ESTIMATION OF SOLUBILITY PARAMETER USING FEDORS AND SMALL METHOD FOR IONIC LIQUIDS

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ESTIMATION OF SOLUBILITY PARAMETER USING SMALL AND FEDORS METHOD FOR IONIC LIQUIDS

MUHAMMAD RIDHWAN BIN SALMAN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

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JUNE 2015

SUPERVISOR’S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

Signature :
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Position : SENIOR LECTURER
Date : 30 JUNE 2014

STUDENT’S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Name : MUHAMMAD RIDHWAN BIN SALMAN
ID Number : KC11047
Date : 30 JUNE 2015

Dedication

To my family, my lecturers, my friends & to whom it may concern.

ACKNOWLEDGEMENT

First and foremost, I have to thank my parents for their love and support throughout my life. Thank you both for giving me strength to reach for the stars and chase my dreams. My sister and brother deserve my wholehearted thanks as well.

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To all my friends, thank you for your understanding and encouragement in my many, many moments of crisis. Your friendship makes my life a wonderful experience. I cannot list all the names here, but you are always on my mind.

Thank you, Allah for always being there for me.

This thesis is only a beginning of my journey

ABSTRACT

Corrosion required three things to be formed such as water, iron and oxygen. The effect may harmful to pipeline equipment and also will cause operation and other maintenance issues. In the industry, different solvents are used in order to remove the present of iron oxide (Fe_2O_3) contaminants from pipeline. Thus, ionic liquids (ILs) as a solvent are used to study the solubility of Fe_2O_3 in removing if as contaminant from pipelines. Fedors' and Small group contribution method are chosen applied as an estimation method in order to identify the suitable ILs. From the estimation method, 2-hydroxy-N-(2-hydroxyethyl)-N-methylethanolammonium acetate [HEME] Ac, 2-ethyl-N-(2-hydroxyethyl)-N-methylethanolammonium ethyl sulphate [HEME] ESO_4, 1-ethyl-3-metylimidazolium ethyl sulphate [EMIM][ESO_4] and 1-ethyl-3-methylimidazolium acetate, [EMIM] Ac were chosen and synthesized based on its solubility parameter. Each synthesized ILs will be tested by adding 0.0015g of Fe_2O_3 into 1.5mL ILs to observe their dissolution performance. From the observation, [HEME] Ac has reduced the amount of Fe_2O_3 better compared with other ILs. It can be concluded that low value of solubility parameter for both cation and anion can dissolve Fe_2O_3.

ABSTRAK

Kakisan akan terjadi dengan kehadiran tiga komponen seperti air, besi dan oksigen. Kesannya boleh membahayakan peralatan saluran paip dan juga akan menyebabkan isu-isu operasi dan penyelenggaraan. Dalam industri, pelarut yang berbeza digunakan untuk menyingkirkan ferum oksida (Fe_2O_3) iaitu bahan enapcemar daripada paip. Oleh itu, cecair ionik (ILs) digunakan sebagai pelarut untuk mengkaji keterlarutan parameter Ils terhadap Fe_2O_3 berdasarkan kaedah Fedors dan Small sebagai anggaran untuk mengenal pasti ILs sesuai. Melalui kaedah tersebut, 2-hydroxy-N-(2-hydroxyethyl)-N-methylethanolammonium acetate [HEME][Ac], 2-ethyl-N-(2-hydroxyethyl)-N-methylethanolammonium ethyl sulphate [HEME][ESO_4], 1-ethyl-3-metylimidazolium ethyl sulphate [EMIM][ESO4] and 1-ethyl-3-methylimidazolium acetate, [EMIM][Ac] telah dipilih dan disintesis berdasarkan parameter keterlarutan itu. Setiap ILs akan diuji dengan menambah 0.0015g Fe_2O_3 ke dalam 1.5mL ILs untuk melihat potensi larutan. Berdasarkan pemerhatian yang telah dijalankan, [HEME][Ac] telah mengurangkan jumlah Fe_2O_3 yang lebih baik berbanding dengan ILs yang lain. Kesimpulannya, kation dan anion yang lebih rendah nilainya berdasarkan kepada parameter keterlarutan (Fedors 'dan Small) boleh malarutkan Fe_2O_3 dengan lebih baik.

