 2.1	+35 ± 5.9	+32.2 ± 8.1	+11.7 ± 2.8
ΔS (J mol ⁻¹ K ⁻¹) at 298 (K)		+23.8 ± 5.4	+27.5 ± 7.1	-2.3 ± 0.3	+97.4 ± 7.3	+86.4 ± 8.5	+13.1 ± 4.2

From the data of the table, it is logical that the reactions of the extractions are nonspontaneous owing to ΔG being positive. The enthalpies of BT and DBT extraction are endothermic, because of the difficulty to form holes due to the high surface tension. From the values of Entropy, it is clear that ΔS drives BT and DBT extraction.

Recently, Abbott and co-workers,³⁹ have expanded the study of the effect of solute hydrogen bonding on their extraction by DESs. The authors found that if the solute being transferred to the DES has a larger enthalpy of interaction with the DES than that between the chloride and the HBD of the DES, then the transfer should be exothermic and the partition coefficient should be significantly larger than that observed for less polar solutes such as those listed in Table 3.4 and Table 3.5. To test this idea, the transfer of four aliphatic solutes with different functional groups was tested from cyclohexane to Ethaline. The results are shown in Table 3.6.

Table 3.6: Partition coefficients and Gibbs energy change for functional groups partition from cyclohexane to Ethaline ($T \pm 0.6$ °C).³⁹

Solute	K_p at		ΔG (kJ mol ⁻¹) at 25 °C		ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹) at 25 °C
	25 °C	40 °C	25 °C	40 °C		
Butanoic acid	100	100	--	--	--	--
1-Pentanol	1.22 ± 0.02	0.95 ± 0.02	-0.5 ± 0.04	+0.1 ± 0.06	-12.7 \pm 0.3	-44.4 \pm 3.1
Ethyl acetate	0.10 ± 0.01	0.20 ± 0.06	+5.5 ± 0.3	+4.0 ± 0.7	+38.4 \pm 3.6	+110 \pm 12
2-Pentanone	0.02 ± 0.02	0.04 ± 0.02	+9.4 ± 1.5	+8.4 ± 1.1	+30.0 \pm 6.4	+69.0 \pm 5.7

The four solutes chosen were butanoic acid, 1-pentanol, ethyl acetate and 2-pentanone as they all have approximately the same size, but visibly the first two are strong hydrogen bond donors whereas the last two are significantly weaker. The data in **Table 3.6** show that the butanoic acid is extensively completely transferred to the DES whereas the corresponding alcohol lies predominantly in the DES. The enthalpy of transfer cannot be calculated by this method but it is fair to assume that it is exothermic as is that for 1-pentanol. It is interesting to note that the transfer of 1-pentanol causes a slight ordering of the DES unlike the other solutes. For both ethyl acetate and 2-pentanone the enthalpy of transfer is endothermic but the partition coefficient is very much into the alkane phase rather than the DES.

It has previously been shown that the energy of hole formation is very important at controlling diffusion and conductivity so it is not surprising that it should also be involved in the thermodynamics of solvation and phase equilibria.²¹

3.3 Applications on real diesel fuel

Owing to the variety of polyaromatic and heterocyclic compounds (mercaptans and thiophene derivatives) in real fuel oils, the ILs-EDS is technically complex; therefore, only limited studies have been carried out on EDS for real fuel oils.⁴⁰ **Table 3.7** summarises the results of some EDSs by ILs for real fuel oils at optimised conditions.⁴⁰

Table 3.7: EDS by ILs for real fuel oils at optimised conditions.⁴⁰

ILs	Oil	Initial S: (ppm)	IL-oil mass ratio	Temp. (K)	Time (min)	S extraction efficiency (%)
[BMIM][N(CN) ₂]	Gasoline	300	1 : 1	298	20	18.63
[BMIM][N(CN) ₂]	Diesel	380	1 : 1	298	20	32.82
[HPy][BF ₄]	Diesel	83.2	1 : 1	RT	15	16.7
[OPy][BF ₄]	Diesel	83.2	1 : 1	RT	15	24.3
[BMIM][BF ₄]	Diesel	1572	1 : 5	RT	20	8.23
[C ₄ Py][BF ₄]	Diesel	1572	1 : 5	RT	20	7
[C ₈ Py][BF ₄]	Diesel	1710	1 : 5	RT	20	8.16
[BMIM][BF ₄]	Diesel	385	1 : 1	303	30	55.8
			1 : 3	303	30	40.1
			1 : 5	303	30	27.7
[BMIM][BF ₄]	Gasoline	180	1 : 1	303	30	70
			1 : 3	303	30	59.2
			1 : 5	303	30	44.8
[EMIM][OAc]	Gasoline	240	1 : 1	298	20	38.7
	Diesel	1000	1 : 1	298	20	12
[HMpy][NTf ₂]	Gasoline	240	1 : 1	298	20	30
	Diesel	1000	1 : 1	298	20	37.8

Owing to their interest for green chemistry, more than 16 companies worked with QUILL to develop generic ionic liquid technologies for industrial applications.^{41,42} Moreover, in 2000, NATO sponsored an initiative entitled “Green Industrial Applications of Ionic Liquids” to encourage development of new strategies for ILs in industrial applications.^{41,}

43

Real diesel fuel contains a mixture of components, including alkyl-aromatic, paraffinic, aromatic and a range of polyaromatic hydrocarbons,⁴⁴ therefore, to illustrate the difference of extractive desulfurisation and polymerisation performance of DESs between decane and real diesel, a complementary experiment is conducted using commercial diesel which had been partially desulfurised and this was re-sulfurised using the compounds tested above. The same approach has also been used by other articles in the literature.⁴⁵⁻⁴⁷

3.3.1 Th in real diesel

Thiophene has been used as an example instead of other aromatic sulfur compounds for removal by DESs under optimisation of the operational conditions. Thus, prepared diesel fuel samples were extracted with the six DESs used above at the same optimum

desulfurisation conditions. Each prepared Th-containing fuel was then added to freshly prepared DESs in an initial mass ratio of 1/1 (17.47 mmol L⁻¹ Th in a treated diesel oil). The two-phase mixture was vigorously stirred for 1 hour at 30 °C, after which it was allowed to separate. In all cases, the diesel samples needed up to 15 min for complete separation.

GC-FID spectra have taken from all used diesel samples at all extraction procedures. A similar result was found in the case of real diesel. In each sample of the diesel extraction (**Figure 3.13**), the DES steadily lowered the sulfur content.

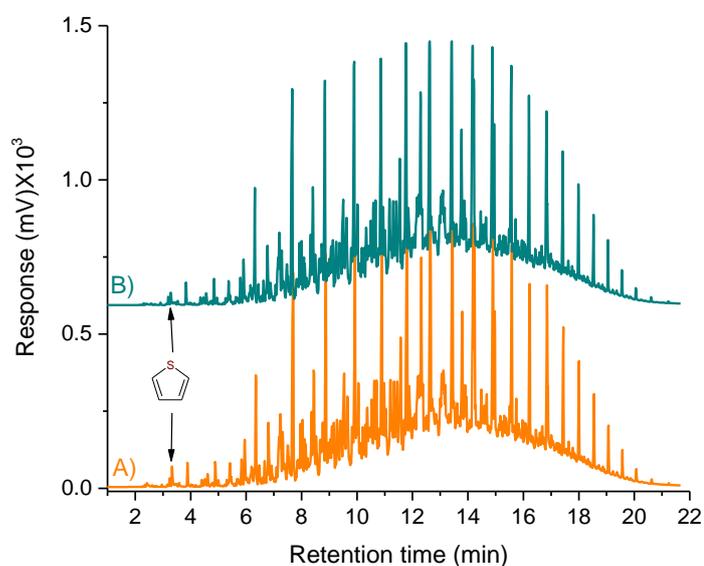


Figure 3.13: Chromatograms of Th-based commercial diesel fuel A) before, B) after extraction by Pentaline.

Figure 3.14 shows the results of extractive desulfurisation of the true diesel with 6 DESs. Pentaline displays the highest S-removal capability from diesel in a single stage extraction. The order of extraction efficiency is the same as those presented in **Figure 3.2** for decane as for diesel.

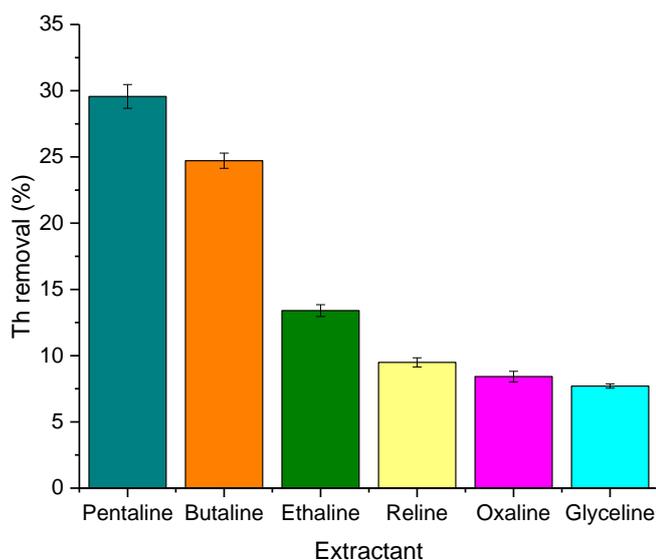


Figure 3.14: Th percentage removal from commercial diesel fuel measured by GC-FID. Extraction conditions; diesel/DES ratio = 1, at 30 °C, 750 rpm during 1 hour.

However, the extraction efficiency for thiophene removal from diesel fuel by Pentaline, Butaline and Ethaline is decreased to 30, 25 and 13 % respectively. This is probably due to the extraction of other constituents of the fuel oil which are then saturating the DES. With respect to ability of Reline, Oxaline and Glyceline, their efficiency for reducing Th concentration from diesel fuel remains almost constant which is principally due to their low capability.

3.3.2 Multi-EDS and regeneration of DES

For the technical application of the DES-extraction, the regeneration and subsequent recycling of the IL is of significant concern. The most promising re-extraction mediums are low-boiling hydrocarbons like pentane, hexane or ether (DEE). The structure of the regenerated Butaline was confirmed by ^1H NMR. Butaline was extracted by diethyl ether (2 times) and evaporated under vacuum for 3 hrs at 303 K. Analysis of the DES by ^1H -NMR⁴⁸ spectroscopy indicated that its purity was retained. The results of the DES recycling experiment are shown in **Table 3.8**.

Table 3.8: Recycling of Butaline, extraction condition: 30 °C, 1 hour; mass ratio diesel oil/ DES, = 2/1; initial sulfur content, 17.47 mmol L⁻¹.

Run	Extraction (%)
1	20.4 ± 0.9
2	19.9 ± 0.4
3	19.8 ± 0.7
4	19.6 ± 0.6

For four consecutive extraction cycles, commercial diesel fuel samples were separately treated with the same sample of Butaline (after regeneration), the results of which are shown in **Table 3.8**. It can be seen that Butaline was utilised repeatedly four times with negligible apparent loss of extraction power.

Although a second high S-removal by Butaline is obtained as shown in **Figure 3.14**, the final S-content in fuels cannot meet the definite requirement of low sulfur fuels (e.g. 0.11–0.6 mmol L⁻¹). Consequently, multistage extractions need to be performed, and the results are shown in **Table 3.9**.

Table 3.9: Multi-stage desulfurisation of treated desulfurised real diesel oil. Extraction conditions: 30 °C, 60 min; mass ratio diesel oil/ DES 2/1; initial sulfur content, 17.47 mmol L⁻¹.

Stage	Extraction (%)
1	20.4 ± 0.9
2	31 ± 1
3	44.1 ± 1.6
4	52 ± 1.7
5	66.6 ± 5

The S-content in diesel reduced from 17.47 to 5.8 mmol L⁻¹ (66.6 % of S-removal) after 5 cycles with fixed mass ratio of model fuel to DES as 2:1, within 60 min at 30 °C. As a result, multiple extractions are effective for the reduction of S-content of liquid fuel an

acceptable level. Nevertheless, as shown in **Table 3.9**, more extraction steps are necessary in case of commercial diesel oil to reach future technical sulfur content specifications.

It is clear from a practical and financial perspective that simple liquid-liquid extraction is not a viable procedure to remove thiophenic compounds from diesel oil. To carry out multiple extractions followed by multiple back extractions not a practical process for a relatively low value product. An alternative approach is to drive the equilibrium by making a solid product from the thiophenic materials.

3.4 Extractive polymerisation

3.4.1 Extractive electropolymerisation of Th into DESs (Ethaline)

One option to form a solid product from the thiophenic compounds would be to polymerise thiophene to polythiophene (PTh).



In addition, thiophene could be converted to a solid thiophene sulfoxide catalysed by DESs in the presence of H₂O₂ as oxidising agent.⁴⁹ The issue with this approach is that H₂O is introduced as an aqueous solution as a by-product which will contaminate the oil. In the current study it is proposed that Th could be converted into a solid by polymerising it to polythiophene (PTh). This is an interesting material which has been used in numerous electronic devices as a semiconductor and electrochromic material.⁵⁰⁻⁵²

Usually, polythiophene has been prepared from homo-polymerisation of un-substituted thiophene. There are many groups who have studied the polymerisation of thiophene in molecular solvents. Totirillon and Garnier reported the preparation of polythiophene in the acetonitrile (CH₃CN) in the presence of N(Bu)₄ClO₄.⁵³ They found that thin or thick film polymer deposits could be reproducibly obtained with similar conducting properties and chemical composition. They concluded that unsubstituted polythiophene is very stable under vacuum and in the air. In addition, Li et al. formed polythiophene nanoparticle in the presence of the trace amount of cetyltrimethylammonium bromide with ferric(III) salt and CH₃CN as oxidant and aqueous solution respectively.⁵⁴ Several groups have also studied the polymerisation in ionic liquids, for example Pringle and coworkers⁵⁵ utilized 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) amide (EmimTFSA) and N,N-butylmethylpyrrolidinium bis (trifluoromethanesulfonyl) amide (P_{1,4}TFSA) to form polythiophene. Their results showed that the physical properties and

the growth of the polymer was different in the two liquids owing to the nature of the imidazolium cation which is planar and aromatic compared to the pyrrolidinium cation which is non-planar, larger and aliphatic. It was concluded that polythiophene films produced from the pyrrolidinium based ionic liquid have a higher electroactive surface area and are denser and slightly smoother than those produced from their imidazolium analogues. Moreover, Janiszewska and Osteryoung carried out successfully unsubstituted polythiophene formation by (Bmim)Cl/ AlCl₃ at +1.7 V.⁵⁶ They found that the reaction of polythiophene preparation was appeared in an ambient room temperature molten salt and was completely irreversible.

In this study, Ethaline has been used to extract and electro-polymerise thiophene by cyclic voltammetry (CV) at different scan rates, at 30 °C. Ethaline has been attempted with and without FeCl₃ as Lewis acidic, using Pt working and counter electrodes and a Ag wire reference electrode. The cyclic voltammetric response of thiophene in Ethaline is shown in **Figure 3.15**.

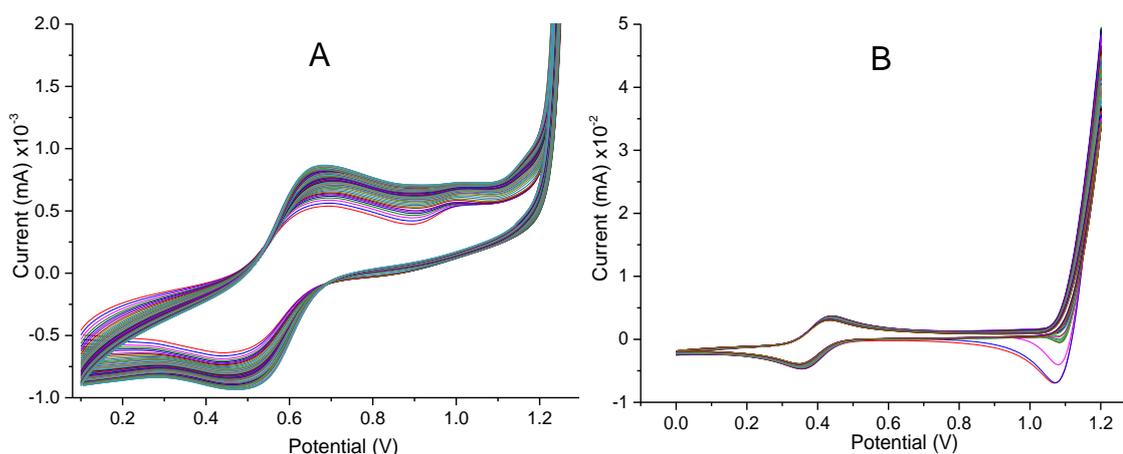


Figure 3.15: CVs for polymerisation of (0.15 mol/L) thiophene in (A) Ethaline, (B) mixture of Ethaline with (0.077 mol/L) of FeCl₃, 40 cycles, scan rate: 50 mV s⁻¹.

Figure 3.15A shows the clear oxidation and reduction of the thiophene with a half-wave potential of approximately 0.6 V. Scans to 1.2 V do not show the further oxidation to form the polymer growing on the electrode surface. The main reason for this is probably because Ethaline is a protic solvent containing a hydroxyl group and it could also possibly contains small amounts of water. A large number of studies have shown that the presence of traces of water in the medium precludes the electropolymerisation of thiophene through

reaction of the water molecule with thiophene radical cations which make a passivating layer on the working electrode.⁵⁷⁻⁵⁹

The same experiment was repeated using ferric chloride as an electrocatalyst. Ferric chloride is known to be a good chemical catalyst for the polymerisation of thiophene. A redox process is again observed in **Figure 3.15B**, but this time the redox half wave potential is at a lower over-potential (0.4 V) suggesting that it is the Fe^{II/III} redox couple. Again no signal for the polymer was observed which again is probably due to the protic nature of Ethaline.

3.5 Conclusion

A variety of DESs have been used for the extractive desulfurisation (EDS) of thiophenic species in oil-like liquids. It has been shown that EDS efficiency increases slightly as a function of temperature and time but the main factor affecting partitioning of species into the DES is the solubility of S-compounds in the DES. In general, stirring has only a small influence on thiophene removal except in Reline where it is probably the high viscosity which results in a low extraction efficiency due to taking a long time to reach equilibrium. The polarity parameters of the DESs are all very high and do not correlate with the extraction efficiency.

It was shown, however that the extraction process could be dominated by the energy required to make holes of suitable dimensions to fit aromatic S-species. There is a good correlation between the extraction efficiency of S-compounds and the energy required to make a void in the DES. It was shown that DES composed of choline chloride and 1,5-pentandiol showed the best extraction performance for Th, BT and DBT. The non-spontaneity of their extraction by DESs is governed by the positive value of ΔG which occurs due to the endothermic enthalpy of solvation. The positive value of ΔS indicates that aromatic S-compounds make the DESs more disordered upon inclusion. The positive value of ΔH is thought to be due to the large energy required to make a hole for the solutes in the DES. This results from the high surface tension of DESs. Moreover, size of solutes also has a direct effect on the partitioning of sulfur molecules into extractors. The extractive performance using DESs followed the order: Th > BT > DBT, depending on the size of the solute. Therefore, removal of S-species from diesel fuel into DESs depends on the average size of the holes in the DES and the size of the S-containing molecules.

Partition into DESs is greatest where the enthalpy of solvation is exothermic. This clearly occurs when the solute is strongly hydrogen bonding and to achieve this the hydrogen bond formed between the solute and the chloride of the DES should be larger than that between the chloride and the HBD of the DES.

Thiophene partitioned into a type 3 DES but could not be electropolymerised and this is thought to be due to the high Brønsted acidity in the form of the HBD and traces of water which will terminate any growing polymer chains. The possibility of reducing sulfur content from commercial real diesel fuel oil by extractive desulfurisation using DESs was examined at optimised conditions. Desulfurisation conditions parameters are optimised for each DES to achieve the desired sulfur reduction and it was applied on diesel spiked with Th as an example. The results showed that extraction capability for Th removal from natural diesel by each one of Pentaline, Butaline and Ethaline is decreased to 29.6 %, 24.7 % and 13.4 % respectively which was slightly lower than that for decane.

After four consecutive extraction cycles of Th, extractant (Butaline) still was pure. In addition, during the processes, after five cycles with a fixed mass ratio of real diesel fuel to DES, 66.6 % of sulfur contaminant was removed by Butaline. The used DES saturated with sulfur compounds could easily be regenerated by back extraction with diethyl ether.

Extractive electrochemical polymerisation of Th and BT was attempted in the DESs but no polymer could be grown on the electrode surface. This was thought to be due to the presence of chloride and water which both terminate chain growth. This chapter has shown that while thiophenic species can be extracted into DESs, it is not possible to separate them using electropolymerisation. An alternative approach that may be possible could be to cool the DES to cause the thiophenic compounds to either precipitate (BT and DBT) or to separate (Th). While this was not studied further during this project it is discussed later in **Chapter 6**. In the next chapter, electrochemical polymerisation of Th, BT and DBT will again be attempted in a 1:1 (Bmim)Cl: FeCl₃ ionic liquid. In **Chapter 5**, the chemical polymerisation of the same thiophenic compounds will be attempted in a 1:2 (Bmim)Cl: FeCl₃ ionic liquid.

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Chapter four: EDS and electropolymerisation using (Bmim)Cl

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4. Extractive electropolymerisation

4.1 Introduction

In the previous Chapter, Ethaline was used to extract Th and its analogues from decane. The partition coefficient was surprisingly found to favour Th remaining in the oil phase and so electropolymerisation was attempted to drive the equilibrium towards the DES phase. However, due to the high proton activity of Ethaline,^{1, 2} polythiophene could not be formed after extraction into the DESs. The aim in this Chapter is to attempt to electropolymerise aromatic sulfur compounds (thiophene and its polycyclic analogues benzothiophene and dibenzothiophene) in (Bmim)Cl based liquids. Firstly, this will be attempted electrochemically with and without an electro-catalyst: ferric chloride. In addition to the amount of polymer produced the reaction rate of the extractive electropolymerisation will also be attempted.

The physical properties of the eutectic formed between (Bmim)Cl and FeCl₃ have previously been reported³⁻⁶ and it was shown that (Bmim)Cl is hydrophilic whereas the 1:1 (Bmim)Cl: FeCl₃ mixture is hydrophobic.^{7, 8} More specifically, the strong acidity of the (FeCl₄⁻) anion forms a complex with the aromatic ring of the Bmim cation.⁹

The main novelty in this Chapter is that (Bmim)FeCl₄ is used as both an extractive phase and an electrocatalytic medium to electropolymerise thiophene. Additionally, the role of the Lewis acidic FeCl₃ in the IL is explained. As highlighted in the previous chapter, solvent extraction is a practically infeasible method of removing thiophenic compounds but an electrocatalytic method where the product phase separates as a solid may be potentially viable.

4.2 Extractive electropolymerisation of Th

To get around the problem caused by the protic DESs, an aprotic liquid was used. In this case a mixture of butyl imidazolium chloride with ferric chloride was used. This has previously been made and characterised by Csihony et al.¹⁰ This should be strong chemical catalyst for thiophene polymerisation and should enable the separation of solid polythiophene from the two liquid phases as outlined in **Figure 4.1**. In addition the strong

Lewis acidity of FeCl_3 should ensure that the activity of Cl^- , which can inhibit polymerisation, is low.