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LIST OF ABBREVIATIONS

δ	Solubility parameter
F_i	molar attraction constant
v	molar volume
M	molecular weight
δ_T	total solubility parameter
δ_d	nonpolar interaction
δ_p	polar interaction
δ_h	hydrogen bonding component
E_{hi}	hydrogen bonding energy

Greek

Δ	delta

Units

J	joule
cm^2	square centimetre
cm^3	cubic centimetre
mol	mol
MPa	megapascals

LIST OF ABBREVIATIONS

SP	Solubility parameter
ILs	Ionic liquids
FTIR	Fourier transform infra-red
NMR	Nuclear magnetic resonance
LPG	Liquefied petroleum gas
QSPR	Quantitative Structure Activity Relationship
CP	Cathodic protection
[HEME][Ac]	2-hydroxy-N-(2-hydroxyethyl)-N-methylethanolammonium acetate
[HEME][ESO_4]	2-ethyl-N-(2-hydroxyethyl)-N-methylethanolammonium ethyl sulphate
[EMIM][Ac]	1-ethyl-3-methylimidazolium acetate
[EMIM][ESO_4]	1-ethyl-3-methyl-imidazolium ethyl sulphate

1 INTRODUCTION

1.1 Motivation and statement of problem

Corrosion is a natural phenomenon that occurred in our daily life. It can be defined as the degradation of material due to a reaction with the environment. Corrosion required three things to be formed such as water, iron and oxygen. Rust, on the other hand, is a type of corrosion which happens to iron and its alloys. The chemical substance that commonly related to rusting is Fe_2O_3 because iron combines readily with oxygen. When iron reacts to water or the moist air, Fe_2O_3 are formed and cause the material to rust.

Meanwhile, black powder consists of various forms of iron sulphide or Fe_2O_3, included with the other unwanted constituents such as water, liquid hydrocarbons and sand in natural gas and fluid transmission delivery systems. Generally, black powder is a typical contaminant in transmission pipeline. It is a general term to describe a main host of corrosion related contaminants found in pipelines transmission that transport natural gas, hydrocarbon condensates, and liquefied petroleum gas (LPG). (Wines et al., 2009)

Pipes are fabricated from different material types to suit its needs and services desired. The most commonly used material for petroleum pipelines is mild steel because of its strength, ductility, weld ability and it is ability to heat treatment for varying mechanical. However, mild steel corrodes easily because all common structural metals form surface oxide films when exposed to pure air but the oxide formed on mild steel is readily broken down, and in the presence of moisture it is not repaired. Therefore, a reaction between steel (Fe), moisture (H_2O), and oxygen (O_2), takes place to form rust. This reaction is represented by a chemical equation of the following type: (Badmos et al., 2009)

$$4Fe + 2H_2O + 3O_2 \rightarrow 2Fe_2O_3 + H_2O \qquad \text{(Eq.1)}$$

The effect may harmful to pipeline equipment and also will cause operation and other maintenance issues. Different solution in order to remove the black powder contaminants from pipeline, but their efficiency is inadequate.

The example of corrosion control such as the principal methods to minimize the corrosion on underground pipelines are coatings and cathodic protection (Peabody, 2001). In the industry, different solvents are used in order to remove the present of Fe_2O_3 contaminants from pipeline. Thus, ILs as a solvent are used to study the solubility of Fe_2O_3.

1.2 Objectives

The following are the objectives of this research:

- To determine the solubility parameter of ILs by using estimation of Fedors and Small group contribution method.
- To synthesize and identify the physical properties of proposed ILs.
- To determine the potential of ionic liquids for solubility study towards Fe_2O_3.

1.3 Scope of this research

The following are the scope of this research:

- Various type of cation and anion of ILs will be considered.
- Estimation the solubility parameter by using Fedors and Small method.
- Synthesize and characterization for proposed ILs.
- Solubility study of ILs to dissolve Fe_2O_3.

1.4 Main contribution of this work

The following are the contributions

- Prior to my supervisor’s guidance in learning and get experience in the study of solubility parameter of ILs.
- Be able to study the estimation of solubility parameter of ILs, characterization of ILs and their solubility towards Fe_2O_3.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 described about the problem statement to carrying this research. Since the pipeline systems cannot avoid from corrosion to occurred, it give a motivation to do a research about dissolve Fe_2O_3 in ILs to solve the problem.

Chapter 2 provides a description of the various type of method used in determining the solubility parameter. There are also the reviews of the type ILs with their characteristics and applications. The related research by others also included in this chapter.

Chapter 3 gives detail on material and method used in this research. The experimental illustration of the study and the sequences of the process for every step were stated in this chapter. There also include all the analysis such as pH analysis, density, viscosity and FTIR analysis for ILs characterization. Besides that, the method to synthesis proposed ILs and their solubility study towards Fe_2O_3 are also described.

Chapter 4 consists of result of laboratory work and analysis study. The discussion was related to the characteristic and analysis results of each ILs.

Chapter 5 draws together a summary of findings and future work which might be derived from the experiment developed in this work.

2 LITERATURE REVIEW

2.0 Overview

This chapter presents about the solubility parameter and ionic liquids. The study of method in determination of the parameter and more details about the ILs.