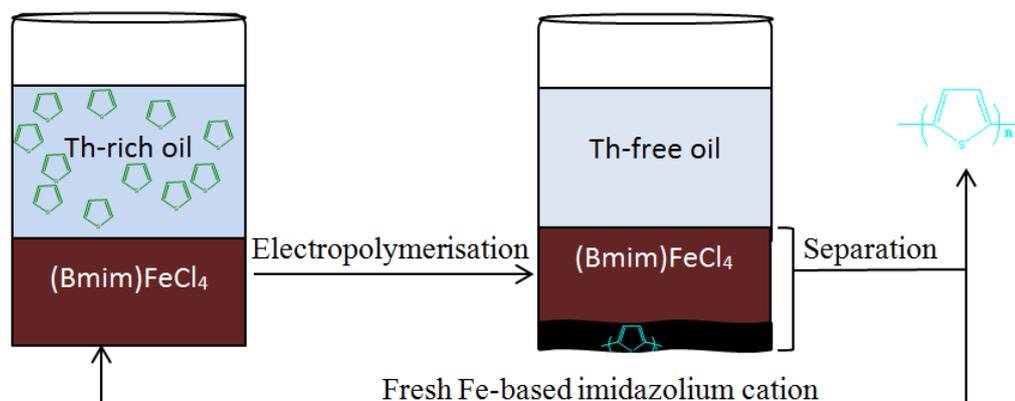


Figure 4.1: Extraction and electropolymerisation of Th in fuel oil.

Equimolar amounts of $(\text{Bmim})\text{Cl}$ with FeCl_3 allowed a less viscous dark brown liquid to be formed. When this was contacted with the decane/thiophene solution a dark brown/black layer quickly formed at the interface between the two liquids suggesting the chemical formation of a polymer.

Dharaskar and coworkers illustrated that after stirring the bilayer system, 59.2% of Th was extracted into the $(\text{Bmim})\text{FeCl}_4$ layer.¹¹ It was proposed that there was a specific interaction between thiophene and the Fe^{III} -based anion. To demonstrate the importance of the metal in the extraction process Li et al.,¹² and Yang et al.,^{13, 14} studied the adsorption of thiophene zeolite Y doped with Ag^+ and Cu^+ . They found that the metals interacted with the thiophene π orbitals with a donation into the vacant σ orbitals of the metal and a back donation of electron charge to the π^* orbital of thiophene from the d orbitals of metals. The authors believed that the same mechanism occur with the Lewis acidic FeCl_3 based-triethyl ammonium chloride.

In the current study, polythiophene (PTh) was prepared and monitored using cyclic voltammetry directly on a Pt working electrode using a Ag wire reference electrode. **Figure 4.2** shows the cyclic voltammetry of thiophene in four comparative systems. The first shows the behaviour of Th in $(\text{Bmim})\text{Cl}$, whereas the second is the same experiment but the thiophene is present in a decane layer contacted to $(\text{Bmim})\text{Cl}$. These two experiment were then repeated using 1 mole equivalent of FeCl_3 to $(\text{Bmim})\text{Cl}$. In all cases the electrodes were in the ionic liquid phase.

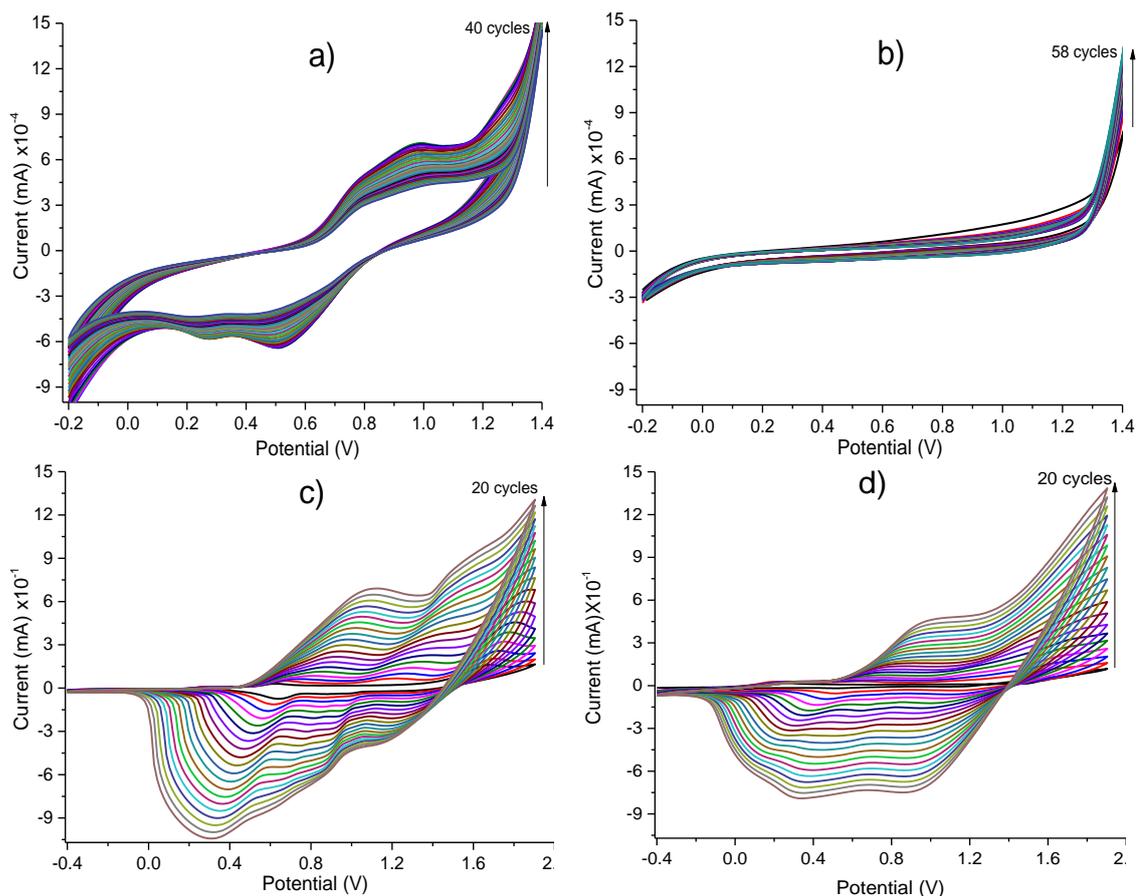


Figure 4.2: CVs of a) 0.4 mol/L Th in (Bmim)Cl, b) 0.4 mol/L Th in decane in contact with (Bmim)Cl, c) 0.5 mol/L (1mmol) Th in 1:1 FeCl₃/(Bmim)Cl and d) as c but with 0.4 mol/L (0.8mmol) Th in decane. All at 25 °C, scan rate: 50 mV s⁻¹, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

Figure 4.2a shows the oxidation of thiophene in (Bmim)Cl in the absence of FeCl₃. It can be seen that the current increases on subsequent scans which is indicative of electropolymerisation but it could also be oligomerisation with only short chain oligomers growing. The signal for the oxidation and reduction of thiophene is clear and there is some evidence of polymer formation although inspection of the electrode after 40 cycles does not reveal any significant growth of the polymer on the platinum surface.

Repeating this experiment by contacting the ionic liquids with the decane containing the same number of moles of thiophene as in **Figure 4.2a** yielded negligible electrochemical activity of the thiophene (**Figure 4.2b**). This suggests that only a small amount of the Th is extracted into the (Bmim)Cl which is insufficient to observe oxidation or polymer formation. To some extent this could be expected since (Bmim)Cl has a high surface

tension and from the results shown in **Chapter 3** it may be predicted that the energy required to form a hole for Th solvation may be quite large compared to the DESs studied in the previous chapter.

Figure 4.2c shows the equivalent experiment in which 1 mole equivalent of FeCl₃ has been added to the (Bmim)Cl. The electrochemical response is significantly different to that in the absence of FeCl₃. It is, however, similar to that carried out in molecular solvents using an Fe^{III} electrocatalyst and is more characteristic of electropolymerisation than that observed in **Figure 4.2a**.¹⁵ With repeated cycling the oxidative and reductive current increases due to the growth of material on the surface which is electroactive. Inspection of the working electrode after cycling shows clear evidence of a black polymer growing on the electrode surface. This is more evidence that in the absence of FeCl₃ the thiophene is only forming oligomers.

At high FeCl₃ concentrations, an acid catalysed reaction can take place with the formation of a polymeric black film which is similar to that synthesised using AlCl₃.¹⁶ It can be seen that there is a good agreement between this and the results obtained in previous study of Janiszewska in terms of the polymer formed.¹⁷

Repeating this experiment this time contacting the ionic liquids with the thiophene in decane solution yields a significant growth of polymer on the electrode. This suggests that the FeCl₃ is responsible for helping the Th to partition into the DES layer. The electrochemical activity contrasts strongly with the response when FeCl₃ is absent (*c.f.* **Figure 4.2b** and **d**).

Visual comparison of **Figures 4.2c** and **d** show similar charges on the oxidative and reductive cycles. The addition of decane should dilute the total concentration of thiophene in the system so the charge observed should decrease. The observation that the charges with and without decane are similar shows that the partition coefficient must be greater than 1. The kinetics of polymerisation can be estimated from the charge data. As mentioned in **Chapter 1**, a charge equivalent to 2.25 electrons per molecule will lead to the addition of one molecule of thiophene and 0.25 doping anions (Cl⁻).¹⁸ Consequently, the electropolymerisation charge, Q_{Th} ,^{18, 19} can be written as:

$$Q_{Th} = nNF \quad (4.1)$$

where, n is the number of electron, N is the number of polythiophene moles formed and F is the Faraday constant.

So as to compare the amount of Th converted to polymer in **Figure 4.2c** and **d**, the reaction rate (R)²⁰ has been calculated by:

$$R = \frac{\Delta(\text{Concentration})}{\Delta t} \quad (4.2)$$

where, R is the rate of reaction (mol dm⁻³/s), Δt is the change in time.

The electropolymerisation rates of Th in (Bmim)FeCl₄ were calculated from **Figure 4.2** and are shown in **Table 4.1**. The rate of the reaction of consumed Th should be equal to the reaction rate of produced PTh. However, owing to the biphasic nature of the system, it was difficult to estimate the amount of Th in the IL phase after 20 cycles from reaction of polymerisation, therefore, reaction rates were calculated in terms of the products.

Table 4.1: Reaction rate of electropolymerisation of thiophene. Scan rate 50ms⁻¹, 20 scans, potential window:(-0.4 to +1.9V), Pt as working electrode ($A=1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

Fig. (4.2)	Q (C)		N of PTh (mmol) from		R (mmol/min)	
	Q_{ox}	Q_{red}	Ox.	Red.	Ox.	Red.
c	0.0183	0.0188	7.6×10^{-4}	8.70×10^{-5}	2.48×10^{-5}	2.84×10^{-6}
d	0.0162	0.0186	6.7×10^{-4}	8.55×10^{-5}	2.2×10^{-5}	2.79×10^{-6}

The data from **Table 4.1** show that the rate of PTh formation in a monophasic system is only marginally higher than that from the biphasic system. Given that an equal volume of decane to (Bmim)FeCl₄ was used the charge should decrease by half but the observation that it decreases by less than 10% shows that the partition coefficient must be significantly greater than 1.

On the other hand, as can be seen in **Figure 4.2c** and **Figure 4.2d**, as the film thickness of the polymer increases, the voltammetric polymer for the reduction of the polymer shifts to more negative potentials and for the oxidation peak shifts to more positive values with consecutive scans which is characteristic of polymer growth. This is possibly due to the polymer conductivity which increases the resistivity of the film on the electrode surface due to slows counter-ion mobility and electron transfer kinetics.^{21, 22} Multiple voltammetric scans caused the electropolymerisation of thiophene from the decane layer.

A black solid polymer formed on the surface of WE which then precipitates into the DES as shown in **Figure 4.3**.

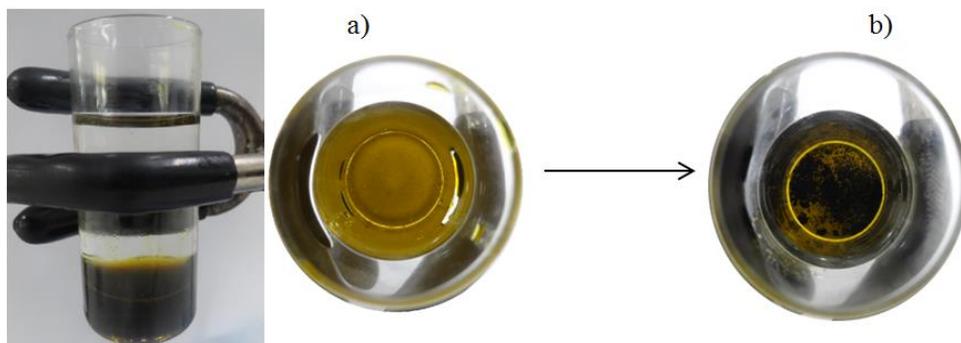


Figure 4.3: Multiple extractive electropolymerisation of thiophene in decane a) before, b) after polythiophene formation, at 50 mV s^{-1} , $30 \text{ }^\circ\text{C}$, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

The Fe-based ionic liquids cannot chemically polymerise thiophene until the molar ratio of FeCl_3 and $(\text{Bmim})\text{Cl}$ is above 1:1. Above this molar ratio the liquid becomes more Lewis acid and coincidentally less viscous. The concentration of free Cl^- is significantly lower as FeCl_4^- dominates. This also prevents the chloride ion reacting with the radical cation causing polymer termination.

4.2.1 EQCM study of polythiophene growth

Electrochemical Quartz Crystal Microbalance EQCM is a technique which enables mass changes on an electrode to be quantified from changes in the oscillating frequency occurring to a quartz crystal onto which an electrode has been vapour deposited. This is a technique which has frequently been applied to the growth and cycling of conjugated conducting polymers.²³⁻²⁷ By collecting not only frequency (and hence mass) data, but also the charge data, mechanisms can be inferred from mass-charge plots.

To find out the mass of electrodeposited polythiophene from the $(\text{Bmim})\text{FeCl}_4$ liquid, a platinum coated EQCM resonator with a platinum flat counter electrode (CE) was used in combination with a silver wire as a reference electrode (RE). The Sauerbrey equation,

relates any change of mass of the surface of a crystal (Δm), with the change of the resonant frequency (Δf) as shown in the equation (4.3):

$$\Delta m(\text{g}) = -1.1 \times 10^{-9} \Delta f(\text{Hz})^{28, 29} \quad (4.3)$$

Figure 4.4 shows gravimetric response achieved on a Pt electrode and the corresponding cyclic voltammogram obtained during extractive electropolymerisation of thiophene from (Bmim)Cl containing FeCl_3 .

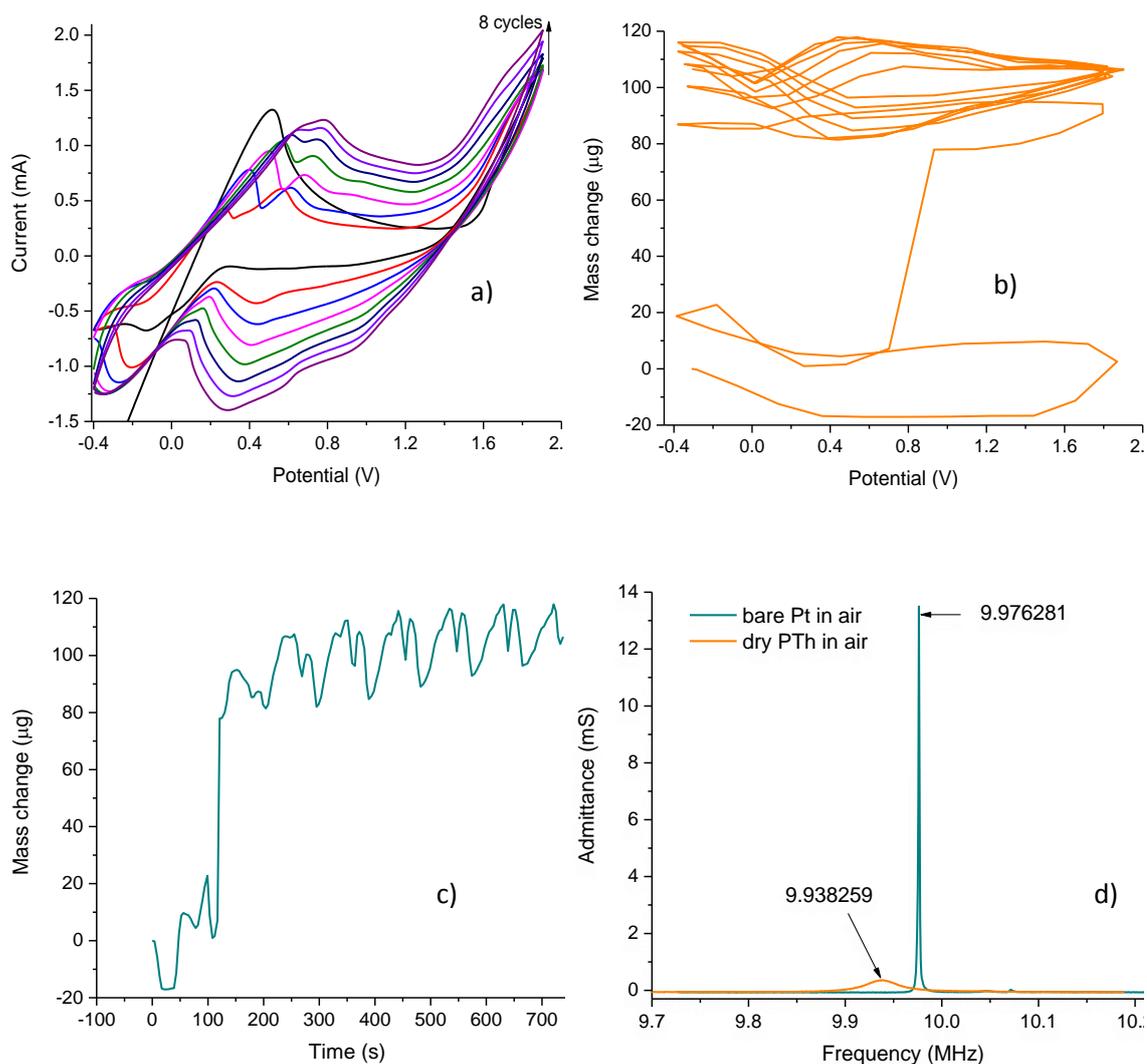


Figure 4.4: (a) CV, (b and c) mass change as a function of potential and time, and d) frequency vs admittance plots for the polymer obtained on Pt electrode in the mixture of 0.4 mmoles Th in equimole of Fe-based DES recorded during 8 polymerisation cycles at 25 °C, scan rate at 50 mV s^{-1} and the area of quartz crystal was 0.23 cm^2 .

The results presented above in **Figure 4.4a** and **Figure 4.4c** show the mass increment observed in this experiment. The data presented in these figures was used to estimate the amount of thiophene monomer converted to polythiophene after eight cycles in ionic liquid mixture by plotting change of mass as a function of potential for the oxidation of the monomer.

In **Figure 4.4c**, a sharp increase in the deposition film mass of PTh was observed on the second cycle which grew more gradually on the subsequent eight cycles. This shows that an initial seeding of the polymer is required on the first cycle which grows rapidly on the second cycle and once the electrode is covered with polymer consecutive cycles have a much slower polymer growth due to decreased conductivity.

The estimated mass of PTh was derived by calculating Δf (from **Figure 4.4d**) using the Sauerbrey equation. This was found to be 42 μg but this is less than the mass calculated against the time; this may be due to the deposition of FeCl_4^- ions and IL within deposited film which increased the mass of the formed PTh to around 120 μg . The reduced polymer mass might also be due to the loss of some amount of PTh after washing the deposited polymer on the WE surface several times with water and drying.

While the $\text{FeCl}_3:(\text{Bmim})\text{Cl}$ has been shown to be a suitable catalyst for the (electro)polymerisation of thiophene, it remains to be shown if it is effective with the other sulfur containing heterocyclic compounds found in oil such as benzothiophene or dibenzothiophene and this topic will be addressed in **section 4.3**.

4.2.2 Morphology of prepared polymer

The solvent exerts a pronounced effect on the resulting polymer film formed in terms of conductivity, electrochemical activity and morphology.³⁰ In this regard, the best polythiophene films are grown in anhydrous aprotic non-nucleophilic electrolytes because nucleophilic species can compete with the polymer for the radicals of monomer regenerated at the working electrode surface.^{30, 31}

The morphology of the polymer was studied using 3D-microscopy to evaluate the homogeneity of the sample and the result is shown in **Figure 4.5**.

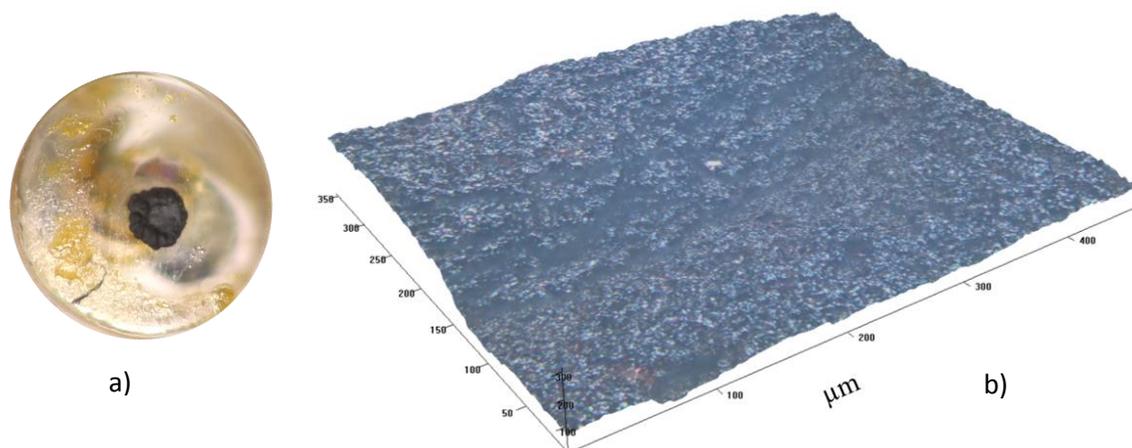


Figure 4.5: a) Photo of WE surface, b) 3D optical microscopy image of polythiophene formed in a mixture of 1:1 of (Bmim)FeCl₄ at 25 °C, after 20 cycles, at 50 mV s⁻¹, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

3D optical microscopy was used to determine the morphology of the deposited film. It can be seen that the surface is smooth and homogeneous.

4.2.3 Characterisation of PTh

Raman spectroscopy has been widely used together with infrared spectroscopy to probe the structure and properties of conjugated polymers by studying the vibrational modes. **Figure 4.6a** shows the FT-IR spectrum of the polythiophene film obtained in **Figure 4.5a**. Many low-intensity vibrational peaks could be seen in the range of 2300-3100 cm⁻¹ which can be attributed to the aromatic C-H stretching vibrations, C=C and C_β-C_β characteristic peaks identified almost at 1566 and 1330 cm⁻¹ respectively.^{32, 33}

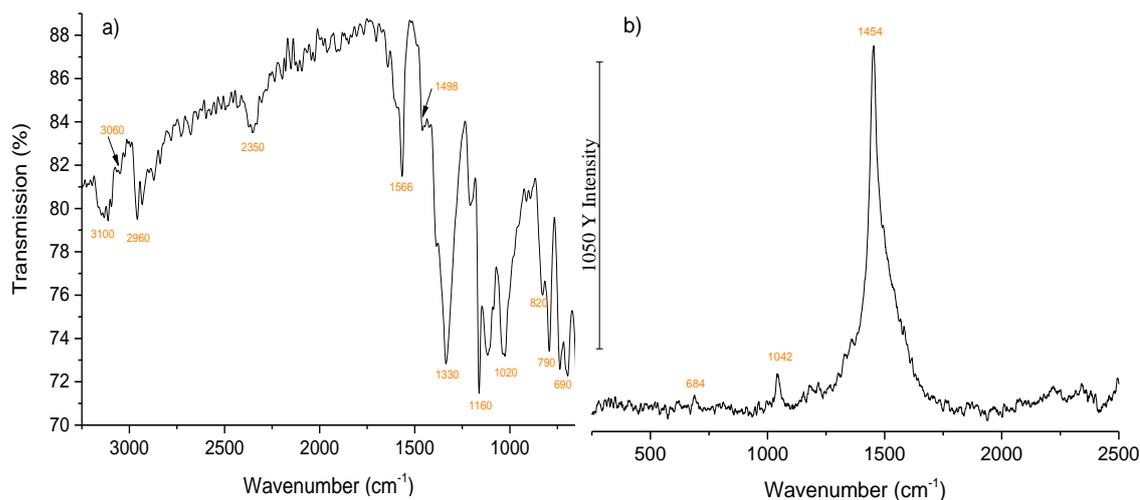


Figure 4.6: a) FTIR spectrum of polythiophene, b) Raman spectrum of polythiophene measured using a 532 nm laser source.