2.1 Solubility parameter

Figure 2.1: Joel H. Hilderbrand, the discoverer of solubility parameter

The term of solubility parameter was introduced by Joel H. Hildebrand and Robert L. Scott. Later in 1931, the concept of cohesive energy was introduced by Scatchard and the others into Hildebrand theories, identifying this quantity with the cohesive energy per unit volume. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density:

$$\delta = (\frac{E}{V})^{1/2} \qquad \text{(Eq.2)}$$

V is the molar volume of the pure solvent, and E is its (measurable) energy vaporization. (Hansen, 2007). The Hildebrand solubility parameters have numerous applications including gas-liquid solubility, solvent extraction and many others.

Then, Charles M. Hansen has pioneered the concept that the total cohesive energy term and thus the total solubility parameter (δ_T) arises from a nonpolar interaction(δ_d), a polar interaction(δ_P), and a hydrogen bonding component(δ_h). The sum of the squares of the Hansen can be expressed as: (Archer, 1992).

$$\delta_T = (\delta_d{}^2 + \delta_P{}^2 + \delta_h{}^2)^{1/2} \quad \text{(Eq.3)}$$

Hansen solubility parameters also define a three dimension “solubility space” in which all liquid or solid substances may be localized. In the “Hansen space”, solvents in which a given molecule is soluble form a cloud of points corresponding in most cases to a sphere whose centre point is the solute coordinates. All solvents and mixtures found in this volume are good solvents for the studied solute and the solvents outside are non-solvents. The more a solvent is close to the solute in the “Hansen space”, the better its affinity for this solute (Bordes et al., 2010).

A low molar mass compound can be described by the three parameter values, δ_D, δ_P, and δ_H. The solvent is described not only by these three values but also by a parameter called interaction radius, R_0, which is the radius of the “solubility sphere” in the “$2\delta_D$-δ_P -δ_H” space. In this space, the three parameters determine a centre of a sphere, which has the R_0 as its radius. Also in this space, a low molar mass compound can be positioned as a dot based on its parameters, and if the compound is within the space limited by the “solubility sphere”, it is a solvent for the polymer, and vice versa. The distance between the centre of the “solubility sphere” and the position the compound belongs to is expressed as below:

$$D_{s-p} = \sqrt{((2\delta_{D,P} - 2\delta_{D,S})^2 + (\delta_{P,P} - \delta_{P,S})^2 + (\delta_{H,P} - \delta_{H,S})^2\ )} \quad \text{(Eq. 4)}$$

where,

S = solvent

And the letter P following refers to polymer.

Usually, the ratio $D_{S\text{-}P}/R_0$ is used as the criterion determined)

$D_{S\text{-}P}/R_0 > 1$ → the compound is a non-solvent;

$D_{S\text{-}P}/R_0 < 1$ → the compound is a solvent;

$D_{S\text{-}P}/R_0 = 0$ → the compound may cause swelling (Wu, 1967).

The solubility parameter is important in the theory of solutions and has been shown to be connected to other physical properties such as surface tension and wettability, the ratio of the coefficient of thermal expansion to compressibility, the boiling points in the case of non-polar liquids, the ultimate strength of materials, and the glass transition temperature of polymers.

Therefore, the ability to estimate the solubility parameters can often be a useful tool to predicting systems physical properties and performance (Miller-Chou & Koenig, 2003).

2.2 Group contribution method

Solubility parameters have been determined as a numerical values in four different ways. Firstly, via measurement based on the measured solubility interaction of one material with another. Secondly, via estimation of the three Hansen Solubility Parameter (HSP) values with correlation, and occasional use of the “Pythagorean Theorem”. Empirical or adjustable constants in the correlations do depend upon characteristics of other solvents. It is somewhat less effective because only two of the three parameters are determined independently. This method is not directly based on the solubility measurements. Thirdly, via theoretical calculation based on thermodynamic. There are some adjustable constants in this calculation methods, and choices of which equation of state to use. Lastly, via group contribution calculation based on regression analysis of solubility parameters. This method determined through a structural analysis of solvent molecules (Durkee, 2013).

Group contribution method is based on the functional group and structural formula of the molecules and presented as empirical Quantitative Structure Activity Relationship (QSPR) approaches. This method is based on the study of property on number of carbon atom or methylene groups which is a hydrocarbon atoms with composition $–CH_2$- in molecules. Any compound was divided into fragment that have a partial value called a contribution and can be calculated from known experimental data usually by Small, Hoftyzer and Van Krevelen, Hoy and Coleman et al. By summing up the values of contributions from the molecule will obtain the property of that compound (Jankowski et al., 2008).

The properties of molecules are investigated by separating them into smaller subgroups. The basic assumption is that the free energy of a molecule transfer between two phases is the sum of its individual contributions of groups, and that these group contributions are independent of the rest of the molecule. There is an obvious trade-off in group contributions. It is possible to define several groups in different ways. The more the subgroups used, the more accurate the group contributions become, but the less likely that there is sufficient statistical data to make predictions (Machui & Brabec, 2012).