In the range of 600- 1500 cm^{-1} vibrational infrared absorption peaks can be used to identify polythiophene by its characteristic fingerprint. The peak at 690 cm^{-1} usually ascribed to the C-S-C bending mode indicating of presence of thiophene, whereas the peak at approximately 790 cm^{-1} is attributed to C-S-C bending mode of 2,5-disubstituted PTh. The band at 820 cm^{-1} is assigned to the C-H out of plane deformation of the Th unit and the weak peak observed at 1498 cm^{-1} is presented for $\text{C}_\alpha=\text{C}_\beta$ asymmetric stretching deformation which are less sensitive due to the energy of excitation lines.^{34, 35}

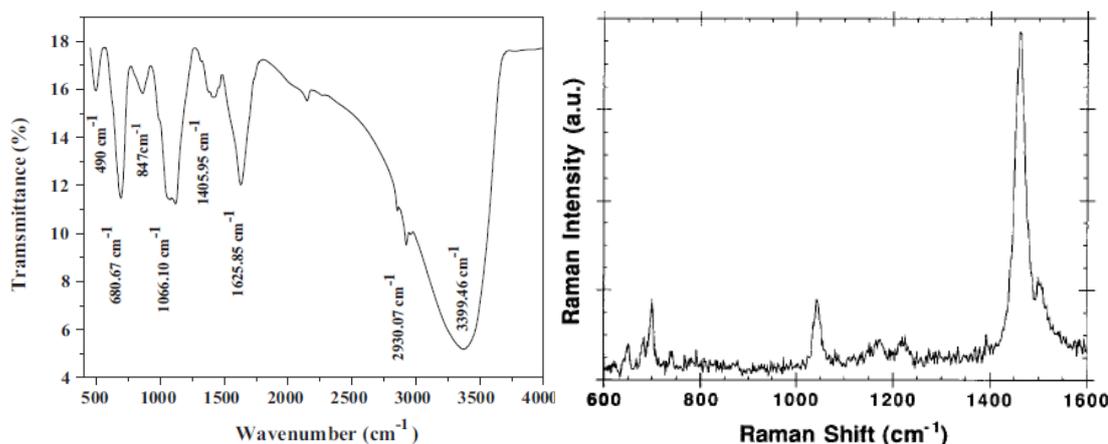


Figure 4.7: FT-IR and Raman spectroscopy of un-substituted PTh.^{36, 37}

Generally, three main peaks coupled to the electronic transition of the unsubstituted polythiophene can be shown by Raman spectra as seen in **Figure 4.6b**. This spectrum illustrates the most important line of the solid polythiophene occurs at 1454 cm⁻¹ for C α =C β stretching region which is completely symmetric deformation, in phase vibration and spread over the whole polymer chain. The weak C-H stretching vibrations and C-S-C bonding vibrations can be assigned around 1042 and 684 cm⁻¹ respectively. All of these signals prove that neutral polythiophene has been synthesised in Fe-based imidazolium DESs.^{32, 38} **Figure 4.7** shows the literature spectra of unsubstituted polythiophene in which the finger print of the PTh does not change.

4.2.4 Electrochemical activity of polymer

The electroactivity of polymers makes them attractive as materials particularly in capacitors. The redox process demands a familiar interaction between deposited polymer films and the liquid for ions to not only penetrate through the polymeric matrix, but also to keep neutrality of the process electrically, which eventually increases the charge storage.^{39, 40}

Can and co-workers,⁴¹ illustrated the stability and electroactivity of conducting polythiophene grown by cyclic voltammetry in non-aqueous media. Poly(3-methylthiophene) is not electro-active when cycled in acetonitrile-water mixtures, which is thought to be due to the hydrophobicity of polymer and the inability of ions and solvent to penetrate into the polymer to balance the charge.⁴² In contrast, Naudin et al.⁴³ prepared and characterised poly(3-(4-fluorophenyl)thiophene) electrochemically in imidazolium based ionic liquids and they demonstrated that the electroactive polymer was rapidly lost when it was repeatedly cycled in pure ionic liquids.

To study the stability of PTh, a sample of PTh (15 cycles) was prepared in (Bmim)FeCl₄ on a working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) using CV following which it was washed and dried. The electrode was then transferred to a different DES and cycled 30 times in Ethaline, Pentaline and Reline. A fresh PTh film was prepared for each experiment. The results in **Figure 4.8a** suggest that the PTh rapidly loses its redox activity from the first to the 30th cycle. The same experiment was repeated using pure Fe-based imidazolium ionic liquid. As can be seen in **Figure 4.8b**, the current from 1st cycle decreased rapidly within cycling in pure IL and the redox stability of the polymer decreased gradually until

the 41st scans where no electrochemical activity was observed. This means that the cyclic stability of polythiophene thin film at the scan rate 50 mV s⁻¹ decreased gradually.

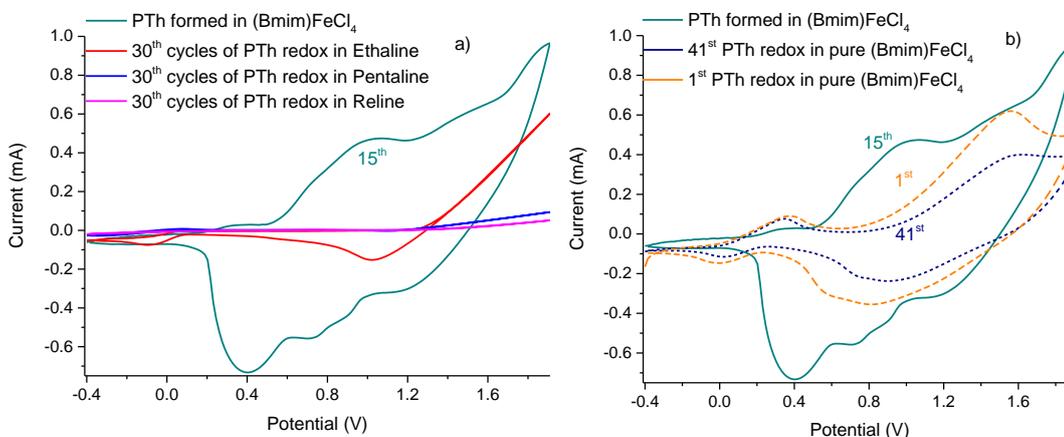


Figure 4.8: CVs of polythiophene activity as grown and then redox CVs of PTh film stability a) after 30 cycles in DESs, b) after 1st and 41st cycles in (Bmim)Cl:FeCl₃ without monomer, at 30 °C, 50 mV s⁻¹, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

A possible reason behind the loss of electroactivity after cycling in the DES is due to deswelling of the film. During cycling, easy and fast mass transport of ionic species in to and out of the polymer is needed balance the charge.^{43, 44} The conjugated polymer completely loses electroactivity of the redox reactions from the 42nd cycle. This is because of the loss of the adherence of the film to the surface of electrode. This implies that the prepared polythiophene has limited stability upon repeated cycling once it is transferred to a protic DESs. These results are in agreement with Naudin's study.

4.2.5 Optimisation of electrocatalytic polymerisation

The above study shows that PTh can be effectively electropolymerised in (Bmim)FeCl₄ by extracting thiophene and growing a polymer simultaneously. In order to be able to investigate the efficacy of this method for sulfur extraction from diesel, it is necessary to optimise the process parameters. Some of the most important parameters which affect the rate of polymer formation include; temperature, electrolyte composition, monomer

concentration, shape and type of electrode material, cell geometry and applied potential. All of these effect the structure and physicochemical properties of the resulting polymer from electropolymerisation of 5-membered heterocyclic compounds.³¹ Ionic liquids offer possibilities for preparing conducting polymers with different properties compared to those grown using molecular organic solvents. The topic of electropolymerisation in ionic liquids has been reviewed by Pringle.⁴⁵

4.2.5.1 Effect of scan rate

Kellenberger and coworkers,⁴⁶ reported that at high scan rates, the number of nucleation sites generated at the surface of the working electrode is larger than at slow scan rates, but the nuclei are smaller since the electrode is maintained for a shorter time at the oxidation-reduction potential. At lower scan rates the number of nucleation sites is lower, but their dimension is increased.

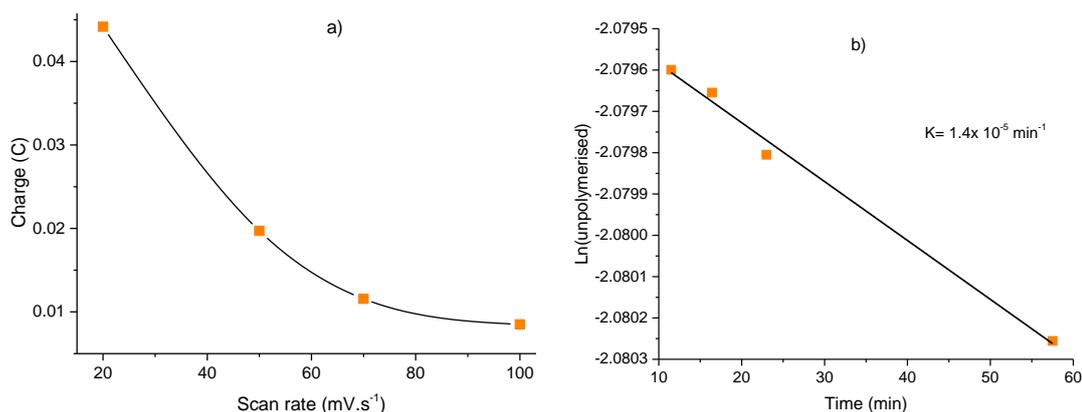


Figure 4.9: Plot of a) deposition charge (from reduction peak) against number of scan rates, b) $\text{Ln}(\text{unpolymersed Th})$ vs time for the electrochemical polymerisation of thiophene into 6.87 mmoles FeCl_3 in $(\text{Bmim})\text{Cl}$ (1:1), with 0.25 mmoles Th in 2ml decane, at 30 °C, 15 cycles, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

Stilwell et al.,⁴⁷ showed that the time spent in the oxidation region is evidently longer at slower scan rates than at faster ones. **Figure 4.9** shows that increasing the scan rate for PTh growth results in a decrease in the charge for the polymer film formation as shown previously by Patil et al.³⁹

If the amount of material grown is just time dependent then it should be possible to carry out more cycles at a faster scan rate e.g. 15 cycles at 100 mV s^{-1} should be equal to the deposited charge of 3 cycles when the scan rate is 20 mV s^{-1} . This was carried out for the system shown in **Figure 4.9a** and the charge for deposition at 100 mV s^{-1} after 15 cycles was $8.57 \times 10^{-3} \text{ C}$ compared to $8.63 \times 10^{-3} \text{ C}$ after 3 cycles at 20 mV s^{-1} . This shows that the amount of polymer grown is just dependent upon the length of time spent in the growth region of the cycle.

4.2.5.2 Stoichiometry effect of IL mixture mass ratio

For this methodology to be effective, the process needs to function at approximately the same rate at as low a catalyst loading as possible. To investigate the influence of the relative phase volume of DES to decane on the electrochemical response, two different volume ratios have been studied as displayed in **Figure 4.10**.

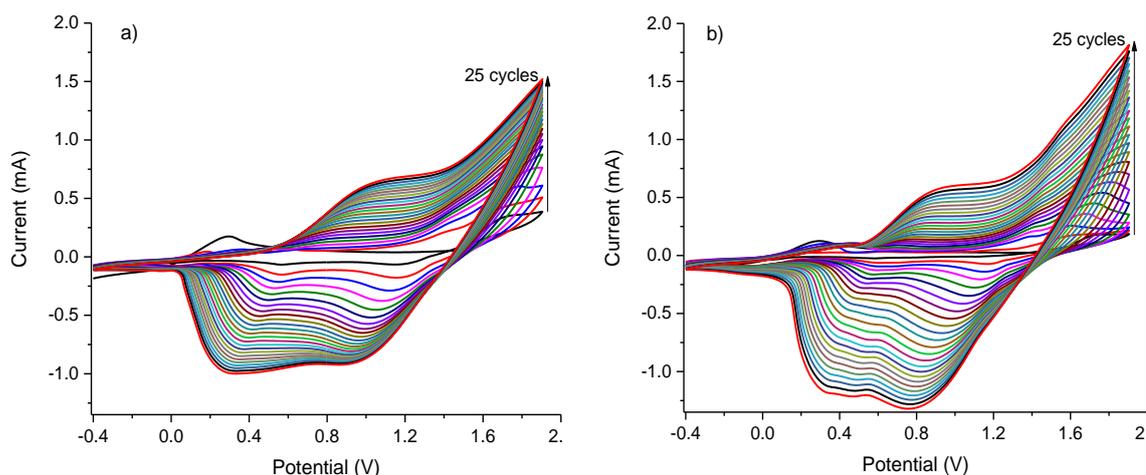


Figure 4.10: CVs of a) 1:7 v/v of DES: decane: 0.3 ml includes 1.43 mmoles of FeCl_3 into 1-1 Fe-DES, 2ml of Th -containing decane (0.21 mol/L), b) 1:1 v/v of DES: decane, Th in 2ml of decane is 0.21 mol/L , 25 cycles, mV s^{-1} , $25 \text{ }^\circ\text{C}$, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

Both CVs show the polymerisation characteristics of thiophene. As expected, as the ratio of DES: decane increases the current for Th polymerisation increases as more Th partitions into the DES.

The number of moles of Th converted to polymer in **Figure 4.10**, was calculated from the charge under the voltammogram using **equations 4.1** and **4.2**. The data are summarised in **Table 4.2**.

Table 4.2: Stoichiometry effect on the rate of the electropolymerisation reaction of Th after extraction from decane. Scan rate 50 mV s^{-1} , 25 scans, potential window: $(-0.4 \text{ to } +1.9\text{V})$, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

IL : Fuel (v/v)	Q (C)		N of PTh (mmol) from		R (mmol/min)	
	Q_{ox}	Q_{red}	Ox.	Red.	Ox.	Red.
1:7	0.0195	0.022	8.09×10^{-4}	1.013×10^{-4}	2.11×10^{-5}	2.62×10^{-6}
1:1	0.0226	0.025	9.36×10^{-4}	1.15×10^{-4}	2.44×10^{-5}	3.0×10^{-6}

The data in **Table 4.2** show the number of moles and the reaction rates for PTh formation from the oxidation and reduction signal. It is interesting to note that while the current increased in 1:1 volume ratio, there was no a significant variance in the amount of PTh deposited when compared with that obtained from 1:7 volume ratio which confirms the observation earlier that polymerisation is rate limiting rather than the solubility of Th in the DES.

Table 4.2 shows that the electrochemical polymerisation rate is relatively slow. To investigate the viability of this method to a practical extraction system a calculation was performed to see how quickly Th could be performed from an oil. Taking a 1 L sample of decane containing 1wt % of Th and 10 x10 cm WE, as illustrated in **Figure 4.11**.

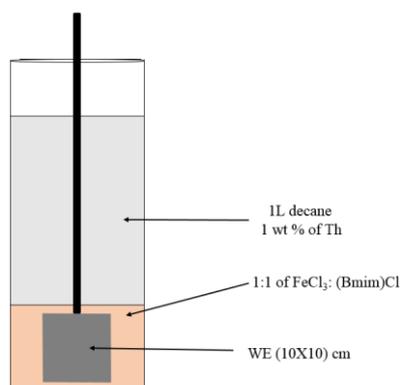


Figure 4.11: Scale up the process of extractive electropolymerisation of Th into IL mixture.

In most homogeneous solution polymerisation reactions, the kinetics of addition reactions are first order in monomer.⁴⁸ The mechanism is harder to interpret for a heterogeneous electrochemical process but the mechanism could be approximated from the data in **Figure 4.9**. Assuming the charge is proportional to concentration and the sweep rate can be related to the time of polymerisation then a pseudo first order kinetic plot could be approximated.

$$R = -\frac{dA}{dt} = k[A] \quad (4.4)$$

where, k is the rate constant of the polymer reaction and $[A]$ is the initial concentration of monomer. It can be seen from **Figure 4.9b** that a plot of $\ln [Th]$ vs t gives an approximately straight line correlation suggesting that the process is pseudo first order with a rate constant of $1.4 \times 10^{-5} \text{ min}^{-1}$.

To determine the amount of Th that could be turned over in a given time, the rate of oxidation from **table 4.2** (1:7) was used with the initial monomer concentration (0.21M) to calculate the rate constant. This was found to be $1.0 \times 10^{-7} \text{ min}^{-1}$. As seen in **Figure 4.11**, the time to remove 75 % of the Th from 1wt % in 1 L fuel using electropolymerisation would be 4.5 hrs. This is clearly far too slow to be practically viable.

4.2.5.3 Monomer effect

Several groups have studied the effect of the monomer on the rate of polymer formation. Pekmiz and coworkers showed that there is a considerable decrease in the polymer yield by increasing the monomer concentration.⁴⁹ Lee and Choi found that with increasing monomer concentration the polymerisation is affected by the precipitation of the monomer on the film surface which prevents polymerisation.⁵⁰ Janiszewsk et al. also mentioned that excess thiophene monomer may inhabit redox reactions on the surface of electrode due to their absorption.¹⁷ In the current study different Th concentrations were used to see their influence on the electropolymerisation after partitioning into an IL mixture until the concentration of Th became equal to the FeCl_3 concentration in the IL mixture.

It is clear from **Figure 4.12** that adding different amounts of thiophene to the decane layer behaves in the same way observed for electropolymerisation in molecular solvents or ionic liquids. The deposition charge produced from electropolymerisation of PTh was

5.5×10^{-2} and 6.1×10^{-4} C when the monomer concentration in decane was 0.5 and 4.7 mmol respectively. Lee and Choi⁵⁰ proposed that the monomer blocks the electrode surface at high concentration which decreases the rate of polymer formation.

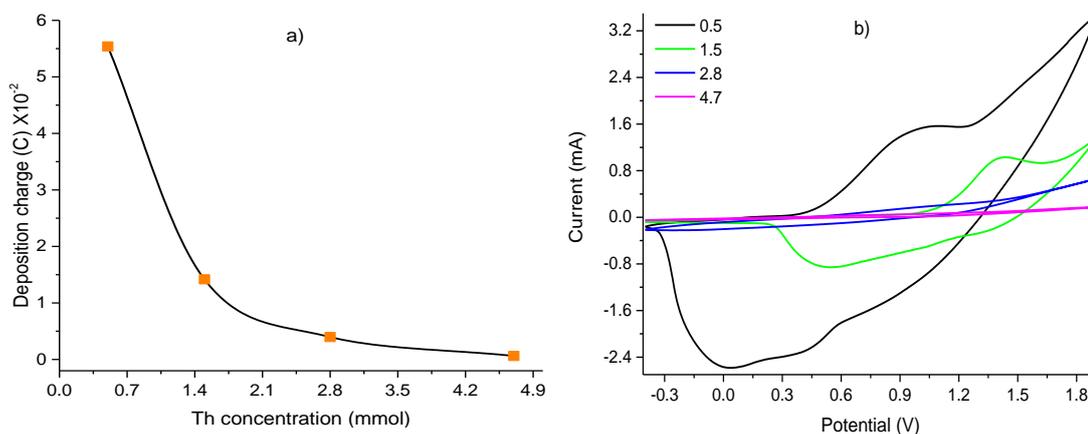


Figure 4.12: a) Plot of maximum cathodic charge (Q) versus various Th concentration in decane, b) polymerisation CV of different Th mmoles in decane connected to a 1:1 FeCl_3 (Bmim)Cl DES; 50 mV s^{-1} , after 20 cycles, at 25°C , Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

Moreover, the rate of PTh formation was $8.34 \times 10^{-6} \text{ mmol min}^{-1}$ when the Th-based decane concentration was 0.5 mmoles, but decreased to $9.3 \times 10^{-8} \text{ mmol min}^{-1}$ when Th concentration increased to 4.7 mmoles as illustrated in **Figure 4.13**.

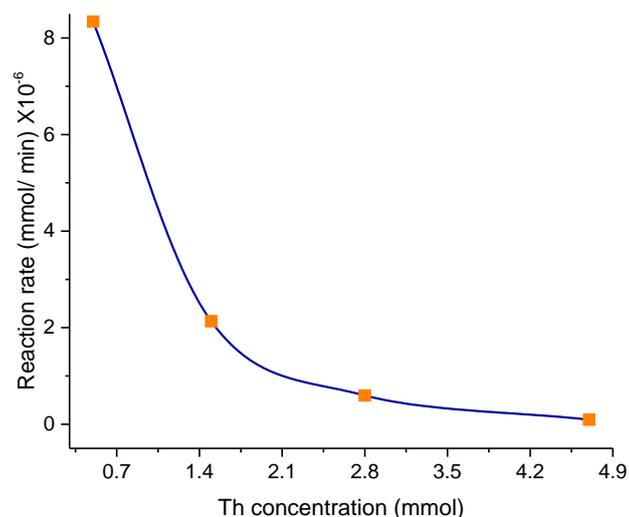


Figure 4.13: Reaction rate of Th electropolymerisation as a function of monomer concentration, scan rate: 50 mV s⁻¹, after 20 cycles, at 25 °C, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

As a result of the reaction rates discussed, it is clear that electropolymerisation functions best when there is a relatively low Th concentration. Fortuitously this corresponds to the typical concentrations of Th found in oil.⁵¹ Martin showed that the amount of S-compounds in gasoline, light naphtha and kerosene is (0.3-3 %).⁵¹

4.2.5.4 Effect of temperature

All spontaneous polymerisation reactions are exothermic as the formation of a polymer decreases the entropy of the system. Because the enthalpy of formation is large and negative the extent of the reaction will not be significantly affected by increasing the temperature. The temperature does however have a significant impact on the kinetics of polymerisation as well as on the conductivity, mechanical characteristics and redox properties of the films in an electropolymerisation process.^{52, 53} At high temperature, a lower conductivity and less conjugated polymer tends to form.^{31, 54} Hotta et al. and Waltman and Bargon reported that PTh films in diethyl sulphate [(C₂H₅)₂-SO₄] found to be more electrical conductive, dense and rigid at the lower temperature than those produced at room temperature.⁵⁵⁻⁵⁷ Conversely, Hotta et al. found that polythiophene

containing AsF_6 (prepared in tetra-*n*-butyl ammonium hexafluoroarsenate) is more tough, highly conductive and more dense at higher temperature than those at room temperature.⁵⁷

With increasing temperature, polymer formation decreases, due to the formation of a polymer layer which delays further reaction resulting in more diffusion of FeCl_3 in the polymer film.⁵⁰ Unlike the previous results, increasing temperature has a significant effect on the extraction and electropolymerisation of thiophene into $(\text{Bmim})\text{FeCl}_4$ as seen in **Figure 4.14**, because the larger the charge, the more the formation of the polymer according to Faraday law (equation 4.1)

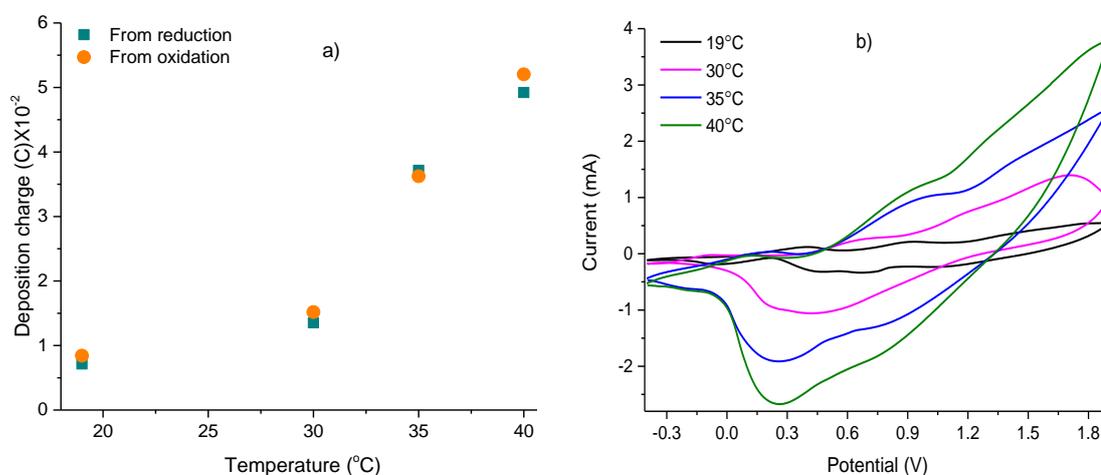


Figure 4.14: a) Plot of charge against temperature b) CV of current vs. potential of 20 scans of 4.7 mmoles FeCl_3 into $(\text{Bmim})\text{Cl}$ with 0.25 mmoles Th in decane, at 50 mV s^{-1} , Pt as working electrode ($A= 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

According to Faraday law, the mmoles of PTh formed at different temperature reactions have been calculated and explained in **table 4.3**.