Group contribution method is also used as predicting solubility parameter with expression as following:

$$\delta_P = \rho \left|\frac{\Sigma F_i}{M}\right| = \frac{\Sigma F_i}{v} \qquad \text{(Eq.5)}$$

where F_i is the molar attraction constant; M is the molecular weight of the repeat unit (molar mass); v is the molar volume. Values of "v" can be estimated by group contribution methods either v=$\sum v_r$ or $\sum v_g$ while v_r is the molar volume group contribution in the rubbery amorphous state and v_g is the molar volume group contribution in the glassy amorphous state (Robeson, 2007).

The development of the theories have given rise various type of method to determine the solubility parameter. In 1976, Hoftyzer and Van Krevelen's method was introducing the solubility parameter can be predicted from a group contribution method. The expression of the method using the following equations:

$$\delta_d = \frac{\sum F_{di}}{V} \quad \delta_P = \frac{\sqrt{\sum F_{pi}^2}}{V} \qquad \delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \qquad \text{(Eq.6)}$$

F_{di} Is the molar attraction constant, E_{hi} is hydrogen bonding energy, V is the molar volume (Elidrissi et al., 2012).

Later in 1985 and 1989, the Hoy Solubility Parameter method have extended for structural features like: cis, trans, ortho-, meta-, para- substitution (aromatics), and branching (i.e. isopropyl, t-butyl, conjugation of double bond, and rings). The complex molecules in ascertaining the cohesional energy density can be determined by the Fedor's method. This method also may be predicted from the group contribution method and applicable to bioactive molecules such as imipenum and efrotomycin (Aerts, 2002).

Group contribution methods are essentially empirical estimation methods. A large variety of these models have been designed during last centuries, differing in a field of their applicability and in the set of experimental data. During last years also models for ionic liquids and their variable properties were developed, for example density, thermal expansion and viscosity of cholinium-derived ionic liquids, the glass-transition temperature and fragility experimental data of mixture with ionic liquid were compared with group contribution methods or thermo physical properties were studied.

Some of these group contribution methods were developed for only limited number of compounds, for some family of compounds, for example, fluorinated olefins hydrocarbons, fatty acid methyl esters most of approaches were established for a wide range of organic compounds (Kolská et al., 2012).

2.3 *Fedors' group contribution method*

Fedors' compiled a table of molecular parts and their contribution to cohesive energy and molecular volume. Fedors' method is especially useful when two parts: a single molecule have different polarity, as in surfactant and proteins (Vaughan 1993). The solubility parameter of the dissolved, δ, can be either be obtained from literature or calculated from group contribution method. If the structure of the solvents is known, δ of many complex solutes can be calculated using Fedors' group contribution method. This is done by adding up the contribution of the individual groups to the vaporization energy (J/mol) and the molar volume of overall structure (cm^3 /mol), $\sum_{i=1}^{n}(\Delta E_i)$ and$\sum_{i=1}^{n}(\Delta v_i)$. The solubility parameter for the solute is calculated as the square root of the ratio of the summation of all energy contributions to the summation of the all the group volumes. The solubility parameter values estimated using the Fedors' method are consistent with those obtained from other sources (Kumoro & Hasan, 2006).

The determination of solubility by Fedor's method can be calculated from the equation and based on Hoy solubility parameter:

$$\delta_h = \left[\frac{\sum \Delta e_i}{\sum \Delta v_i}\right]^{1/2} \quad \text{(Eq.7)}$$

where Δe_i and Δv_i are the additive atomic group contributions for the energy of vaporisation and the molar volume respectively at a given temperature (Hamerton et al., 2010).

2.4 *Small group contribution method*

Small has published a table of molar attraction constants which allows the estimation of the δ from the structural formula of the polymer and its density. Small data can be found in the Polymer or Chemical Rubber Company (CRC) handbooks of Chemistry and Physics. The molar attraction constants, G are additive over the formula and are related to the solubility parameter by the following equation:

$$\delta = d \sum G/M \tag{Eq.8}$$

where, ∑G is the sum of the molar attraction constants for all the atoms and groups in the polymer, d is the density and M equals the molar mass of the repeat unit.

Hoy has also determined the solubility parameter again using values for molar attraction constants he has determined. His values differ from Small's values and are shown in the polymer handbook. Hoy uses the following equation to determine the solubility parameter by using the group additively principle as expressed in the following equation:

$$\delta = \sum F_t + \frac{135.1}{V_m} \tag{Eq.9}$$

where V_m is the molar volume found by dividing the molecular weight by density. Van Krevelen uses cohesive energy values to compute the solubility parameter using his data and the following equation: (Amelia et al., 2014)

$$\delta = \frac{(E_{coh})^{\frac{1}{2}}}{V} \tag{Eq.10}$$

2.5 *Ionic liquids*

Figure 2.2: Paul Walden, the discoverer of ionic liquids

The field of ionic liquids began in 1914 with an observation by Paul Walden who reported the physical properties of ethylammonium nitrate ([EtNH$_3$][NO$_3$] which was formed by the neutralisation of ethylamine with concentrated nitric acid. It is extremely instructive to revisit this paper, as the thinking behind the work, and some of the issues of association are as relevant today as they were in 1914. Today, however, this is widely acknowledged as the start of the field of ionic liquids, and it has left an important legacy. The current definition for ionic liquids is derived from here: ionic liquids are most commonly defined as materials that are composed of cations and anions which melt at or below 100^{o}C. This temperature does not have any chemical or physical significance, but has persisted until the present day; it is only now that it is being queried (Plechkova & Seddon, 2008) .