Table 4.3: Quantity of PTh formation at different temperatures using CV, after 20 scans of 4.7 mmoles FeCl_3 into $(\text{Bmim})\text{Cl}$ with 0.25 mmoles Th in decane, at 50 mV s^{-1} , Pt as working electrode ($A= 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

Temperature (°C)	Q_{Red} (C)	N of PTh (mmol)
19	0.00714	3.29×10^{-5}

30	0.01352	6.23×10^{-5}
35	0.03716	1.71×10^{-4}
40	0.04922	2.27×10^{-4}

As seen in **Table 4.3**, mmoles of polythiophene obtained is increased by a factor of 6.8 (PTh formation increased from 3.29×10^{-5} to 2.27×10^{-4} mmoles) when the temperature was raised from 19 to 40 °C. This could be attributed to increased mass transport to the electrode surface. It is clear now that high temperature has a significant effect on the polymer growth film into (Bmim)FeCl₄ mixture whereas viscosity of equimolar ratio of (Bmim)Cl-FeCl₃ at 25 °C is 47.44 cP, viscosity should decrease as temperature arises. Luo et al., studied the effect of functional groups and temperature in poly-(3,4-ethylenedioxythiophene) and they illustrated that decreasing the temperature not only caused a slower diffusion rate of the monomers, but also lowered the electrochemical polymerisation reaction rate which is possibly, the main reason behind the regularity of structure formation.⁵⁸ Similarly, Saraji and Bagheri,⁵⁹ reported that the rate of electrochemically polyindole formation in aqueous solution increases linearly with the temperature.

4.3 Extractive electropolymerisation of BT into 1:1 (Bmim)FeCl₄

Conducting polymers such as polythiophene, polyaniline and polypyrrole are generally produced from oxidation or reduction of the monomer by means of a chemical or an electrochemical process.^{42, 60} While the electropolymerisation of thiophene has been studied in depth that of benzothiophene has been studied significantly less.

Although, polybenzothiophene (PBT) is a known low band-gap polymer, very few publications have been reported concerning its electro-synthesis.⁶⁰ Heishoku and Seki⁶¹ electropolymerised BT into C₆H₅CN and CH₃CN using various supporting electrolytes. In addition, Ishizawa et al. electropolymerised BT in LiBF₄/acetonitrile solution.⁶² The authors suggested that the active centres in BT for polymerisation are C(2) and C(5) as seen in **Figure 4.15**.

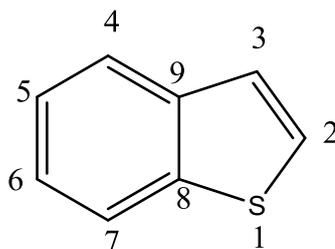


Figure 4.15: Chemical structure of BT.

Lu et al.,⁶³ also successfully electropolymerised BT in three different solvents (boron trifluoride, diethyl etherate and trifluoroacetic acid) and it has been reported that polymerisation probably most occurs at the C(2), C(4) and C(7) positions. Similar to Ishizawa's group's work, Wang et al. illustrated the structure of conjugated delocalised polybenzothienophene at the same positions.⁶⁴ Furthermore, Xu and co-researchers electro-synthesised polybenzothienophene in mixed electrolytes of boron trifluoride diethyl etherate and trifluoroacetic acid without mentioning the reactive sites of the polymer linkage positions.⁶⁰

Figure 4.16 shows the cyclic voltammogram for 125 mmol L⁻¹ of BT in decane which was contacted with 1:1 of (Bmim)Cl:FeCl₃ mixture at 30 °C. The voltammogram clearly shows an electrochemical signal for the reversible Fe^{II/III} couple between -0.4V and +0.5V, but the characteristic polymer growth signal shown in **Figure 4.16** are absent which should be grown significantly around +1.4V. Despite numerous attempts no sign of polymerisation was obtained.

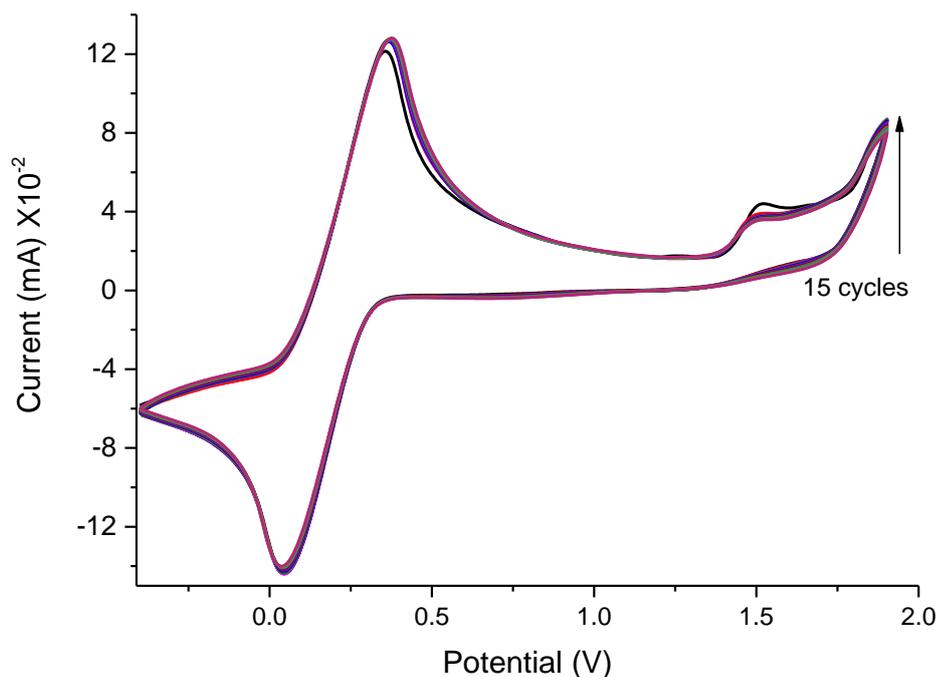


Figure 4.16: Voltammetric profile obtained during electropolymerisation of 0.25 mmoles (125 mmol L^{-1}) of BT in decane with 1:1 of (Bmim)FeCl₄ at 30 °C, 15 scans, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

The difficulty to electrochemically polymerise BT is probably due to the higher oxidation potential required compared with Th. The BT radical formed will be more reactive than the corresponding Th radical and may undergo fast reaction with the solvent (Bmim) or anions (Cl⁻) to produce soluble products rather than to electropolymerise monomers and form polybenzothiophene.

4.4 Reactivity of BT and Th copolymerisation into 1:1 (Bmim)FeCl₄

The previous section showed that BT could not be electropolymerised to form a homopolymer but because BT and Th occur together in mineral oil it is important to see whether they can co-polymerise. Seki et al.,⁶⁵ grew a highly conductive copolymer by electrochemical copolymerisation from BT with pyrrole into acetonitrile and benzonitrile. They found that copolymerisation strongly depended on the type of electrolyte, the current density, type of solvent and monomer composition.

Three blends of Th and BT were prepared in decane and electrochemical copolymerisation was carried out in 1:1 (Bmim)Cl: FeCl₃. **Figure 4.17** shows the voltammetric profiles recorded during the co-electro-oxidation of Th and BT.

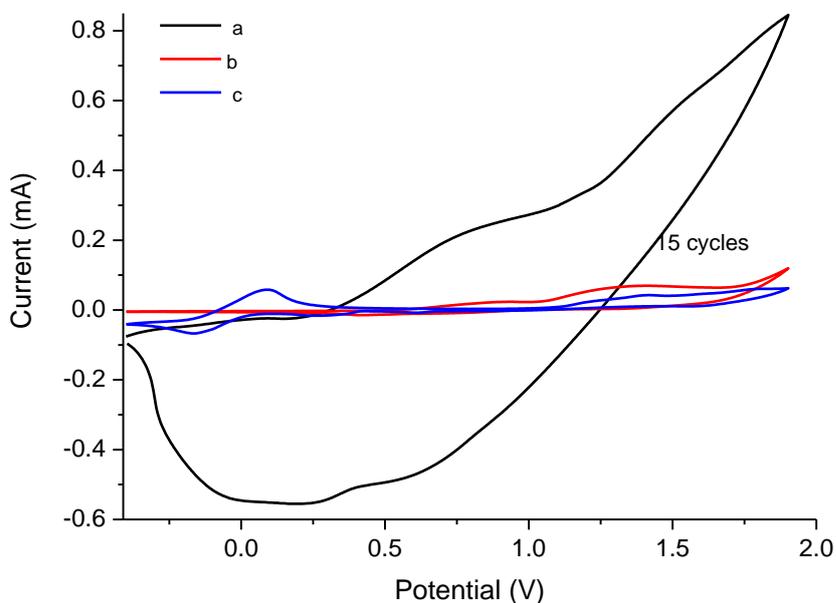


Figure 4.17: CV of electropolymerisation of 1:1 (Bmim)FeCl₄ containing (7 mmoles FeCl₃) with a) 125 mmol L⁻¹ Th, b) 125 and 35 mmol L⁻¹ of Th and BT respectively, c) 125 mmol L⁻¹ of each Th and BT in decane at 30 °C, 50 mV s⁻¹, 15 cycles, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

It is immediately clear from **Figure 4.17** that the addition of BT to decane significantly decreases the current for electropolymerisation. Even though all three liquids contain the same concentration of Th, the presence of BT clearly poisons the growth of polymer on the electrode surface as the charge decreased with BT addition to oil phase. This could be because it terminates polymer growth on the WE surface. Moreover, after increasing the amount of BT in the solvent (**Figure 4.17c**), the current efficiency of polymerisation significantly decreased. It implies that copolymerisation cannot be accomplished from this mixture. This is significant as it suggests that if there is a relatively high BT content in the diesel then it will prevent polymerisation and this method of sulfur removal will become inefficient

4.5 Application of PTh formation in commercial diesel

In this section the methods developed in **Section 4.2** will be studied using commercial diesel samples. Samples of diesel from which sulfur containing compounds had already been largely removed were spiked with thiophene (0.2 mol L^{-1}) and extracted using an equal mass of 1:1 (Bmim)Cl: FeCl_3 . **Figure 4.18** shows the voltammogram obtained after 20 cycles at 25°C and a scan rate of 50 mV s^{-1} .

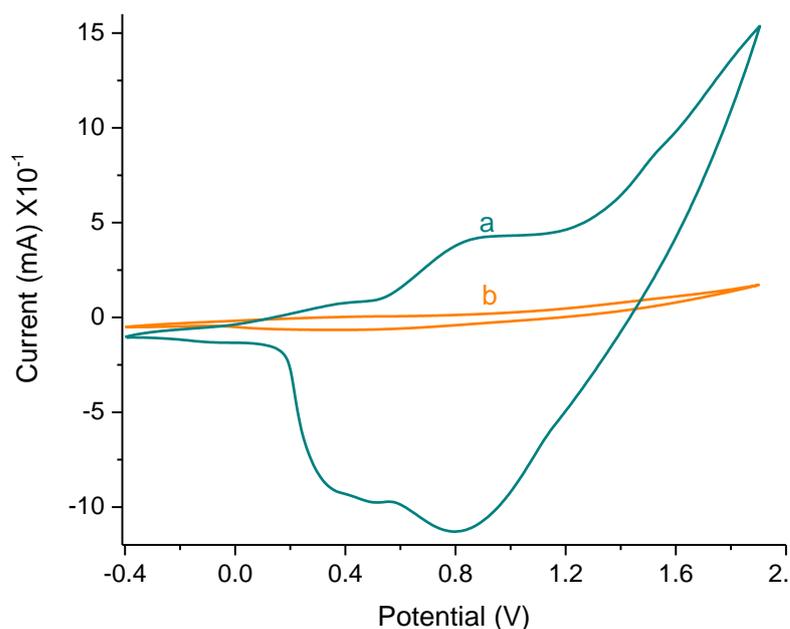


Figure 4.18: CVs of polythiophene formation electrochemically after 20th cycle into (Bmim)FeCl₄ from a) 0.2 M Th in decane, b) 0.2 M Th in commercial diesel fuel, equal molar ratio of IL and organic layer at 25°C , 50 mV s^{-1} scan rate, Pt as working electrode ($A = 1.963 \times 10^{-3} \text{ cm}^2$) and Ag wire as reference electrode.

As can clearly be seen from current charge in **Figure 4.18**, polythiophene clearly appears to grow when the thiophene is put into decane, because, current charge was grown, however, the polymerisation efficiency is significantly lower when commercial diesel is used due to the reduction of current charge. This is probably due to the complex range of additive included into diesel such as pour point suppressants and surfactants. Commercial diesel also contains traces of water which may also prevent polymerisation as shown by Downard and Pletches.

Table 4.4: PTh formation from (C₄mim)FeCl₄ connected with 0.2 M Th in commercial diesel fuel and decane fuel at 25 °C and 50 mV s⁻¹ scan rate, 20 scans, potential window: -0.4 – 1.9V.

PTh in	Q (C)		N of PTh (mmol) from		R (mmol/min)	
	Q _{oxi}	Q _{red}	Oxi.	Red.	Oxi.	Red.
Decane	0.01469	0.01699	6.1x10 ⁻⁴	7.83x10 ⁻⁵	1.99x10 ⁻⁵	2.55x10 ⁻⁶
Diesel	0.00167	0.00148	6.92x10 ⁻⁵	6.82x10 ⁻⁶	2.26x10 ⁻⁶	2.23x10 ⁻⁷

The rate of the reactions of polymer formation after partitioning the monomer from both organic phases into IL mixture were calculated and it is clear that the values of the rate of PTh formation differ by almost an order of magnitude. To understand why this occurs it is important to understand the types of additives used in diesel fuel and why they may inhibit the electropolymerisation process. While the exact composition of commercial diesel will differ for each manufacturer and is clearly proprietary information, some publications have describe the general components of diesel fuels. In general, these components of diesel fuels are; saturated and aromatic hydrocarbons including monoaromatics such as alkylated benzenes, polycyclic aromatic hydrocarbons such as naphthalenes, fluorenes, and phenanthrenes, antioxidant stabilizers (dibasic metal phosphate), cold flow improvers (poly(ethylene-vinyl)acetate), cetane improvers (2-ethyl-hexyl nitrate), trace amounts of nitrogen compounds (quinoline) and moisture.⁶⁶⁻⁷² Oxygen and nitrogen containing compounds in commercial diesel fuel might absorb on the surface of electrode or react with the monomer radical cations causing polymer chain termination.

4.6 Conclusion

In this chapter it has been shown that thiophene can be successfully partitioned into an ionic liquid composed of a 1:1 mixture of (Bmim)Cl and FeCl₃ from a decane layer. This is thought to occur because (C₄mim)FeCl₄ has a relatively low surface tension and so the issues seen in the previous chapter with the enthalpy of hole formation are decreased by adding ferric chloride to the liquid. Cyclic voltammetry in the (Bmim)FeCl₄ phase shows a response characteristic of electropolymerisation for thiophene in an aprotic liquid. This

means that Th not only successfully partitioned from decane but could also be polymerised to PTh.

The black layer formed on the electrode through repetitive cycling was characterised using Raman and FT-IR spectroscopy and was shown to correlate well with PTh described in the literature. It was shown that (Bmim)FeCl₄ acts as an electrocatalyst for polymer formation rather than a chemical catalyst. This was determined by analysing the mass- charge plots obtained using a Pt coated QCM resonator and employing the Sauerbrey equation.

The conditions required for electropolymerisation were optimised. It was found that increasing the concentration of thiophene in decane decreased the rate of polymerisation. This agrees with other studies in molecular solvents and it was concluded that this was due to adsorption of the monomer on the electrode film surface which poisoned the electrode surface. The sweep-rate effects were only a function of the length of time spent at the growing potential. As expected, the amount of polymer that grows on the electrode surface increases with increasing temperature which probably results from a significant decrease in the viscosity of the liquid.

Removal of BT from decane into IL mixture followed by electropolymerisation was also attempted. It was found that no polymer could be formed with this monomer which was thought to be due to the high reactivity of radical BT cations, which can undergo fast reaction with the chloride anions or with the imidazolium cation. The electro-copolymerisation of Th and BT was also attempted but it was found that BT acted as a poison in the polymerisation process.

The final part of this chapter investigated the extraction and electro-polymerisation of Th from commercial diesel fuel. A sample of low-sulfur commercial diesel fuel was spiked with an appropriate concentration of Th and extracted using the imidazolium-based IL mixture. It was found that the charge for electro-polymerisation of Th from the commercial diesel was an order of magnitude less than that from decane. This was thought to be due to numerous aromatic and aliphatic O or N-based compounds in real commercial diesel fuel in addition to the additives like glycols and contaminants such as water. These are all good terminating agents for the polymerisation process on the surface of WE.

In conclusion this chapter has shown that while electrochemical polymerisation of Th is a possible methodology for the removal of sulfur containing compounds from oil, it is not

practically viable due to the slow reaction kinetics and the possibility of chain termination from other sulfur containing compounds such as BT and other additives in the fuel such as glycols. In the next chapter the possibility of using different BmimCl:FeCl₃ ratios will be studied with the aim of carrying out chemical polymerisation with the electrochemical regeneration of the Fe^{III} centre.

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Chapter 5: Chemical EDS by 2:1 FeCl₃: (Bmim)Cl

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5 EDS and chemical polymerisation using (Bmim)FeCl₄

5.1 Introduction

As has been shown in **Chapters 3** and **4** DESs have some ability to extract sulfur compounds from oil, but surprisingly this appears to be limited by the enthalpy of hole formation and partition is driven by the change in entropy. The extraction efficiency is improved by adding ferric chloride to an aprotic ammonium salt as this decreases the surface tension making hole formation easier. In the equimolar (Bmim)Cl: FeCl₃ partition of Th into the ionic liquid phase is high but the electropolymerisation of Th is relatively slow and is certainly rate limiting. In addition, it was shown that other thiophenic compounds such as BT and DBT could not be electropolymerised. It is known that if the ferric chloride content of the mixture is increased then the liquid becomes Lewis acidic enough to enable chemical polymerisation of both Th and BT. Therefore, the main objective in this Chapter will be the study of chemical polymerisation in the (Bmim)Cl: FeCl₃ system.

As in **Chapters 3**, all the extraction data were collected using GC-FID and UV-Vis spectroscopy. As mentioned in **Chapter 2**, the absorption spectra of unextracted Th, BT and DBT in organic layers were around 231.5 nm and the retention times for the gas chromatograms were at about 3.14, 9.88 and 14.7 minutes respectively which is in agreement with the results arising from Lobodin and co-workers.¹ Owing to the UV-Vis absorbance maxima of all three heterocyclic sulfur compounds being similar, most analysis was carried out using gas chromatography.

This chapter focuses on:

- 1- Characterisation of the 2:1 FeCl₃: (Bmim)Cl system
- 2- Biphasic extractions of thiophenic compounds and chemical polymerisation of Th and BT using 2:1 FeCl₃: (Bmim)Cl. ILs.
- 3- Regeneration of the IL.
- 4- Application using commercial diesel fuel.

5.2 Characterisation of (Bmim)Cl / FeCl₃ mixtures

To enable large scale use of DESs, it is important to understand the physical and chemical properties of the liquids, species mobility, conductivity and mutual-solubility of the two phases. These measurements were carried out for both the 1:1 and 2:1 FeCl₃: (Bmim)Cl.

5.2.1 Mutual-solubility of the IL mixture and decane

The key factor in evaluating the applicability of an extractant is the cross-solubility of the IL and the model fuel in each other. In this work, the solubility of 1: 1 and 1: 2 of FeCl₃: IL in the model oil was investigated by UV-Vis spectroscopy and GC-FID. The results indicated that no detectable Fe-based solubility was found in decane which would be expected given the difference in polarity of the phases. This is naturally an advantage as it means no contamination of the oil with a potential oxidising agent.

The solubility of the IL in decane was determined gravimetrically (**Table 5.1**), by weighing the mass difference of a given amount of Fe-loaded imidazolium cation and the corresponding imidazolium-based ILs saturated with model fuel after stirring and separating.

Table 5.1: Solubility of model fuel in modified IL at 25 °C in mass percentage.

FeCl ₃ : (Bmim)Cl	1: 1	2: 1
oil solubility in IL mixture, wt %	0.1	0.2

As seen in the **Table 5.1**, the solubility of model fuel in imidazolium-based ILs is quite small and will have the advantage of decreasing viscosity of the ionic liquid.

5.2.2 Conductivity analysis

The conductivity of ionic liquid provides information about the mobility of the ions this in turn has been shown to be controlled by the void volume of the liquid.² In general, the conductivity of ionic liquids is significantly less than aqueous electrolyte solutions and quaternary ammonium electrolytes in polar organic solvents. (Bmim)BF₄ and (Bmim)PF₆ have conductivities of 1180 and 860 $\mu\text{S} \cdot \text{cm}^{-1}$ respectively which are comparatively low compared with aqueous solutions which are between 10 - 20 $\text{mS} \cdot \text{cm}^{-1}$.^{2,3}

Figure 5.1 shows the conductivity of FeCl₃/ (Bmim)Cl mixture in two different molar ratios.