There are many synonyms used for ionic liquids, which can complicate a literature search. “Molten salts” is the most common and most broadly applied term for ionic compounds in the liquid state. Unfortunately, the term “ionic liquid” was also used to mean “molten salt” long before there was much literature on low-melting salts. It may seem that the difference between ionic liquids and molten salts is just a matter of degree (literally); however the practical differences are sufficient to justify a separately identified niche for the salts that are liquid around room temperature. That is, in practice the ionic liquids may usually be handled like ordinary solvents.

Synonyms in the literature for materials that meet the working definition of ionic liquid are: “room temperature molten salt”, “low-temperature molten salt”, “ambient-temperature molten salt”, and “liquid organic salt” (Welton, 2002).

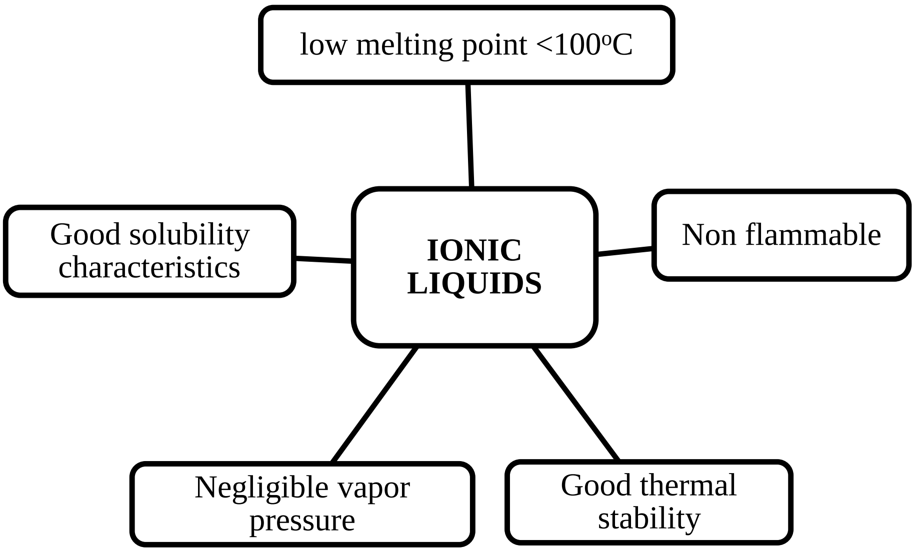


Figure 2.3: Ionic liquids properties

The important for evaluating and selecting ILs for each application as well as this case study is by the knowledge of the physical properties of ILs as shown in Figure 2.3 and the phase behaviour with gases, liquids, and solids. ILs is widely used in application in science and industries because of its unique properties, such as negligible vapour pressure, good thermal stability, non-flammable, and good solubility characteristics.

The two most important features of ILs that have driven research into their use as solvents for engineering separations have been their very low to virtually negligible vapor pressures (< 10 mbar at 300^{o}C) and tunable structures and properties. The lack of a vapor pressure is a desirable characteristic in many separations applications, as solvent losses due to evaporation are unlikely to occur and volatile solutes may be recovered cleanly without residual solvent entrainment. ILs present many potential advantages over conventional organic solvents and water, and consequently have created new opportunities to reconsider conventional chemical engineering processes (Shannon & Brazel, 2014).

Ionic liquids are highly viscous, low toxic and non-ionizing in nature. Non-flammable and non-volatile property of ionic liquid makes it a good option for the development. The selectivity and variety of chemical reactions can be alter by the ionic nature of the ionic liquids. The cationic and anionic properties of ionic liquids have some basic properties such as, polarity, hydrophobicity and other chemical and physical properties. Ionic liquids can be used as a designer solvents because of their ability properties and it increases the potential application (Chatterjee, 2013).

Table 2.1: Physiochemical properties of Ionic liquids (Gilmore, 2007).

Physiochemical property	**Ionic liquid**
Conductivity	Good ionic conductivity compared to organic solvents/electrolyte systems. This is inversely linked to viscosity.
Viscosity	Generally more viscous than common molecular solvents. Viscosity is determined by van der Waals forces and hydrogen bonding and alkyl chain length in the cation.
Density	More dense than water.
Melting point	Melting point <100°C.
Solubility	Ionic liquids can act as both hydrogen bond acceptors (anion) and donors (cation) and therefore interact with substances with both accepting and donating sites. Ionic liquids can be divided into two groups (water-miscible and water immiscible) according to their solubility in water.
Thermal stability	Highly thermally stable (some up to temperatures of 450°C)
Chemical stability	Most are stable towards organic and inorganic substances.

In the past decade, ionic liquids have been increasingly used for diverse applications such as organic synthesis, catalysis, electrochemical devices and solvent extraction of variety of compounds. ILs are made of positively and negatively charged ions, whereas water and organic solvents, such as toluene and dichloromethane, are made of molecules. The structure of ILs is similar to the table salt such as sodium chloride which contains crystals made of positive sodium ions and negative chlorine ions, not molecules. While, salts do not melt below 800 ◦C, most of ILs remain liquid at room temperature (Keskin et al., 2007).

While the cations may be organic or inorganic, the anions are inorganic. The important properties include high heat capacity, high density, extremely low volatility, non-flammability, high thermal stability, wide temperature range for liquid, many variations in compositions, and a large number of possible variations in cation and anion conformation, allowing fine-tuning of the IL properties for specific applications (Domańska, 2005).

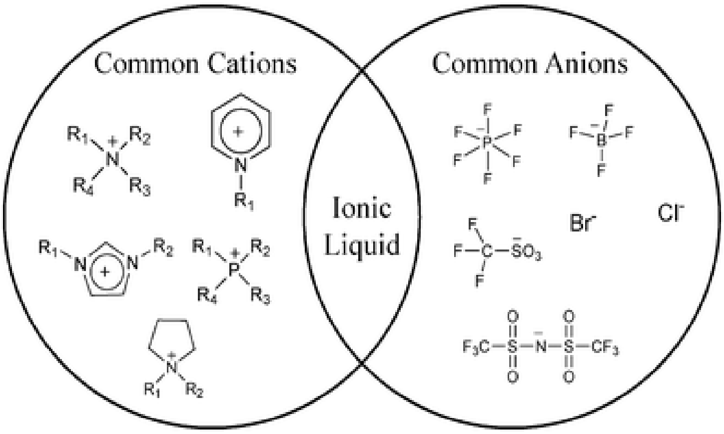


Figure 2.4: Classification of Ionic liquids

The common ILs includes ammonium, phosphonium, sulfonium, guanidium, pyridinum, imidazolium, and pyrolidinium cations. The most common anions are Cl^-, Br^-, $[BF_4]^-$ and $[PF_6]^-$. For simplicity, trifluoromethanesulfonyl $[CF_3SO_2]^-$ anion is abbreviated as [OTf], bis(trifluoromethanesulfonyl)imide $[(CF_3SO_2)_2N]^-$ anion as $[NTf_2]^-$ where ‘Tf’ is a short-hand notation for triflate, and dicyanamide $[N(CN_2]^-$ anion as [dca]. There are several examples of alkylsulfanate anions, which abbreviate as $[C_nSO_4]^-$, where *n* is the carbon number of alkyl chain (Koel, 2008).

Table 2.2: List of various cation and anion

CATION	ANION
Ammonium	Bis(fluorosulfonyl)imide
Imidazolium	Bistrifluoromethanesulfonylimide
Pyridinium	Methyl-phosphonate
Pyrolidinium	Bistriflimide
Phosphonium	Dicyanamide
Sulphonium	Hexafluorophosphate
	Butyl-sulfate
	Acétate
	Methanesulfonate
	Salicylate
	Diethyl phosphate
	Tetrafluoroborate
	Methyl-phosphonate
	Ethylsulfate
	Lactate
	Thiocyanate
	Tosylate
	Tetrafluoroborate

Table 2.3: List of various cation with their molecular structure.

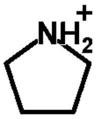
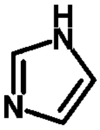
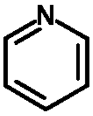
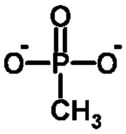
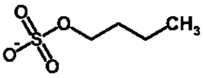
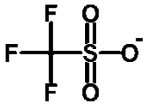
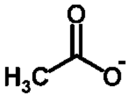
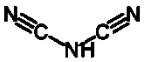
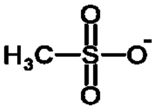
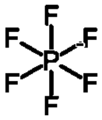
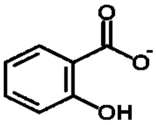
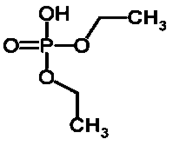
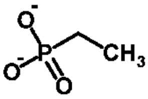
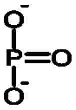
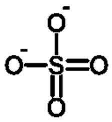
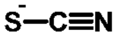
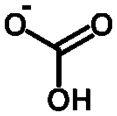
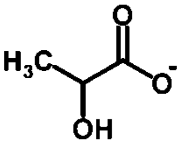
Ammonium (H_4N)	NH_4^+	Pyrolidinium ($C_4H_{10}N$)	
Imidazolium ($C_3H_4N_2$)		Phosphonium (PH_4)	PH_4^+
Pyridinium (C_5H_5N)		Sulphonium (H_3S)	H_3S^+