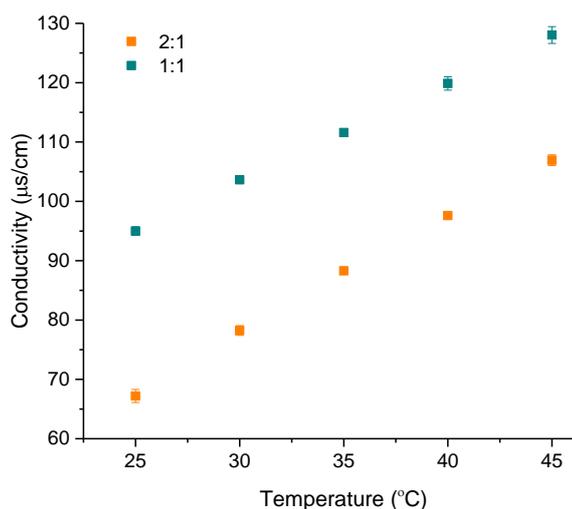


Figure 5.1: Conductivity of $FeCl_3/(Bmim)Cl$ mixtures as a function of temperature.

While in this chapter the polymer is not synthesised by electrochemical means the intention is to regenerate the ionic liquid by bulk electrolysis. For electrochemical applications ionic liquids should ideally have conductivities between $1000 - 10000 \mu S cm^{-1}$ at room temperature,⁴ however, the 2:1 and 1:1 $FeCl_3:(Bmim)Cl$ mixtures have conductivities of 67 and $95 \mu S cm^{-1}$ respectively. The low conductivities are due to the high viscosity of the liquids.

5.2.3 Surface tension and void radius measurements

It has previously been shown that the surface tension gives a measure of the void volume in ionic liquid and this in turn controls the viscosity and conductivity of the liquid. The lower the surface tension the larger the void volume and the lower the viscosity. Measuring the surface tension of two different molar ratios of the 2:1 and 1:1 $FeCl_3:(Bmim)Cl$ mixtures enables the average void radius to be calculated using equation (3.6). These data are presented as a function of temperature in **Table 5.2**.

The surface tension values are very similar in both compositions and do not change significantly over the temperature range measured. The values are similar to some other metal based ionic liquids such as $ChCl: 2ZnCl_2$ ($50.9 mN m^{-1}$) but less than others $ChCl: 2CrCl_3 \cdot 6H_2O$ ($77.3 mN m^{-1}$). As shown in **Chapter 3**, the best solvents for extraction of Th, BT and DBT, Pentaline ($46 mN m^{-1}$), had similar surface tensions to the data in **Table 5.2**. This shows that in these liquids the formation of a hole is still important in controlling the Th partition coefficient.

Table 5.2: Void radius and surface tension measurements for (Bmim)Cl-FeCl₃ as a function of temperature ($T = \pm 0.4$).

Molar ratio FeCl ₃ : (Bmim)Cl	Temperature (K)	Surface tension (mN. m ⁻¹)	Void radius(Å)
1:1	298	46.4 ± 0.4	1.57 ± 0.003
	308	44.6 ± 1.2	1.62 ± 0.001
	318	45.4 ± 0.9	1.64 ± 0.001
2:1	298	46.4 ± 0.2	1.57 ± 0.003
	308	46.0 ± 1.1	1.60 ± 0.004
	318	44.8 ± 0.6	1.65 ± 0.002

5.3 Chemical removal of different S-containing compounds

Removing sulfur compounds from gasoline or diesel fuels to below 30 ppmw and 15 ppmw respectively is called deep desulfurisation or ultra-deep desulfurisation.⁵ To determine the rate of the desulfurisation of different sulfur containing compounds, experiments were first performed with different mixtures in decane. Liquid-liquid extraction was carried out using the same biphasic procedure described in the previous chapters but in this case using Lewis acidic imidazolium-ferric chloride mixtures. Here, different amounts of thiophene and its derivatives were added to the decane phase.

For several decades, the lowest sulfur content achieved by HDS of fuels was around 500 ppmw (around 6 mmol/L or less).⁶⁻⁸ To demonstrate the efficacy of the DESs to chemically remove sulfur compounds mixtures of Th, BT and DBT were prepared in decane. The initial concentrations were around 100-fold more than the amount of S-compounds found in diesel. The two phases were stirred together for 20 min after which no change was observed in Th concentration and the system was considered to be at equilibrium. These data are presented in **Table 5.3**.

It can be seen from **Table 5.3** that in all cases 99.9 % or more of the thiophenic compounds were partitioned each time from the decane layer into the IL mixture and a black viscous solid formed in the ionic liquid layer. An example of a chromatogram of the decane layer before and after extraction is shown in **Figure 5.2** to demonstrate the efficacy of the extraction process.

Table 5.3: Extractive chemical desulfurisation of Th, BT and DBT mixture in decane at 25 °C, stirring (500 rpm) within 20 min, mass ratio of IL/oil (2:1).

S-compounds	Initial concentrations (mmol L ⁻¹)	Final concentration (mmol L ⁻¹)	extraction (%)
Th + BT	125 48	0.022 0.022	>99.9
Th + BT	125 125	0.025 0.025	> 99.9
Th + BT	125 188	0.007 0.007	> 99.9
Th + BT+ DBT	125 96 96	0.004	>99.9
Th + BT+ DBT	125 128 130	0.009	>99.9
Th + BT+ DBT	125 155 197	0.028	>99.9
DBT	108	0.01	>99.9
BT	112	0.033	>99.9
Th	125	0.038	>99.9

It is also clear that adding BT and DBT compounds into Th-based decane does not influence the partition coefficient or hinder the formation of the polymer unlike the case with the electrochemical polymerisation.

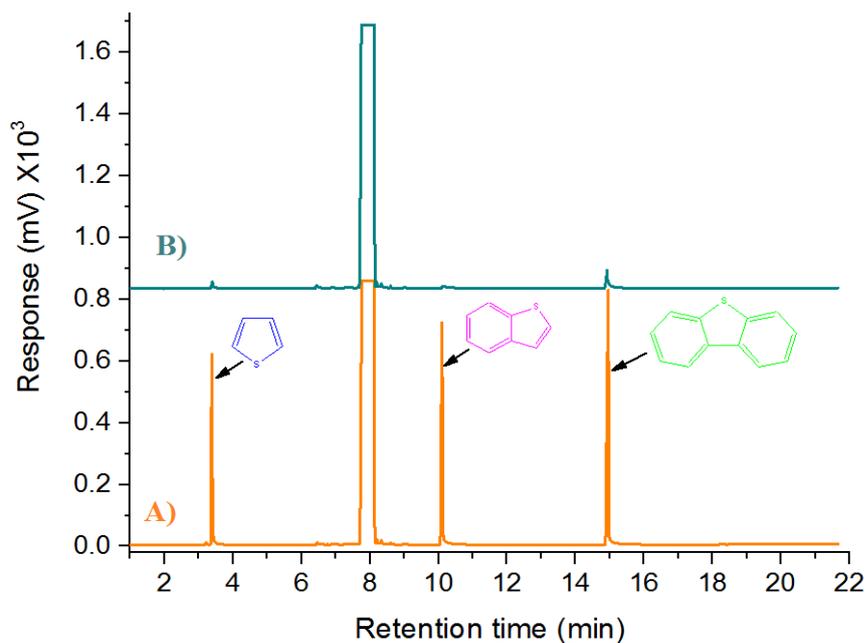


Figure 5.2: GC-FID chromatograms of 125 mmol L⁻¹ of each of three S-compounds in model fuel A) before extraction, B) after extraction. Extraction conditions: 20 min stirring, at 25 °C, 750 rpm and equal molar ratios of two phases.

5.4 Optimisation of EDS by 1(Bmim)Cl : 2FeCl₃

The partitioning of the S-containing molecules into the ionic liquid cannot be simply analysed in the same terms as was carried out with the DESs in **Chapter 3**. Previously the process could be estimated to be a dynamic equilibrium between the two phases however with the Lewis acidic liquids the Th in the IL phase is constantly being oxidised to form PTh and driving the equilibrium towards to IL phase.

By analysing the effect of the time, stirring rate and temperature on the extraction efficiency, the factors affecting the pre-equilibrium and the rate of polythiophene formation can be determined.

5.4.1 Effect of temperature

Extraction temperature is one of the most important factors which can affect the desulfurisation efficiency. Jiang and co-researchers investigated the extraction capability by N-butyl-N-methyl piperidinium tetrachloroferrate as an extractant. The authors found that sulfur removal increased as the temperature increased.⁹ Ban and coworkers published

the results concerning the extraction of sulfur compounds to IL mixture which consist of 1-methyl-3-octylimidazolium chloride system ([Omim]Cl:FeCl₃) that was consistent with that in Jiang's study.¹⁰ Although not expressly mentioned by the authors, this shows that the extraction of thiophene in these liquids is an endothermic process.

On the other hand, Li et al.,^{11, 12} Wang et al.¹⁵ and Sacal et al.¹³ described a desulfurisation procedure with imidazolium salt mixtures with iron halides where the extraction efficiency decreased with increasing temperature. These results strongly agree with the results outlined in **Table 5.4**. The extractive ability of (Bmim)FeCl₄ shows that the extraction must be an exothermic process as the position of the equilibrium is shifted toward the reagents when the temperature is increased in accord with Le Chatelier's principle.

Table 5.4: Extractive desulfurisation of 35 mmol L⁻¹ of each one of Th, BT and DBT into (Bmim)Cl 2FeCl₃ mixture, as a function to time, 500 rpm, fuel/IL mass ratio: 2:1.

Temperature (°C)		25		40		
Time (min)		5	10	5	10	20
Extracting (%)	Th	85.7 ± 5	>99.9	76.3 ± 2	95 ± 4	>99.9
	BT	67.5 ± 3	>99.9	75.3 ± 3	92.8 ± 4	>99.9
	DBT	58 ± 6	>99.9	65.8 ± 3.8	90.6 ± 2	>99.9

Table 5.4 shows that studying the reaction after 5 min extraction time the process is not at equilibrium at either 25 or 40 °C. Comparing the data at the different temperatures it is clear that Th extraction into the DES is lower at the higher temperature which suggests that the transfer is exothermic. Transfer of BT and DBT are quite similar once experimental errors are taken into account but either way neither are significantly affected by temperature. This could suggest that the equilibrium is governed by the rate at which the monomer is converted to the polymer (oligomer). After 10 min the extraction at 25 °C is all but complete whereas those at 40 °C have still not quite gone to completion. This further suggests that the transfer is slightly exothermic. This contrasts with the transfer in the DESs in **Chapter 3** which were endothermic. This could be caused by a complex formed between the iron centre and the thiophene ring. In the previous studies, the reactivity of organosulfur rings in HDS processes has been reported by some researchers

and it was investigated that the reactivity follows the order: Th > BT > DBT.¹⁴⁻¹⁷ This could be due to two factors, increasing the size of the solute molecule increases the size of the hole required to accommodate the solute, the interaction between the iron species and the heterocyclic sulfur atom is probably precluded due to steric factors.

It should also be noted that the extraction efficiency is quoted for **Table 5.4** rather than the partition coefficient as the thiophene in the ionic liquid phase is being converted to PTh which is shifting the equilibrium away from Th in the organic phase. This also explains why BT and DBT are slower to partition into the ionic liquid since polymerisation of these monomers will be slower due to steric hindrance and deactivation.

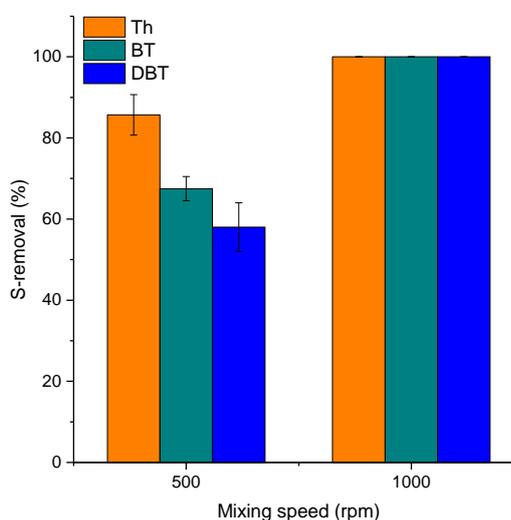


Figure 5.3: Effect of stirring speed on the extraction of sulfur compounds, IL: fuel mole proportion 1:2. Extraction time 5 min.

If the transfer of materials is dependent upon the thermodynamics of hole formation then one method of aiding transfer would be to increase agitation (stirring) enabling better contact between the two phases. The influence of the stirring speed on the sulfur compound extractions is statistically significant as seen in **Figure 5.3**. Doubling the rotation speed of the stirrer in the ionic liquid phase ensured that all the S-containing species were extracted from the decane at 25 °C within 5 min which took about double the time with a slower stirring rate.

5.4.2 Effect of Phase ratio

To investigate the effect of the mass ratio of the organic and DES phases on the extraction efficiency, different mass ratios were employed and the results are shown in **Figure 5.4**. The DES: fuel mass ratios were 1: 1, 1: 2, 1: 3, and 1: 4 and all were mechanically agitated (500 rpm) with a magnetic stirrer for 5 min and then left to settle for 5 min to ensure complete thermodynamic equilibrium at 25 °C.

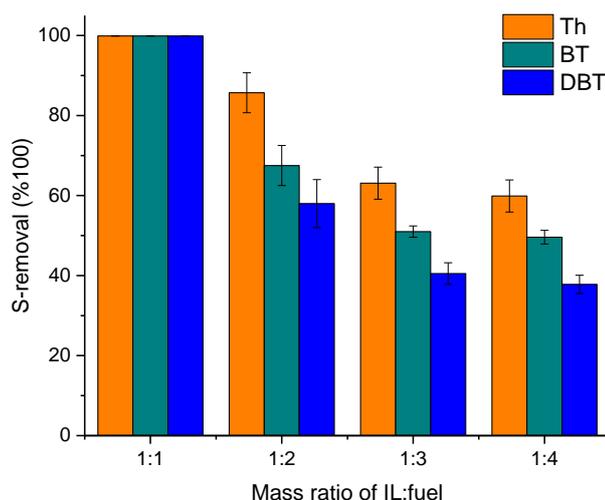


Figure 5.4: Desulfurisation of a mixture of sulfur compounds from decane containing 35 mmol L⁻¹ of Th, BT and DBT into (Bmim)FeCl₄.

It can clearly be seen that the amount of (Bmim)FeCl₄ was an important factor in EDS. Since the iron chloride is still in vast excess to thiophene it is probably a mass transport effect which is still controlling the conversion rate. This could be enhanced by increasing the surface area of the DES by streaming it as droplets through the oil phase as demonstrated at the end of this Chapter.

5.4.3 Effect of time

To understand the extraction and polymerisation processes in more detail mixtures of Th, BT and DBT were extracted with different oil to IL ratios, firstly all in one mixture and then secondly in isolation to try to elucidate the rate limiting factor. **Figure 5.5a** shows the efficiency of extracting 35 mmol L⁻¹ of Th, BT and DBT from the decane phase into

2:1 FeCl₃: (Bmim)Cl ionic liquids in an unstirred system. This was done at an IL: oil mass ratio of 1:1.

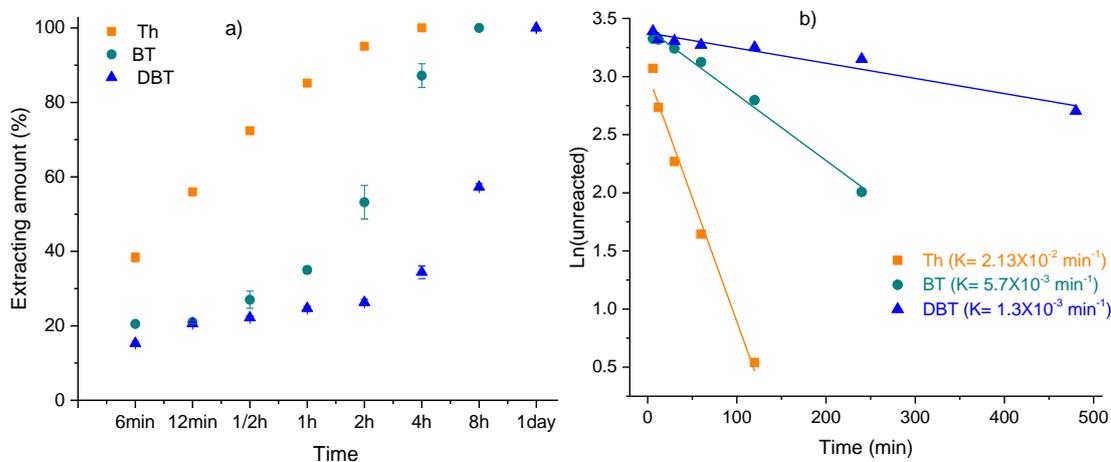
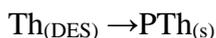
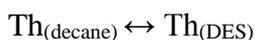


Figure 5.5: Extractive desulfurisation of Th and its derivatives as a mixture from decane into 2:1 FeCl₃: (Bmim)Cl at 25 °C, with equimass ratio of IL to fuel: a) extracting S-compound (%), b) ln (monomer) vs time.

Where an equal mass ratio of IL and decane were used (**Figure 5.5a**), after 6 min, 38 % of Th had been extracted and it required about 4 hours to extract all the Th. Compare of with the stirred system in **Figure 5.3**, it can be seen that mass transport is a very important factor governing extraction and conversion to the polymer. With respect to BT, after 1 h, only 35 % extracted and then reached 100 % after 8 hrs. Removal of DBT was the slowest process with only 34 % removed after 4 hrs. This fits in with the earlier observation that the polymerisation of Th is the fastest followed by BT and DBT.

The overall removal of the sulfur containing species is given by;



The reaction could either be limited by the transfer of species into the DES or by the activation of the monomer. If it is the latter of these then the reaction could be thought of as a pseudo-first order reaction since the catalyst is present in excess. The rate equation for this type of reaction should therefore approximate to

$$\ln([\text{Th}]/[\text{Th}]_0) = -kt \quad (5.1)$$

A plot of $\ln [\text{S-compound}]$ should give a straight line plot. The data in **Figure 5.5a** were tested in this way and the results are shown in **Figure 5.5b**. It can be seen that the extraction of all of the sulfur containing compounds follow this pseudo first order plot. However, it should be stressed that this is by no means proof that this is the definite mechanism for the extraction process. The data do not, however fit well to a second order plot or to a half order plot as may be appropriate if diffusion was the limiting factor. It can therefore only be suggested that a pseudo first order polymerisation may be an appropriate model that fits the observed data relatively well.

If the pseudo-first order polymerisation model used in **Figure 5.5** is appropriate then the rate constants decrease in the order $\text{Th} > \text{BT} > \text{DBT}$ which would seem logical given the size and reactivities of the monomers.

When the same experiment was repeated with the same concentrations of thiophenic compounds but separately (i.e. without the other two sulfur containing species in solution) the results for extraction rates were found to be different as can be **Figure 5.6**.

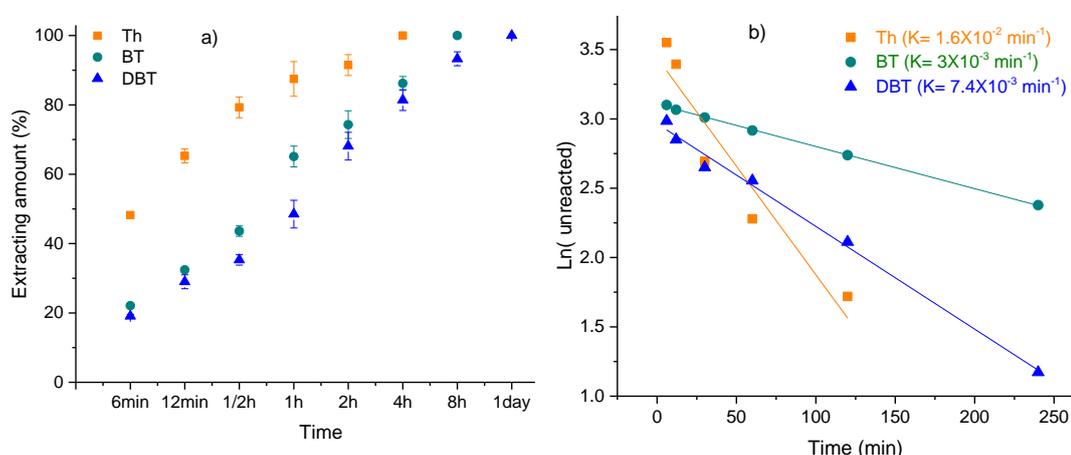


Figure 5.6: Removal of Th and its derivatives individually from decane into 2:1 FeCl_3 : $(\text{Bmim})\text{Cl}$ at 25°C , mass ratio of IL to fuel: 1:1, a) extracting S-compounds (%), b) integrated unreacted S-species vs time.

As previously observed the rate of Th removal was more rapid than BT and DBT when an equal mass ratio has used. Comparing the results for **Figure 5.6** with those for **Figure 5.5**, it can readily be seen that the rates for thiophene removal is comparatively similar

whether the other two sulfur containing compounds are there or not i.e. thiophene polymerises faster than the other two and its polymerisation is not impeded by the others. In contrast the rate at which BT is removed is significantly slower when the other compounds are not present. This implies that it forms co-polymers with Th at least which speeds up the rate of extraction. The same is also true for DBT. This suggests that copolymers form when all the monomers are present. If Th is preferentially extracted and added faster to any growing polymer than BT or DBT then it is not surprising that Th impedes the extraction of the other two monomers.

Finally, it is important to note the comparative rate constants for the electrochemical and chemical rates of polymer production. Comparing the data for Th from **Figure 5.6b** with those presented in **Figure 4.9b**, it can be seen that the rate for the chemical production of Th is approximately 1000 times faster than the electrochemical process. This would be expected given that the chemical process is a 3-D rather than a 2-D reaction as would be the case for the electrocatalytic process. It should also be noted that the concentration of FeCl_3 is significantly higher for the chemical process.

5.4.4 Exhaustive thiophene extraction

Having shown that a mixture of 2:1 FeCl_3 / (Bmim)Cl can be used to extract and polymerise thiophene an experiment was carried out to see how many moles of Th could be turned over in total by a given number of moles of FeCl_3 .

Figure 5.7 shows the number of moles of Th extracted from decane by 5 mmoles of FeCl_3 . Since Th polymerisation is a stoichiometric reaction rather than a catalytic process, the FeCl_3 will have to be regenerated to make the process viable. The stoichiometry of the reaction will show how efficient the reaction is. Theoretically, the number of the moles of thiophene reacted with FeCl_3 should be equal to 2.5 mmoles which is around half number of Fe^{+3} ions in the ionic liquid.

In this experiment aliquots of Th were added to the decane layer every 5 minutes. **Figure 5.7** shows the total amount of Th extracted from the decane layer over time.

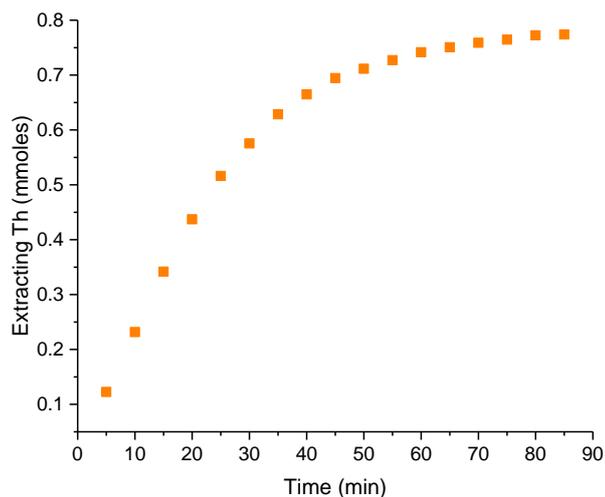


Figure 5.7: Thiophene extracted with 5 mmol Fe^{III} in 2:1 molar ratio of $FeCl_3/(Bmim)Cl$ as a function of time.

The total amount of Th extracted was 0.77 mmol which is considerably less than should be extracted. It is thought that the polymer forms a gel with the remaining ionic liquid preventing further polymerisation and leading to a low extraction efficiency. In addition it should also be noted that if too much of the Fe^{III} is reduced to Fe^{II} then the liquid will also not be Lewis acidic enough to oxidise Th. The same experiment was repeated twice; once under O_2 gas and once under N_2 gas but in both cases the solid black precipitate formed and a similar number of moles were extracted. It can be seen that approximately 4 moles of $FeCl_3$ were required to oxidise each mole of Th.

5.5 Alternative ionic liquids

5.5.1 Alternative metal-based ionic liquids

In principle if iron based ionic liquids were just catalysts for electron transfer then any metal salt with a redox potential above that of the $Fe^{III/II}$ couple should also act as a suitable catalyst for the polymerisation of Th. To show the catalytic behaviour of iron vs other metals the experiment was repeated using copper (II) chloride. The redox potential for the $Fe^{III/II}$ couple in DESs is relatively similar to the $Cu^{II/I}$ couple meaning that they should have similar oxidising power.¹⁸ As has been mentioned before, when thiophene in decane solution was contacted with the DES the deep brown colour of the $(Bmim)FeCl_4$

rapidly changed to a black solid as shown in **Figure 5.8**. However, the orange/brown colouration of the (Bmim)CuCl₃ liquid remained unchanged.

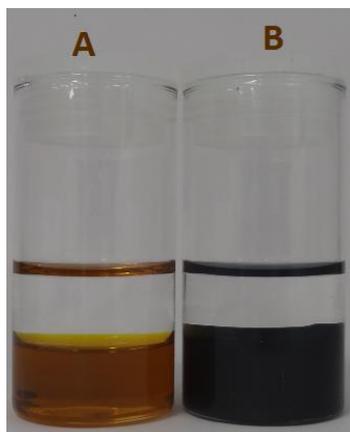


Figure 5.8: 100 mmol L⁻¹ thiophene in decane with (A) 1:5 molar ratio of CuCl₂:(Bmim)Cl, (B) 2:1 molar ratio of FeCl₃:(Bmim)Cl.

To check the fate of the thiophene samples were removed after 48 hours without stirring from the upper-layer and analysed in triplicate using GC-FID as presented in **Figure 5.9**. As a result, the chromatogram data shows that no peak of thiophene after polymerisation appeared with the Fe-containing ionic liquid, but there is still a significant monomer peak in decane after extraction by (Bmim)CuCl₃.

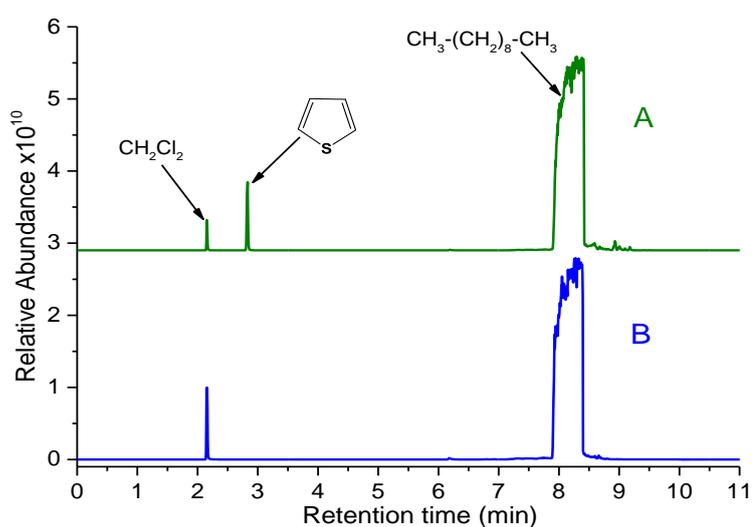


Figure 5.9: The chromatograms of organic phase after separating from (Bmim)Cl with (A) CuCl₂, (B) FeCl₃.

In addition to using GC-FID, the absorbance of the remaining amount of thiophene in the organic phase has been measured by UV-Vis spectrometer as illustrated in **Figure 5.10** and essentially, the same results were observed.

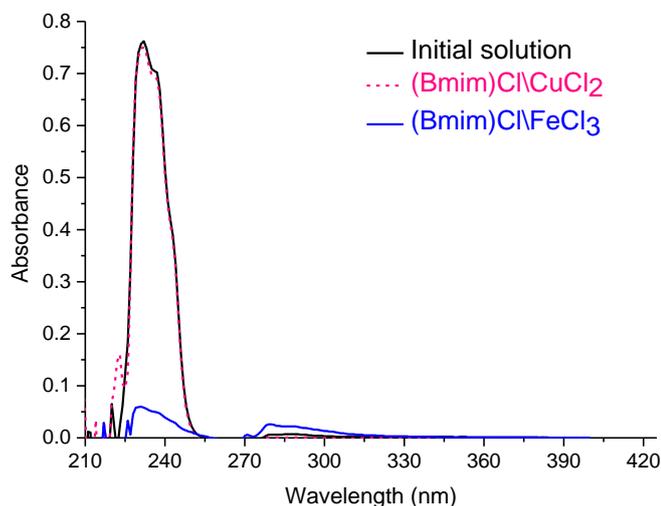


Figure 5.10: Absorption spectra of remained Th in decane before and after extraction by (Bmim)Cl with oxidising agents.

Whereas copper(II) was used as a strong oxidant in this project, Cu(I) has a stronger π -complexation interaction with thiophene.^{19, 20} Moreover, There are such methods in the literature that utilised copper(II) as oxidant for the preparation of high molecular weight polymer.²¹ However, in such cases, CuCl₂ works as a catalyst for polymerisation but does not work as a stoichiometric oxidant.²² The unpolymerised quantity of thiophene which was detected after reaction with Fe-based imidazolium cation was 3.8%. This implies that (96.2 \pm 1 %) of thiophene might be removed and polymerised on account of the strong catalyst FeCl₃.

The result also shows that after polymerisation; almost no Th was extracted into the Cu-based ionic liquid in comparison with that by the Fe-containing imidazolium cation. Abbott and coworkers¹⁸ reported that redox potential (E°) of Cu^{III/I} in DES is more positive and stable on account of the complexity formation with chloride which can be considered that Cu^{II} in DES has similar property in the high chloro environment. It can therefore be concluded that 2:1 FeCl₃ / (Bmim)Cl acts as a Lewis acid reagent. This ties in with the

work by Boesman who showed that the 2:1 $\text{AlCl}_3/(\text{Bmim})\text{Cl}$ also acted as a Lewis acidic reagent for the chemical polymerisation of Th.

5.5.2 Alternative cationic ionic liquids

While iron chloride is a sustainable and hence inexpensive compound to use as a catalyst, imidazolium chloride is comparatively expensive and moderately toxic. In most of the previous studies,²³⁻²⁵ π - π electronic interaction was thought to be the predominant extraction mechanism between aromatic sulfur compounds and aromatic rings based-ILs owing to the excellent S-species removal ability such as pyridinium and imidazolium salts. However, Wilfred and co-authors²⁶ dispelled these ideas using non-aromatic ammonium salts (tributylmethyl ammonium methylcarbonate) and were still able to demonstrate high extraction efficiency.²⁷ To circumvent the use of imidazolium salts of the chloroaluminate based ionic liquids, Abbott et al.²⁸ used benzyltrimethylammonium chloride (BTEAC) and benzyltriethylammonium chloride (BTMAC) instead (**Figure 5.11**).

Analogous liquids were made with BTEAC and BTMAC in a 2 FeCl_3 :1QAS molar ratios and these were tested for their efficacy for sulfur compounds removal.

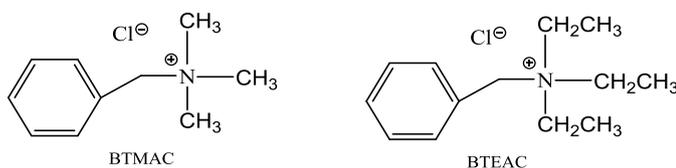


Figure 5.11: Ammonium salts used in desulfurisation operation.²⁸

So, the experiment was carried out by preparing 35 mmol L⁻¹ of Th, BT and DBT in decane. After mixing and stirring (600 rpm) with equal mass of Fe-based ammonium cation at 50 °C in a water bath for 30 min. On completion of the reactions, the upper decane phase was removed and analysed by GC-FID. In both cases no Th or its homologues were found, meaning that complete extraction had been achieved and in all cases a black solid was obtained. While the QASs are cheaper than imidazolium salt with relatively lower toxicity²⁹ it should be noted that the reactions took place at 50 °C as the liquids were too viscous to use at room temperature.

5.5.3 Alternative anionic ionic liquids

In the previous section, it has been shown that polythiophene is difficult to separate from (C₄mim)Cl: 2FeCl₃ ionic liquids. It was proposed that the reason for this difficulty is because the liquid is so viscous and because when the Fe^{III} complex is reduced to Fe^{II} it solidifies. According to Zhong et al.,³⁰ (Bmim)₂Fe(II)Cl₄ has an approximately tetrahedral symmetry and this symmetry gives it a high melting point of 58 °C which could be why the ionic liquid phase solidifies after PTh formation. An alternative method is to dissolve FeCl₃ in an ionic liquid with a less basic anion than Cl⁻. This would mean that less moles of FeCl₃ would be required to make the liquid Lewis acidic and the liquid would be less viscous.

To demonstrate this, chemical polymerisation of Th was carried out with a 1:1 molar ratio of FeCl₃-(Bmim)OTf and (Emim)NTf₂. It should, however, be noted that with (Emim)NTf₂ chemical catalysis could be achieved with less than 1 mole equivalent of FeCl₃ because NTf₂ is not very Lewis basic. FeCl₃ is soluble in both liquids. When chemical polymerisation was carried out under the same conditions used above for the (Bmim)Cl systems, a black deposit was obtained showing that the solution is more Lewis acidic with less FeCl₃ than was required with (Bmim)Cl.

To investigate the phase behaviour of the ionic liquid, FeCl₂ was dissolved in (Bmim)OTf and (Emim)NTf₂ and the results are shown in **Figure 5.12**. In (Bmim)OTf, FeCl₂ is soluble but it forms a thick paste. In (Emim)NTf₂ however, it does not appear to be soluble and it phase separates forming a fine suspension. This may ultimately provide a route by which to regenerate the ionic liquid. The important aspect of this study is that it shows that the ionic liquid phase remains fluid.



Figure 5.12: 1:1 equimolar of chlorometalate (II) anion in a) (Bmim)OTf, b) (Emim)NTf₂ at 50 °C.

5.6 Recyclability of ionic liquids

5.6.1 2FeCl₃: (Bmim)Cl recycling by extraction

From a practical perspective, regeneration of the ionic liquid extractant is vital to make this process viable. Several attempts have been made to regenerate (Bmim)FeCl₄ mixtures. For instance, Lee and co-workers attempted the recovery of Fe-based imidazolium chloride from its mixtures with H₂O using an electromagnet (the liquid is known to be ferromagnetic); however, this way was unsuccessful as only 20 wt% of IL was recovered as the rest of the material was too soluble in water.³¹

One mechanism by which the issue of solid polymerisation could be circumvented was to remove the sulfur by C-S-C bond cleavage as shown in **Figure 5.13**.

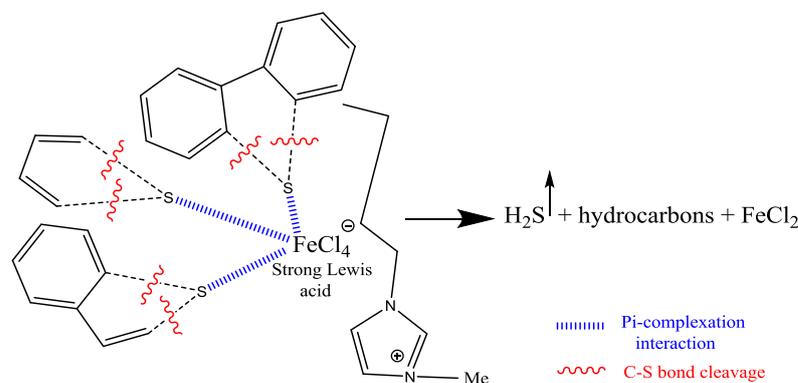


Figure 5.13: One of the estimated mechanism reaction of extractive polymerisation of aromatic S-compounds by (Bmim)FeCl₄.

It was proposed that employing a strong Lewis acid such as ferric chloride with IL could possibly break the C-S bond.³² Diradical-dication formation was proposed as the product after C-S bond breaking; which probably destroyed the structure of the IL in the process. Additionally, if cleavage of the the C-S-C aromatic bond happens, then some of Th, BT and DBT probably would probably be converted to hydrocarbons with the formation of some H₂S gas. To illustrate the presence of this side mechanism a piece of wet Litmus paper was held close to the top of decane surface and after a while, its yellow colour became a deep red indicating the emission of H₂S gas. The characteristic smell was also noted although it only takes a trace of this to be detected with the nose. GC-FID of the decane was carried out to see if any hydrocarbon product was back extracted. Unfortunately, no peaks of hydrocarbons were detected probably due to their low concentrations.

To overcome the above difficulties, Wang et al.,³³ illustrated a simple chemical method for the successful recovery of (Bmim)FeCl₄ from the homogeneous solution using saturated NaCl solutions together with a molecular organic solvent like chloroform or carbon tetrachloride to form a three phase system. This approach was tested on the spent ionic liquids and the results are shown in **Figure 5.14** for the ionic liquid after exhaustive extraction of Th, BT and DBT.

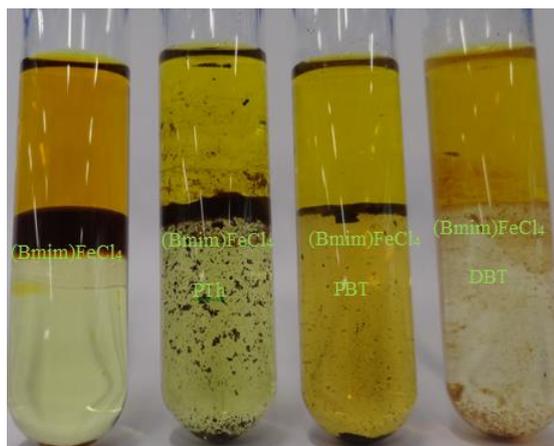


Figure 5.14: Recovery of used FeCl₃-based IL after S-compounds extraction using super centrifuge to isolate saturated sodium chloride, polymer and a volatile CHCl₃ chloroform from IL mixture.

The unused (Bmim)FeCl₄ was unaffected by this back extraction process. Using this approach for the extraction of PTh left an incomplete separation with a black polythiophene precipitate in the bottom of the tube and on the wall of the tube but it was impossible to recover the ionic liquid in a pure form. For the polymerisation of BT two coloured layers form showing that the separation is not clean and a deep black/ brown deposit was formed in the bottom of the tube and at the interface between the two liquids. For PDBT no appreciable solid was formed suggesting that it is not possible to polymerise DBT as mentioned in **Chapter 4**. These results suggest that this method of recovery for the IL mixture may not be suitable.

5.6.2 2FeCl₃: (Bmim)Cl recycling by electro-oxidation

The second method attempted for solving the solidification of the ionic liquid phase was to use an electrochemical bulk electrolysis to reoxidise the Fe^{II} to Fe^{III}. This was attempted using a simple two-electrode set up as shown in **Figure 5.15**.

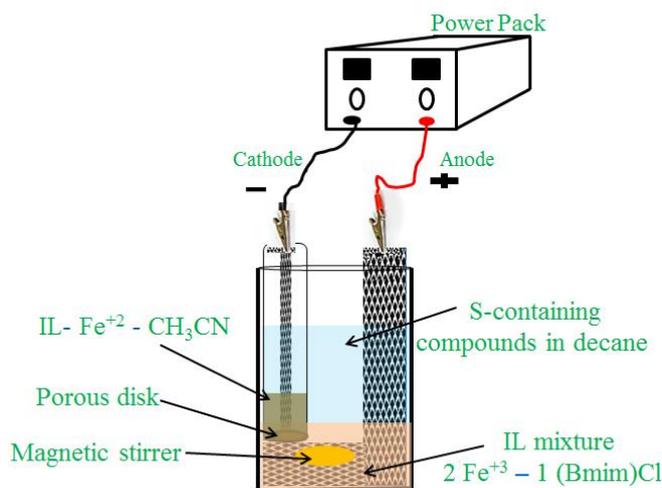


Figure 5.15: Simplified schematic of potentiostat system for IL modification during extractive polymerisation.

The cell for ionic liquid regeneration is shown in **Figure 5.15**. The aim was to reoxidise the Fe^{II} formed from the oxidation of Th back to Fe^{III} . A small glass cell containing the two electrodes separated by around 1 cm was positioned in it. The anode was an iridium oxide coated titanium mesh. The cathode consisted of thin glass tube containing (Bmim)Cl, FeCl_2 and a trace amount of CH_3CN circuit by Ti mesh. A constant voltage of 5.5 V was applied across the two electrodes. The current density was between 2 and 5 mA cm^{-2} . The experiment was run by adding 7.5 μL Th to the decane layer every hour. If the reaction was stoichiometric then each Th needs 2 electrons to oxidise it to PTh. The current density was calculated from the amount of Th that could be oxidised using the Faraday equation (5.3).

$$\text{moles of Th} = \frac{i \cdot t}{nF} \quad (5.2)$$

where, t is the time of reaction, i is the passed current, n is the number of electrons used to oxidise each monomer and F is Faraday constant (96485.3C). To reoxidise Fe^{II} to Fe^{III} from adding 7.5 μL within 1 h, the oxidation of ferrous needs approximately 5mA.

During the experiment, gas was evaluated from the solution when Th was added to the decane layer. The gas was clearly identified as H_2S through its characteristic smell and its effect of wet litmus paper. The polymerisation of thiophene still occurred and a black solid formed in the IL. The same gas was also observed by Zhang and coworkers who

used 2:1 molar ratio of AlCl_3 - MTEACl for the extraction of thiophene.³⁴ Eventually the ionic liquid solidified despite the application of a current which showed that the electrochemical regeneration of the liquid was ineffective.

5.6.3 FeCl_3 : (Bmim)OTf recycling by extraction

In principle the regeneration of the (Bmim)OTf or (Emim)NTf₂ ionic liquids should be easier than that discussed above for (Bmim)Cl: FeCl_3 . The method attempted to use a methanol/water mixture to dilute and extract the reaction products. **Figure 5.16B and D** show mixtures of (Bmim)OTf and (Emim)NTf₂ with FeCl_3 before and after the reaction with Th.

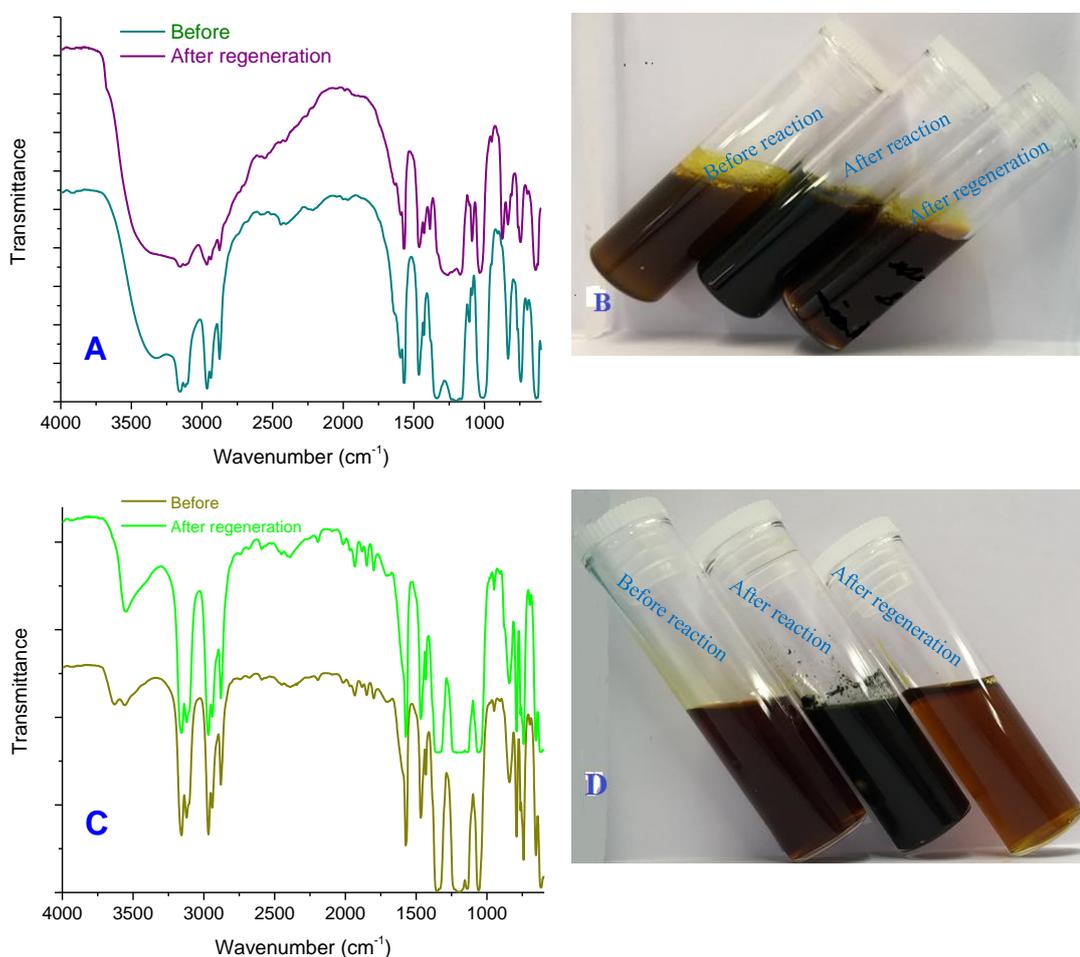


Figure 5.16: Regeneration of used ILs and their IR spectra analysis before and after adding Th; A,B- equimolar ratio of (Bmim)OTf- FeCl_3 , and C,D- 0.22 grams of FeCl_3 in 2grams of (Emim)NTf₂.

The IL phase turned black and viscous when polythiophene formed. The addition of an equal volume of a methanol/water mixture resulted in a more fluid layer which could be filtered. After filtration, the water/ methanol mixtures were removed from the ionic liquids using rotary evaporation. **Figure 5.16A** and **C** show the IR spectra of the liquid before and after recycling and it can be seen that the liquids are essentially the same from an organic perspective.

While the organic component looked very similar after regeneration it can clearly be seen from **Figure 5.16B** and **D** that the IL mixture has become much lighter most probably due to the consumption of FeCl₃ in the chemical polymerisation reaction of thiophene.

The regenerated liquids shown in **Figure 5.16B** and **D** were used to carry out a second polymerisation in the same way as used for the fresh solution and the results are shown in **Table 5.5**. As would be expected the extraction efficiency of the liquid has dropped but most notably no black layer formed showing that the ionic liquid phase is not Lewis acidic enough to chemically polymerise Th.

Table 5.5: Chemical polymerisation of 0.156 mol L⁻¹ Th in 2 ml decane.
Reactions conditions: 35 °C (for OTf) and 25 °C (for NTf₂) IL, 15 min at 900 rpm stirring speed.

IL- FeCl ₃	Extraction (%) before regeneration	Extraction (%) after regeneration
(Bmim)OTf - FeCl ₃	84	58
(Emim)NTf ₂ - FeCl ₃	81	54

5.6.4 FeCl₃: (Bmim)OTf recycling by chemical oxidation

The final method attempted to recycle the spent ionic liquid was to chemically reoxidise the Fe^{II} back to Fe^{III} using a chemical oxidising agent. The general reaction for the polymerisation could be considered as



The aim of the recycling would be to reoxidise the FeCl₂. One method could be to use a halogen. Clearly the use of chlorine gas would be hazardous, but bromine is a good

oxidising agent and relatively easy to handle. Following reaction of FeCl₃: (Bmim)OTf with Th, a black precipitation formed as previously. Addition of an equimolar amount of Br₂ liquid initially coloured the decane layer but this gradually decolourised as the bromine was transferred to the ionic liquid. Unfortunately, the ionic liquid layer did not change its viscosity and so centrifuging the ionic liquid phase did not bring about phase separation of the polymer.