Table 2.4: List of various anion with their molecular structure.

methyl-phosphonate (CH_3O_3P)		Butyl sulfate ($C_4H_9O_4S$)	
Triflate (CF_3O_3F)		Acetate ($C_2H_3O_2$)	
Dicyanamide (CH_2N_3)		Mesylate (CH_3O_3S)	
Hexafluorophosphate (F_6P)		Salicylate ($C_7H_5O_3$)	
diethyl phosphate ($C_4H_{11}O_4P$)		ethyl-phosphonate ($C_2H_5O_3P$)	
Phosphonate (HO_3P)		Sulfate (SO_4)	
Thiocyanate (CNS)		Tosylate ($C_7H_7O_3S$)	

Bicarbonate (CHO$_3$)		Lactate (C3H5O3)	

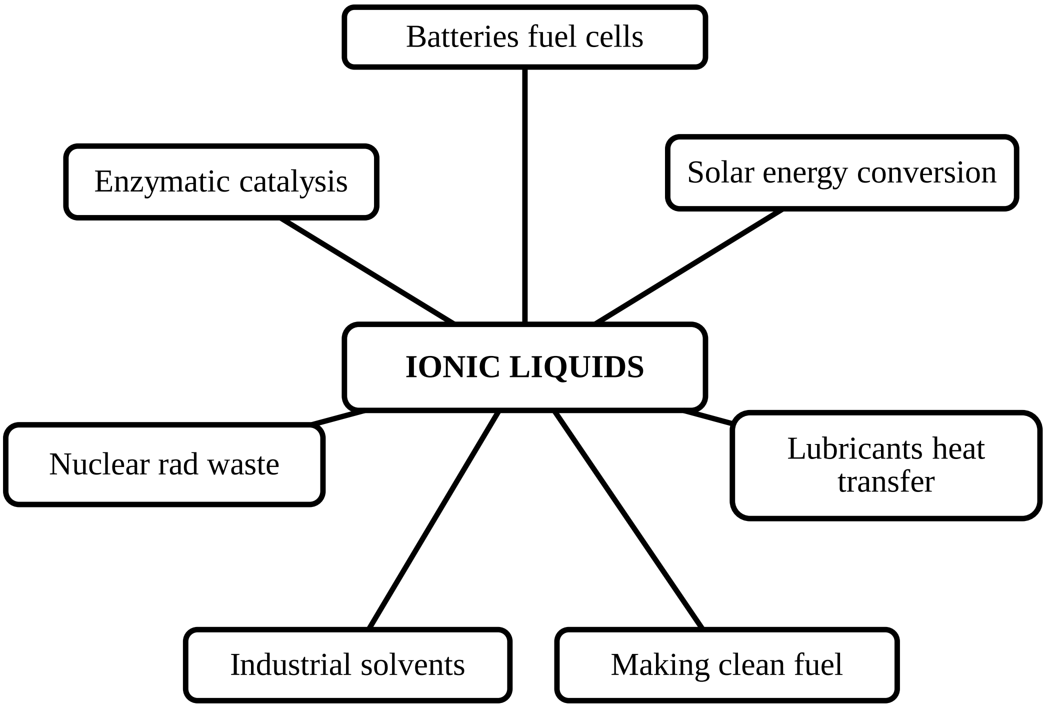


Figure 2.5: Ionic liquids applications

New studies have explored fast reactions in ionic liquids by pulse radiolysis and have shown that charged species, such as a bare electron surrounded by solvent, move more slowly in ionic liquids in comparison to neutral species, just the opposite of what is seen in normal solvents. Also discovered was a reactive and highly mobile form of the electron that exists for only a few trillionths of a second in normal solvents but persists thousands of times longer in ILs. ILs are found to be promising solvents in many of the organic reaction such as esterification, isomerization reactions and many coupling reaction (Khupse & Kumar, 2010).

The most important properties of ionic liquids enable the use of ILs in a wide range of applications, as shown in Figure 2.5. It is also a suitable solvent for synthesis, catalysis and purification. It is also used in electrochemical devices and processes, such as rechargeable lithium batteries and electrochemical capacitors. Rechargeable lithium batteries are a ubiquitous energy device that is being worldwide in many types of portable electronic equipment, such as cellular phones, laptop computers, and digital cameras and many more devices. Recently, it has been realized that variation of the type of cationic core is a very valuable approach to get more number of ILs (Shukla & Saha, 2013).