This shows that the main issue with recycling the ionic liquid phase is the fact that the polymer gels the ionic liquid phase which makes separation difficult. Any future methodology will probably have to involve a dilution and a reoxidation step. One method that could be used would be to add a third phase which would ultimately decrease the viscosity enabling separation but ultimately be immiscible with the ionic liquid phase. This could be something like an ether which could dissolve the bromine but which will phase separate from the ionic liquid. The issue may still be the similarity in density between the polymer and the ionic liquid.

5.7 Practical desulfurisation

5.7.1 EDS application to commercial diesel using 2:1 Fe-based (Bmim)Cl

Nie and coworkers investigated the EDS process using ILs on commercial diesel samples.³⁵ The authors suggested that S-removal from commercial fuel is much harder than desulfurisation of model fuel without giving the reasons.³⁶ Similarly, Eßer et al,²⁴ reported the K_p for S-removal of commercial diesel is less than K_p of a model oil.

This is thought to be due to the high electron density on O and N-compounds in diesel fuels which induce a strong attraction with Fe-based IL and thus reduce the capability of the IL for desulfurisation. Xiao and co-researchers showed that at a concentration of less than 1 wt%, polyaromatic components such as phenanthrenes have a strong inhibiting effect on the desulfurisation.³⁷ Similarly, Xu et al. and Yu et al. also found that in addition the relatively high moisture content in commercial diesel fuel necessitates additives which have a negative impact on the removal of sulfur compounds.^{37, 38}

Thus, the extraction performance of the IL mixture for aromatic sulfur species decreases because of the complicated composition of the real diesel including impurities of many organic N and O compounds as well as aromatic compounds present in it.^{24, 39} Similarly,

Shu et al,⁴⁰ reported that more complex components contained in real fuel lowers the desulfurisation efficiency than that for a model fuel. Zhu and co-workers proved that olefins and aromatic compounds in real diesel have a negative influence on the extraction efficiency.^{41, 42}

GC analysis of the commercial diesel fuel was carried out using the same procedure previously described in **Chapter 4**. Numerous peaks highlighted the complexity of the diesel fraction but precise identification of these compounds was not possible due to the unavailability of standards. Extraction was carried out using a biphasic $2\text{FeCl}_3:(\text{Bmim})\text{Cl}$ / diesel system. Commercial diesel was used but it was spiked with Th, BT, and DBT each at a concentration of 35 mmol L^{-1} . The concentration of the thiophenic compounds were determined by GC at the same operational reaction conditions as those described above. In addition, the effects of mixing rate, temperature, and extraction time were determined.

The efficiency of Fe-loaded IL extractant toward the extractive desulfurization are shown in **Figure 5.17**:

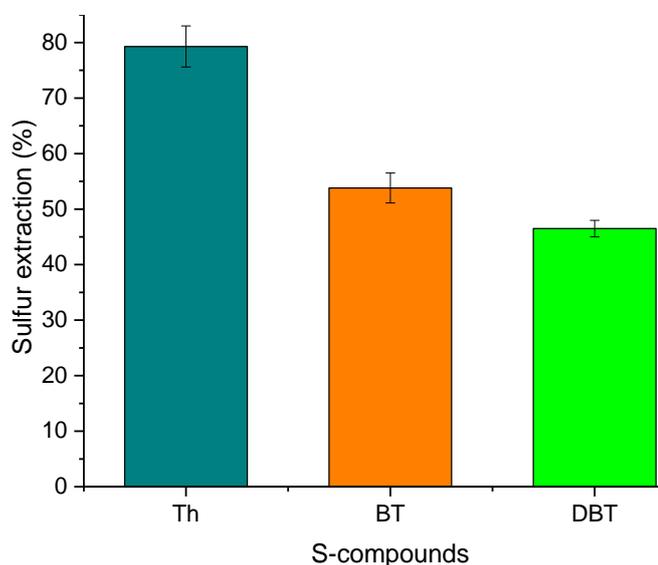


Figure 5.17: Removal of S-containing compounds by imidazolium IL from real diesel fuel. IL: fuel mass ratio: 1:2, 550 rpm, at 25 °C for 5 min.

For the commercial diesel fuel (**Figure 5.17**), the desulfurisation ability of the studied ionic liquid follows the same trends as in the case of the decane. During the process, the

sulfur levels in the upper phase (35 mmol L^{-1}) of each one of Th, BT and DBT could be extracted to (27.8 , 18.8 and 16.3 mmol L^{-1}) respectively through the optimisation of reaction conditions; which means 79.3 , 53.8 and 46.5% of Th, BT and DBT respectively were removed just after 5 min. This compared with 85.7 , 67.5 and 58% respectively for the corresponding extraction from decane. As expected, the extraction data for removing Th, BT and DBT from commercial diesels are lower than from decane. This may be attributed to the coexistence of many aromatics, oxygen and nitrogen additives which compete with the partition of S-compounds in the $(\text{C}_4\text{mim})\text{FeCl}_4$ and saturate the ionic liquid phase. It should however be noted that the extraction efficiency was much higher than by the electrochemical method described in **Chapter 4**.

Peak identification of some of the compounds present in the commercial diesel fuel sample was gathered and the elution time was compared with some standards as well as some data available in the literature. Co-elution of hydrocarbons along with sulfur compounds present in the fuel, can affect retention times e.g. from decane the retention times for Th, BT and DBT by GC were 3.14 , 9.88 and 14.7 min which compare with 3.36 , 10.10 and 14.97 min from commercial diesel fuel.⁴³

Saturated hydrocarbons are generally unaffected by the treatment with acidic imidazolium cation mixture under the stated conditions. The investigated IL mixture showed similar behaviour as indicated by GC-FID data. The diesel compositions appear to be practically unchanged in all extraction stages by DESs except for the fact that sulfur compounds were removed.

Figure 5.18 shows the gas chromatography profiles of the diesel fuel before and after extractions. It is clear that the main content of the diesel fuel does not change before and after extraction. However, after checking the peak areas of the diesel components after extraction, plenty of peak areas reduced and were not the same as in the original in the case of IL- FeCl_3 .

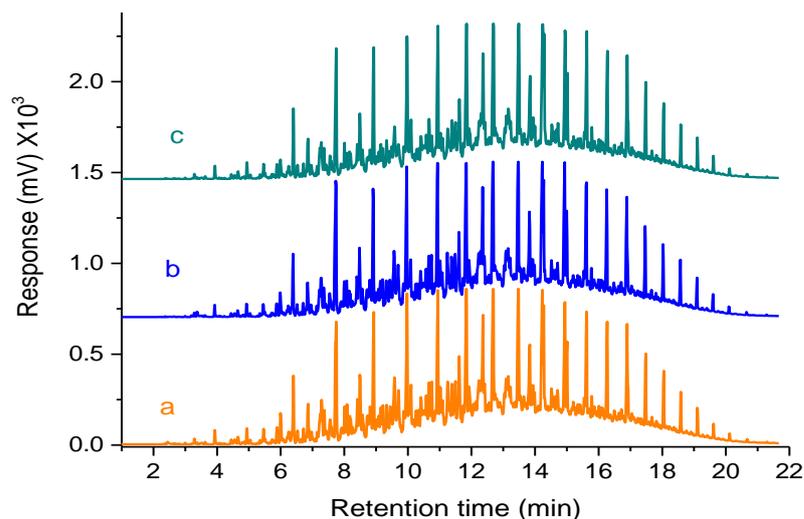


Figure 5.18: GC profiles of commercial diesel fuel a- original, b and c- after extraction using (Bmim)FeCl₄ and DES respectively.

These results are similar to those reported by Adlard using GC-FID as shown in **Figure 5.19**.⁴⁴

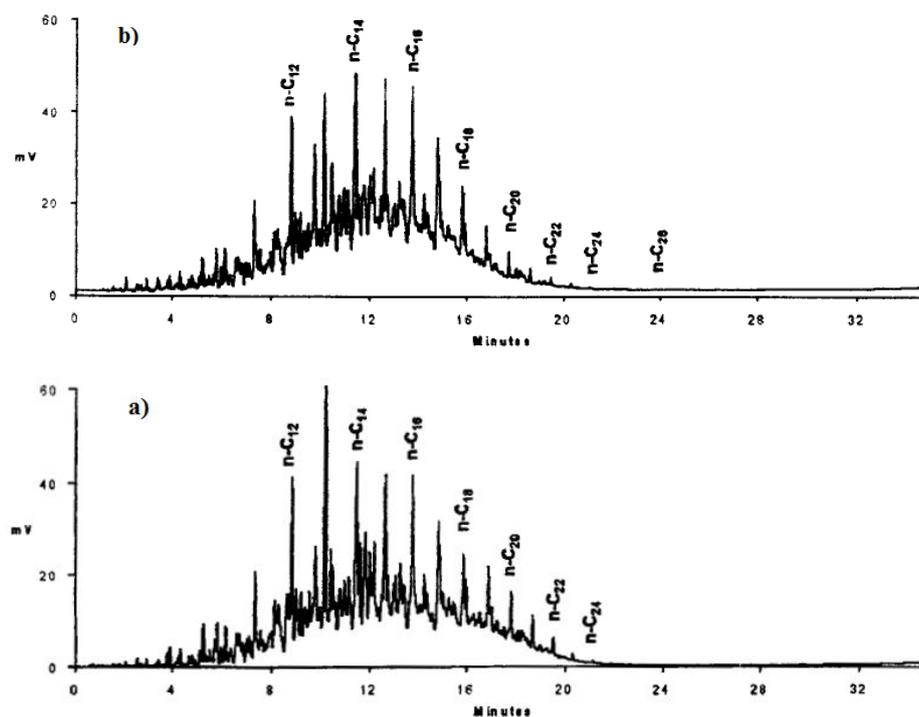


Figure 5.19: FID chromatograms of a) 332 mg/kg sulfur in diesel fuel oil, b) 26.5 mg S L⁻¹ in diesel fuel.⁴⁴

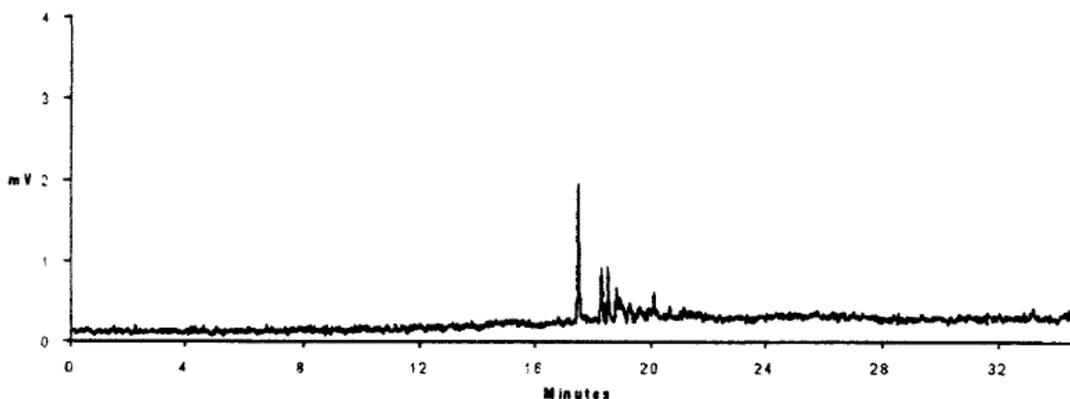


Figure 5.20: SCD chromatogram of low S- containing real diesel fuel in **Figure 5.19b**.⁴⁴

The presence of so many hydrocarbons and heterocyclic compounds in the chromatograms, meant that it was preferable to use GC coupled to sulfur chemiluminescence detector (SCD) rather than GC-FID for S-compounds detection in the commercial diesel sample, because the SCD detector just quantifies S-compounds. GC-(SCD) was utilised by Adlard,⁴⁴ due to the complex specification of sulfur compounds as shown in **Figure 5.20**.

The main issue in the analysis of real diesel fuel is the complexity of this natural mixture including hundreds of different aromatic and aliphatic components with a boiling point range from 498 to 623 K.⁴⁵ Variations in the composition of diesel fuels depend on refinery processes and on the source of the crude oil.⁴⁵ Recently, Wang and coworkers⁴⁶ reported that progress has been made in the identification and separation of petroleum components. The authors identified 121 aromatic hydrocarbons in diesel fuel by capillary GC-MS.

5.7.2 Process Design

In 2001, a first paper describing deep desulfurisation using chloroaluminate ionic liquids and its application on the real diesel fuel was published by Boesmann et al.^{47,48} Although 80 % of the sulfur components were removed successfully, its practical use was difficult. It has been proposed that the main advantages of ILs for deep desulfurisation is that they can be used at low pressure and low temperature.^{49, 50}

To apply the ideas described above, a deep desulfurisation plant would need to be constructed which could ensure the maximum liquid-liquid contact surface area. A theoretical schemed diagram of an experimental apparatus that could achieve this is pictured in **Figure 5.21**. The apparatus comprises a feed bank of thiophene containing diesel, a pipeline reactor in which the IL and oil could be contacted and an electro-regeneration system.

The diesel flow rate would be regulated by a pump (3) and this would have to be adjusted to ensure the correct level of desulfurisation. The inlets (4) would spray the IL from the top of the reactor with multiple nozzles to create small droplets of IL to optimise the liquid-liquid contact area. The IL would be regulated using a pump (11). The spray would be collected in a cone shaped funnel and the differential density would ensure good separation from the diesel.

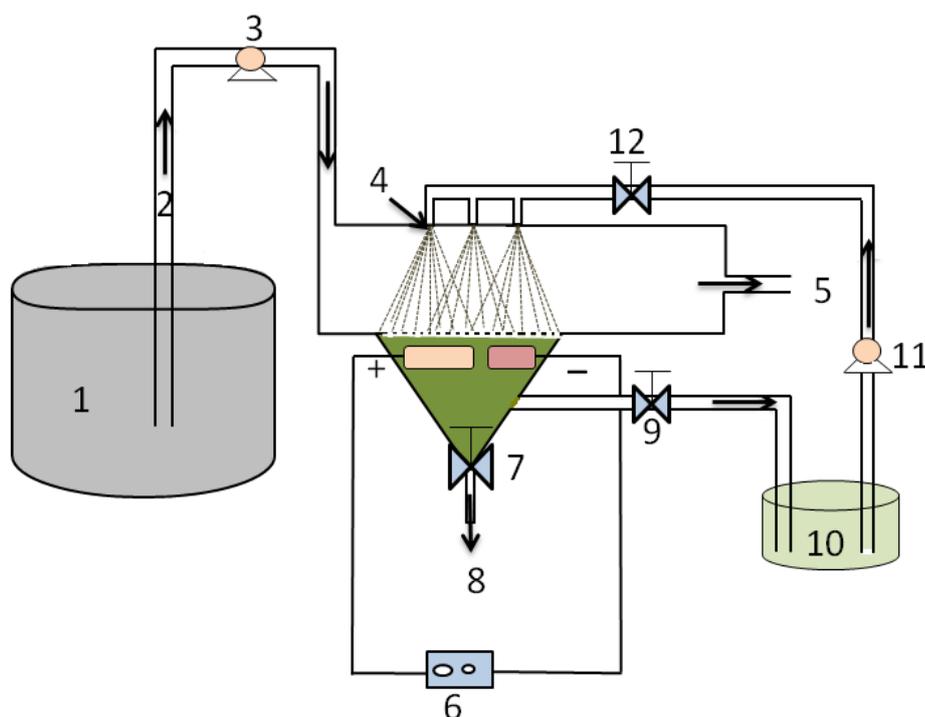


Figure 5.21: Flowchart of experimental set-up 1) feed bank, 2) thiophene-based diesel fuel inlet, 3) influent pump, 4) pump nozzles, 5) free Th diesel fuel outlet, 6) voltage stabilised power, 7), 9), 12) manual valves, 8) PTh outlet, 10) circulation tank and 11) submersible pump.

PTh would be removed from the system through valve 7 and the IL could be regenerated using the electrochemical cell (6) or through mixing with a chemical oxidant such as bromine. For the electrochemical regeneration the anodic reaction would be the

reoxidation of the Fe^{II} . The cathodic reaction would need to be the electrolysis of extraneous water extracted from the diesel yielding a small amount of hydrogen gas. **Figure 5.22** shows the pump nozzles for $(\text{Bmim})\text{Cl} : 2\text{FeCl}_3$ being pumped through decane. As can clearly be seen, a good separation of the two phases is achieved while simultaneously getting a good liquid-liquid contact area.



Figure 5.22: Nebulising $(\text{Bmim})\text{Cl} : 2\text{FeCl}_3$ mixture by injection into the decane fuel.

5.8 **Conclusion**

This Chapter has shown that Lewis acidic tetrachloroferrate based ILs, particularly those containing imidazolium cations, are very efficient at chemically removing sulfur containing compounds from alkane based liquids. The advantage of using an iron-based catalyst is naturally that it is eminently sustainable and hence has a low cost. The use of imidazolium cations on the other hand is more expensive although other quaternary ammonium salts have been demonstrated as being viable in this chapter. While these liquids are more viscous and less highly conducting than some of the DESs used in earlier chapters. Some of the physical properties such as a low surface tension makes them more suitable for solute extraction. A trace amount of organic phase is miscible in IL, but this is negligible and no solubility of the DES in the oil was detectable.

The extractive capability of $(\text{Bmim})\text{Cl} : 2\text{FeCl}_3$ is significantly different from that of the $(\text{Bmim})\text{Cl} : \text{FeCl}_3$ liquid most notably in that the former is exothermic while the latter is endothermic. The extraction of thiophenic compounds from the alkane phase occurs relatively quickly with moderate stirring but it was quite slow in an unstirred system.

Probably due to the breaking interaction between electron pair on the heterocyclic S atom and Fe^{III} ions of ionic liquid anion. The extraction of S-compounds is strongly affected by the stirring rate and on the oil to ionic liquid ratio. Clearly the faster the stirring rate the faster the system comes to equilibrium and the more ionic liquid the more thiophenic compounds are extracted.

Strong interaction between the Lewis acid and S-species made the extraction easier even when the reaction takes place in the absent of stirring. Quantifying the interaction between FeCl₃ and thiophene shows that considerably fewer moles of thiophene are oxidised than there are moles of ferric chloride. This is thought to occur because polythiophene does not separate from the ionic liquid (due to similar densities and high viscosity). The polymer causes the ionic liquid to gel which decreases mass transport and stops the reaction.

Two different approaches have been used to regenerate the IL mixtures. In the first, the recovery of (Bmim)FeCl₄ from the homogeneous solution using saturated NaCl solutions together with a molecular organic solvent. In all cases for the used liquids the polymer did not separate well from the ionic liquid due partially to the viscosity but also due to their similarity in density. The second technique was chemical or electrochemical oxidation to regenerate the iron (III) catalyst. While this may be the most logical approach it was practically difficult due to the high viscosity of the ionic liquid phase once the polymer had formed. This was thought to be due to the same reasons as observed above i.e. the polymer gels the ionic liquid and decreases mass transport.

While recycling the (C₄mim)FeCl₄ is difficult, it was proposed that if an ionic liquid could be used which was less viscous then the separation of the polymer from the ionic liquid would be easier. Experiments were carried out using FeCl₃ in (Bmim)OTf or (Emim)NTf₂ as alternative to (Bmim)Cl. Polythiophene was successfully prepared in both (Bmim)OTf and (Emim)NTf₂ and the mixtures were successfully regenerated and reused. The resulting polythiophene was analysed by UV-Vis and IR spectroscopies.

This procedure has many advantages:

- 1) The preparation of IL is very simple.
- 2) FeCl₃-based ILs showed a good partition coefficient and a relatively fast equilibrium in a stirred system.
- 3) Iron (III) salts are inexpensive and easy handle oxidants. Gao et al.,⁵¹ reported that Lewis acidity (electron-withdrawing ability) follows this order: AlCl₃ > FeCl₃ > ZnCl₂ =

CuCl. The AlCl₃ liquids are too water sensitive and that makes the ferric chloride liquids the best available catalyst.

The major disadvantage is in the recycling of the ionic liquid. While both physical and electrochemical methods have been shown to be unsuccessful in this study, a simple gas phase oxidation probably could be used to reform the FeCl₃ catalyst but the main difficulty with this technology is the similarity in density between the polymer and the ionic liquid makes physical separation of the viscous phase very difficult.

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Chapter six: Conclusions

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6. Conclusion & future works

6.1 Conclusion

This study has focussed on the extraction of thiophenic compounds in oil-like liquids. While this is quite a specific application, it is also part of a larger study within the group to understand the extraction of a wide range of useful molecules into DESs. In the current study the molecules to be removed are contaminants so it is in effect a purification process of the oil-like liquids. The study could just as easily be applied to the extraction and concentration of useful molecules as would be the case for natural product extraction.

In this work, three different methods were chosen to extract the thiophenic compounds; extraction, electrochemical polymerisation and chemical polymerisation. In the first of these, extraction, six different DESs were used for the extractive desulfurisation (EDS) of decane. Three thiophenic compounds were used as typical of those found in crude oil; Th, BT and DBT. The best extractant for the all of the thiophenic compounds was Pentaline. The conditions required for the extraction by DESs were optimised in terms of the time required to reach equilibrium and the effect of temperature and stirring. The partition coefficient was found to decrease in the order Pentaline > Butaline > Ethaline > Glyceline > Reline. Polarity parameters of the DESs were found to all be very similar and do not correlate with the extraction efficiency. It has been thought that the main factor affecting partitioning of species into the DES the enthalpy of transfer. This is turn was thought to be limited by energy required to make a void in the DES.

A good correlation was observed between the extraction efficiency of S-compounds and the surface tension of DESs confirming the importance of hole formation in the extraction process. The positive values of ΔG shows that extraction is non-spontaneous as the enthalpy of extraction is endothermic. So, the equilibrium lies largely towards the S-species being in the oil phase but partitioning into the DES is favoured at higher temperatures. The positive value of ΔS indicates that aromatic S-compounds disrupts the structure of the DESs.

Based on the size of the solute, the extractive performance using DESs follow the trend: Th > BT > DBT. When the hydrogen bond formation between the solute and the HBD of the DES is larger than that between the chloride and the HBD of the DES, then the partition of S-species into DESs is larger and the enthalpy of solvation becomes

exothermic. The extraction of sulfur compounds from commercial diesel fuel using DESs was attempted on a diesel sample spiked with Th. Under comparable conditions the extraction efficiency was slightly lower with commercial diesel than decane which is thought to be due to the large variety of polar additives which are included in diesel samples. A recycling protocol was tested for the DESs but it was quite complex and would not be practically viable.

Extractive electrochemical polymerisation of Th and BT was attempted in the DESs but no polymer could be grown on the WE which probably is due to the presence of Cl^- and H_2O which both terminate chain growth. An alternative approach that may be possible could be to cool the DES to cause the thiophenic compounds to either precipitate (BT and DBT) or to separate (Th). Overall, Pentaline seems to be the best extractant among all used DESs because it has very low surface tension for common extraction at low temperature.

The second approach was to use an electrocatalytic method to oxidise Th to PTh. A 1:1 mixture of (Bmim)Cl and FeCl_3 was used for the process owing to the relatively low surface tension and strong Lewis acidity of the IL mixture. This allowed Th to be successfully partitioned into an aprotic IL from a decane layer and then electropolymerised to PTh. FT-IR and Raman spectroscopy showed that the black layer formed on the electrode through repetitive cycling was PTh. It was shown that (Bmim) FeCl_4 acts as an electrocatalyst by analysing the mass-charge plots obtained using a Pt coated QCM resonator and employing the Sauerbrey equation.

Different factors were studied to optimise Th electropolymerisation such as temperature, monomer concentration and sweep rate. It has found that increasing the concentration of Th monomer in decane decreased the rate of polymerisation, possibly was due to adsorption of the monomer on the electrode film surface which poisoned the electrode surface. As predicted, the amount of PTh that grows on the electrode surface increases with increasing temperature which might be from a significant decrease in the viscosity of the IL mixture.

No polymer could be formed after extraction of BT from organic phase on IL mixture followed by electropolymerisation which was thought to be due to the high reactivity of radical BT cations, which can undergo fast reaction with the chloride anions or with the

imidazolium cation. The electro-copolymerisation of Th and BT was also attempted but it was found that BT acted as a poison in the polymerisation process.

From a sample of low-sulfur commercial diesel fuel which was spiked with Th after extracted and electropolymerised using the imidazolium-based IL mixture, it was found that the charge for electro-polymerisation of Th from the commercial diesel was an order of magnitude less than that from decane. This was thought to be due to numerous aromatic and aliphatic O or N-based compounds in real commercial diesel fuel in addition to the additives like glycols and contaminants such as water.

While electrochemical polymerisation of Th is a possible methodology for the removal of sulfur containing compounds from oil, is not viable due to the slow reaction kinetics and the possibility of chain termination from other sulfur containing compounds such as BT and other additives in the fuel such as glycols.

The final method chosen to remove sulfur from oil-like liquids was by chemically oxidising it using 1(Bmim)Cl: 2FeCl₃. This was found to be very effective at chemically removing S-containing molecules from organic phase into IL phase and the enthalpy of transfer was found to be exothermic. Iron-based catalysts are clearly sustainable and have a relatively low cost. While these liquids are more viscous and less highly conducting than some of the DESs, some of the physical properties such as a low surface tension makes them more suitable for solute extraction. A trace amount of organic layer is miscible in IL, but this is negligible and no solubility of the DES in the fuel was detectable.

The extraction of aromatic sulfur compounds from the alkane phase by 1(Bmim)Cl: 2FeCl₃ occurs not just with moderate stirring, but also in an unstirred system due to the strong interaction between the Lewis acid and S-species. It was found that the removal of S-compounds is strongly affected by the stirring rate and on the oil to IL ratio. It means that the faster the stirring rate, the faster the system comes to equilibrium and, the more ionic liquid, the more thiophenic species are extracted.

Owing to similar densities of PTh and the IL it is difficult to separate the polymer from the IL as the mixed phase has a high viscosity. This results in a sub-stoichiometric yield of the polymer as the unreacted ferric chloride becomes inactive in a gel-like phase. Attempts were made to recycle the liquid using a mixture of saturated NaCl solution and a molecular organic solvent. However, the polymer could not be separated from the IL mixture due to the partly similarity in density and the viscosity of the polymer with the IL mixture causes decreasing mass transport. While recycling the (C₄mim)FeCl₄ was

difficult, two experiments were carried out using FeCl_3 in (Bmim)OTf or (Emim)NTf₂ as alternative to (Bmim)Cl. Polythiophene was successfully prepared in both (Bmim)OTf and (Emim)NTf₂ and the mixtures were successfully regenerated and reused. The resulting PTh was analysed by UV-Vis and FT-IR spectroscopies.

The maximum liquid-liquid contact surface area is ideal for deep desulfurisation. A potential experimental apparatus was suggested. The main difficulty of 1:2 molar ratio of (Bmim)Cl: FeCl_3 is in the recycling of the IL. While both physical and electrochemical methods have been shown to be unsuccessful in this study, a simple gas phase oxidation probably could be employed to reform the ferric chloride but the main difficulty with this technology is the similarity in density between the produced polymer and the IL makes physical separation of the viscous layer very difficult.

6.2 Future works

There are two main aspects of this work that require further study.

The first is the fundamental aspects of extraction using DESs and ionic liquids in general. It appears that the extraction of thiophenic molecules is hindered by the large enthalpy of hole formation and the small enthalpy of solvation. It would be useful to develop models for the enthalpy of solvation based on the enthalpy of interaction between the HBD solutes such as polyphenols and carboxylic acids found in natural products. The enthalpy of interaction could be studied using calorimetry. The enthalpy of hydrogen bonding has recently been calculated using a Hess cycle. The heat capacities of the components and the mixtures were measured and the differences between them were found to be reasonable values (ΔH_{HBond} was 10 to 20 kJmol^{-1}). If the enthalpy of solvation was more exothermic then the partition coefficient should be larger and the solute should partition into the DES. In the petrochemical industry, this could be a simple method for de-watering oil.

In addition to removal aromatic sulfur compounds, DESs might be useful for aliphatic S or N-species removals, named denitrification and de-phenalisation respectively. DESs are also well known to be good solvents for metals removal which can be present in high concentrations in crude oil. It would be interesting to study additives such as strong Lewis acid as catalyst with DESs to improve extraction efficiency of different crude oil contaminants.

Additionally, equimolar ratio of (Bmim)Cl-FeCl₃ might be suitable to electropolymerise other monomers such as substituted Th, substitute pyrroles and aniline to produce conducting polymers which are used for electronic devices as conducting polymers. Characterising 1(Bmim)OTf- 0.5 FeCl₃ as a mixture to electropolymerise different monomers as have been mentioned above.

Moreover, using different methods for regeneration of used Lewis acidic (Bmim) FeCl₄ such as bubbled of a simple halogen such as bromine and then adding a co-solvent to aid separation of the polymer from the DES. There is a significant scope to change the density of the DES by changing cations and HBDs and this could enable easier separation of the polymer from the DES using density.

6.3 Appendix

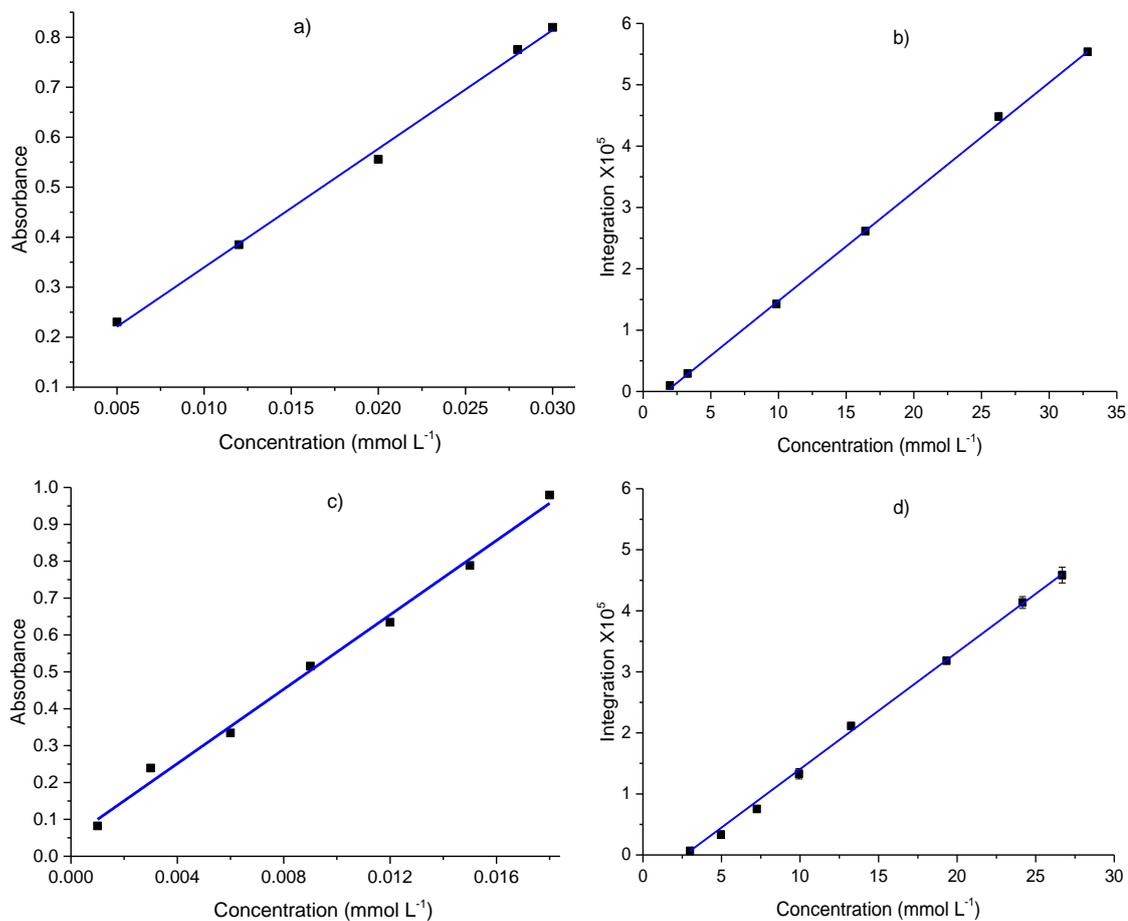


Figure 6.1: a) and c) are absorption spectra, b) and d) are areas absorbance of BT and DBT standard concentrations respectively in decane measured by UV-Vis spectroscopy and GC-FID.

Table 6.1: Th extraction by DESs at 25 °C, 0.8 fuel: 1DES mass ratio and at different stirring rate (rpm).

Stirring rate	500		750		900	
Techn.	UV-Vis	GC-FID	UV-Vis	GC-FID	UV-Vis	GC-FID
DESs	Ext. %					
Butaline	28.1 ± 1.2	27.8 ± 0.7	33.8 ± 1.5	32.5 ± 1	35.9 ± 2	34 ± 1
Oxaline	12.5 ± 0.5	12.6 ± 0.4	12.6 ± 0.5	12.7 ± 0.2	14.0 ± 0.7	13.4 ± 0.34
Pentaline	34.8 ± 1.5	33.7 ± 1	37.6 ± 1.6	36.9 ± 1	40.1 ± 1.8	38.5 ± 2.2
Glyceline	16.4 ± 0.6	15.8 ± 0.5	17.7 ± 0.7	16.7 ± 0.4	19.2 ± 0.7	18.7 ± 0.6
Ethaline	23.9 ± 1	24.6 ± 0.8	24.5 ± 1	25 ± 1	27.3 ± 1.1	26.4 ± 1.2
Reline	12.5 ± 0.5	11.9 ± 0.3	13.3 ± 0.5	12.9 ± 0.4	20.2 ± 0.8	19.3 ± 0.7

Table 6.2: Extraction of Th by DESs at 25 °C, 500RPM, at different phase ratios.

Fuel : DES	2:1		1:1	
Techniques	UV-Vis	GC-FID	UV-Vis	GC-FID
DESs	Ext. %	Ext. %	Ext. %	Ext. %
Butaline	24.4 ± 0.6	23 ± 0.5	28 ± 1.2	27.8 ± 0.66
Oxaline	7.8 ± 0.66	8.5 ± 0.44	12.5 ± 0.5	12.6 ± 0.4
Pentaline	22.5 ± 0.6	23.8 ± 1.15	37.6 ± 1.6	37 ± 1
Glyceline	9.4 ± 0.65	9.2 ± 0.24	16.4 ± 0.6	15.8 ± 0.45
Ethaline	25 ± 0.6	25.2 ± 1.5	23.9 ± 1	24.6 ± 0.8
Reline	8.7 ± 0.6	8.4 ± 0.2	12.5 ± 0.5	12 ± 0.3
Fuel : DES	1:2		1:3	

Techniques	UV-Vis	GC-FID	UV-Vis	GC-FID
DESs	Ext. %	Ext. %	Ext. %	Ext. %
Butaline	57.5 ± 3.1	54.7 ± 4.3	64.6 ± 4	65 ± 3.8
Oxaline	27.1 ± 1	26.0 ± 0.7	33.5 ± 1.5	34.4 ± 1.1
Pentaline	56.8 ± 2.8	54.65 ± 1.4	70.2 ± 4.5	66 ± 3
Glyceline	28.2 ± 1.2	27.5 ± 1.3	41.8 ± 2.1	41.3 ± 1
Ethaline	44 ± 2.1	44.6 ± 1.3	48.3 ± 2.2	49.7 ± 1.7
Reline	23 ± 1	23.7 ± 1.1	31.1 ± 1.4	32.1 ± 1

Table 6.3: Th extraction by DESs at different temperature, 0.8:1 mass ratio and at 500 (rpm) during 2 hrs.

Temp. (°C)	25		35		45	
Technique	UV-Vis	GC-FID	UV-Vis	GC-FID	UV-Vis	GC-FID
DESs	Ext. %	Ext. %	Ext. %	Ext. %	Ext. %	Ext. %
Butaline	28.1 ± 1.2	27.8 ± 0.7	26.9 ± 1.1	27.8 ± 0.3	37.1 ± 1.9	36.1 ± 0.3
Oxaline	12.5 ± 0.5	12.6 ± 0.4	12.9 ± 0.5	12.4 ± 0.1	15.1 ± 0.5	15.7 ± 0.3
Pentaline	37.6 ± 1.6	37 ± 1	37.9 ± 1.7	37.5 ± 0.1	39.8 ± 1.7	38.4 ± 0.3
Glyceline	16.4 ± 0.6	15.8 ± 0.45	16.2 ± 0.6	16 ± 0.2	17.2 ± 0.7	16.4 ± 0.1
Ethaline	23.9 ± 1	24.6 ± 0.8	22.8 ± 1.1	23.5 ± 0.6	26.6 ± 1.1	25.6 ± 0.7
Reline	12.5 ± 0.5	12 ± 0.33	15.9 ± 0.7	15.2 ± 0.2	15.6 ± 0.7	15.1 ± 0.2

Table 6.4: Th extraction by DESs as a function of time, 0.8 decane: IDES mass ratio and stirring speed 500 (rpm) at 25 °C.

Time (min)	60		120		180	
Techniques	UV-Vis	GC-FID	UV-Vis	GC-FID	UV-Vis	GC-FID
DESs	Ext. %					
Butaline	26.2 ± 0.6	28 ± 0.8	28.1 ± 1.2	27.8 ± 0.7	33.2 ± 1.2	32.8 ± 0.8
Oxaline	4.6 ± 1.5	3.9 ± 0.1	12.5 ± 0.5	12.6 ± 0.4	13.9 ± 0.7	13.5 ± 0.4
Pentaline	34.5 ± 0.8	33.9 ± 1.2	37.6 ± 1.6	36.9 ± 1	38 ± 2	37.5 ± 1.3
Glyceline	7.1 ± 1	6.3 ± 0.3	16.4 ± 0.6	15.8 ± 0.5	15.9 ± 0.2	15.7 ± 0.5
Ethaline	21.3 ± 0.5	20.7 ± 0.7	23.9 ± 1	24.6 ± 0.8	26 ± 1.5	24.7 ± 0.8
Reline	7.2 ± 1.5	5.8 ± 0.2	12.5 ± 0.5	12 ± 0.3	18.2 ± 1.1	17.2 ± 0.6

Table 6.5: Surface tension ($mN.m^{-1}$) data of the used DESs as a function of temperature.

DES	Temperature (°C)		
	25	35	45
Pentaline	45.6 ± 0.3	45.5 ± 0.3	45.1 ± 0.2
Butaline	47.8 ± 0.3	47.3 ± 0.2	47.1 ± 0.2
Ethaline	51.8 ± 0.3	50.6 ± 0.3	49.5 ± 0.3
Glyceline	64.8 ± 0.1	63.3 ± 0.8	59.8 ± 0.3
Oxaline	67.5 ± 0.1	59.1 ± 0.4	58.5 ± 0.4
Reline	73.2 ± 0.2	67.1 ± 1.3	61.8 ± 1.2

Table 6.6: Remained Th (%) by multiple extraction times in *n*-C₁₀ using DESs.

Extraction time	Technique	DES	
		Pentaline	Butaline
1st	UV-Vis	73 ± 1.8	63.9 ± 1.5
	GC-FID	72.9 ± 1	63.6 ± 1
2nd	UV-Vis	34 ± 0.5	31.1 ± 2.5
	GC-FID	34.7 ± 2	29.3 ± 3
3rd	UV-Vis	23.7 ± 1.2	17.9 ± 1.1
	GC-FID	22.6 ± 1.7	17.4 ± 1.4
4th	UV-Vis	14.4 ± 0.6	11.3 ± 0.4
	GC-FID	13.6 ± 2.3	11.5 ± 2
5th	UV-Vis	3.1 ± 0.9	2.1 ± 0.7
	GC-FID	2.5 ± 0.4	1.3 ± 0.5

Table 6.7: Extraction of BT and DBT by DESs from decane.

S-compounds	Technique	DES	
		Pentaline	Glyceline
BT	UV-Vis	33.6 ± 0.7	7.1 ± 1.1
	GC-FID	32.9 ± 9	6.3 ± 0.5
DBT	UV-Vis	30.1 ± 0.9	2.2 ± 0.3
	GC-FID	28.8 ± 2.7	2 ± 0.05

Table 6.8: *Th extraction from commercial real diesel by DESs at 30 °C, 0.8 fuel: 1DES mass ratio and at 750 (rpm) during 1 h.*

Technique	UV-Vis	GC-FID
DESs	Ext. %	Ext. %
Butaline	25.1 ± 0.4	24.7 ± 0.6
Oxaline	8.9 ± 1.2	8.4 ± 0.4
Pentaline	30.1 ± 1.1	29.6 ± 0.9
Glyceline	6.9 ± 0.8	7.7 ± 0.2
Ethaline	13.1 ± 0.1	13.4 ± 0.5
Reline	9.9 ± 0.7	9.5 ± 0.3

Table 6.9: *Conductivity of FeCl₃/ Imidazolium-based IL as a function of temperature.*

Temperature (°C)	Conductivity (µs/cm)	
	2:1	1:1
25	67.2 ± 1.1	95 ± 0.7
30	78.2 ± 0.6	103.6 ± 0.5
35	88.3 ± 0.1	111.6 ± 0.1
40	97.6 ± 0.2	119.9 ± 1.1
45	106.9 ± 0.9	128 ± 1.4

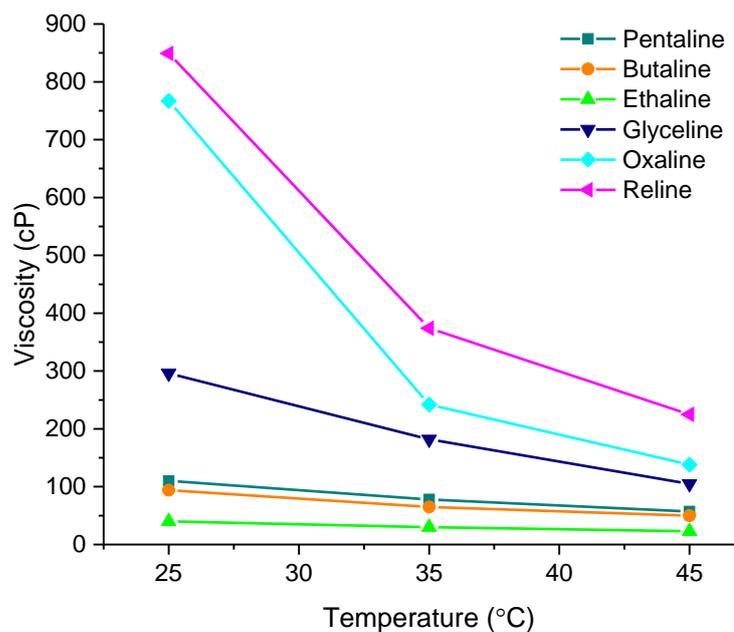


Figure 6.2: Viscosity of used DESs as extractant as a function of temperature.

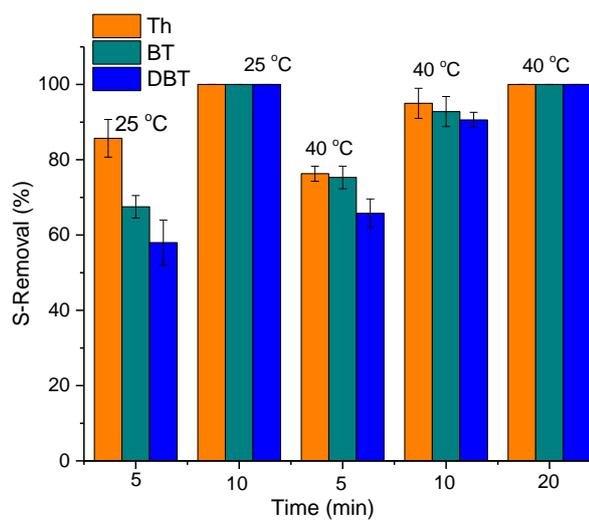


Figure 6.3: Extractive desulfurisation of 35 mmol L⁻¹ of each one of Th, BT and DBT into (Bmim)FeCl₄ mixture, as a function to time, 500 rpm, fuel/IL mass ratio: 2:1.

Table 6.10: Extractive desulfurisation of a mixture of 35 mmol L⁻¹ each of S-compounds into (Bmim)FeCl₄, 500 rpm, 25 °C.

S-species removal (%)		Th	BT	DBT
Mass ratio of (IL: fuel)	1:1	100 ± 0.01	100 ± 0.01	100 ± 0.01
	1:2	85.7 ± 5	67.5 ± 5	58 ± 6
	1:3	63.1 ± 4	51 ± 1.4	40.5 ± 2.7
	1:4	59.9 ± 4	49.6 ± 1.7	37.8 ± 2.3

Table 6.11: Removal of S-containing compounds from true diesel by imidazolium IL. Reaction conditions: IL: fuel mass ratio: 1:2, 550 rpm, at 25 °C for 5 min.

Sulfur molecules	Extraction (%)
Th	79.3 ± 3.7
BT	53.8 ± 2.7
DBT	46.5 ± 1.5

Table 6.12: Extractive desulfurisation of Th and its derivatives as a mixture from model oil into 2:1 FeCl₃: (Bmim)Cl at 25 °C.

		Thiophenic compounds removal (%)		
IL: fuel	1:1			
Time	Th	BT	DBT	
6min	38.4 ± 1.2	20.5 ± 0.4	15.3 ± 0.5	
12min	56 ± 0.8	21 ± 0.4	20.6 ± 0.5	
1/2h	72.4 ± 0.7	27 ± 2.3	22.2 ± 0.5	
1h	85.2 ± 0.4	35 ± 0.9	24.7 ± 0.6	
2h	95.1 ± 0.5	53.2 ± 4.5	26.3 ± 0.8	
4h	99.90 ± 0.01	87.2 ± 3.2	34.4 ± 1.7	
8h	-	99.9 ± 0.01	57.3 ± 0.9	
1day	-	-	99.9 ± 0.01	

Table 6.13: Removal of Th and its derivatives individually from decane into 2:1 FeCl₃: (Bmim)Cl at 25 °C.

	Thiophenic compounds removal (%)		
IL: fuel	1:1		
Time	Th	BT	DBT
6min	48.2 ± 0.6	22.1 ± 0.3	19.1 ± 0.5
12min	65.3 ± 2	32.4 ± 0.6	29 ± 2
1/2h	79.3 ± 3	43.6 ± 1.5	35.3 ± 1.5
1h	87.5 ± 5	65.1 ± 3	48.5 ± 4
2h	91.5 ± 3	74.3 ± 4	68.1 ± 4
4h	99.9 ± 0.01	86.2 ± 2	81.4 ± 3
8h	-	99.9 ± 0.01	93.3 ± 2
1day	-	-	99.9 ± 0.01