3 MATERIALS AND METHODS

3.1 Equipment

AccuPyc II 1340 Micromeritics, Brookfield viscometer (DV-II+ Pro), Mettler Toledo pH meter, FT-IR Spectrometer Nicolet iS10 model, Grant-bio Multifunction Rotators, 360º Vertical. Centrifuge and hot plate and magnetic stirrer was used in this investigation.

3.2 Chemicals

1-methylimidazole ($CH_3C_3H_3N_2$), methyl diethanolamine (MDEA), diethyl sulphate, sodium acetate, 1-ethyl-3-methylimidazole, acetone, toluene and Fe_2O_3.

3.3 Methods

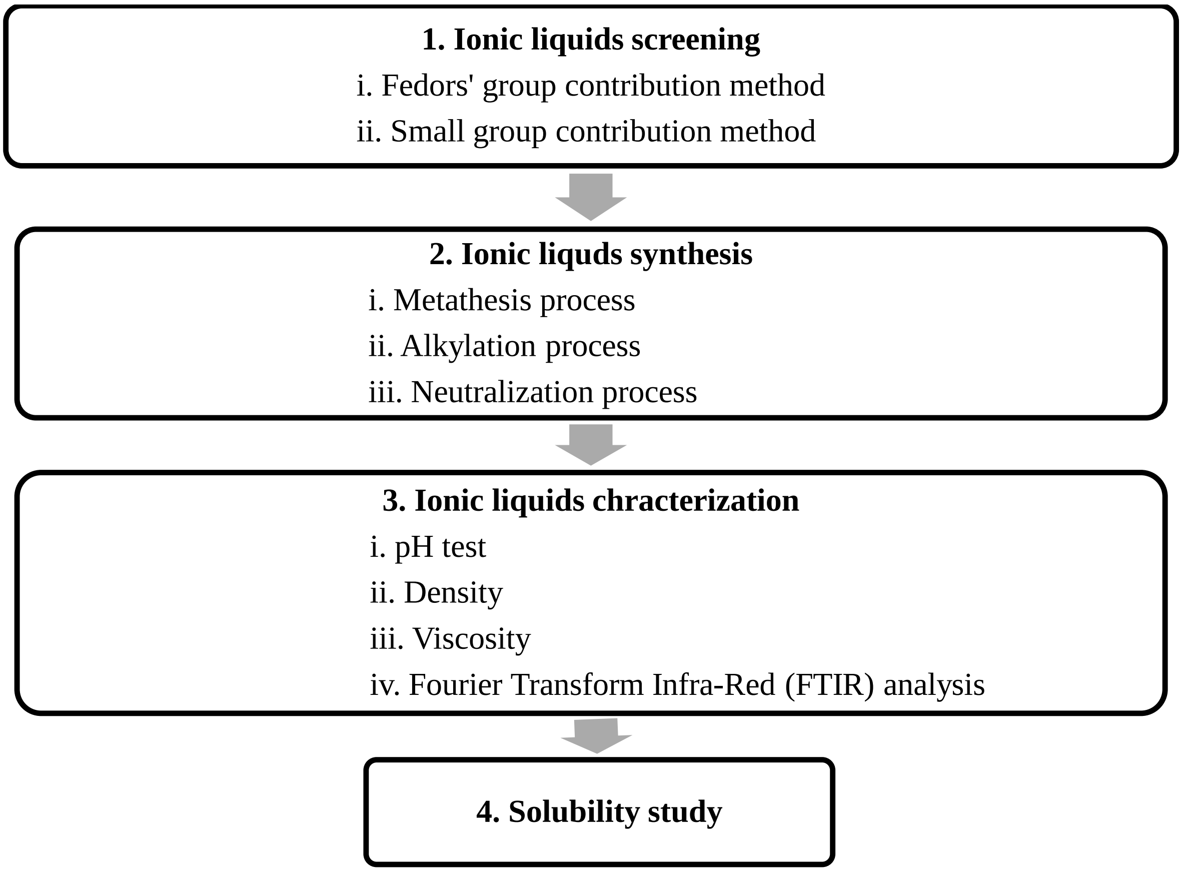


Figure 3.1: Flow chart for the solubility test

3.3-1 Ionic liquids screening

The solubility parameter of ILs was identified by using Fedors' and Small group contribution method. Fedors' and Small have compiled a table of molecular parts and their contribution to cohesive energy and molecular volume to allow the estimation of the solubility parameter as in the Appendix A. The estimation solubility parameter for Fedors group contribution method can be calculated by using Eq.7 while Small group contribution method by using Eq.8. The step of calculation as in Appendix B.

3.3-2 Ionic liquids synthesis

All the selected ILs were synthesized by using different methods. There are three methods to synthesis for different ILs:

i. *Metathesis*

Metathesis, for instance, involves the exchange of ions in a solution containing two ion pairs to produce the thermodynamically most stable ion pairs (Ajam, 2005). This method is to produce 1-ethyl-3-methylimidazolium acetate, [EMIM] [Ac].

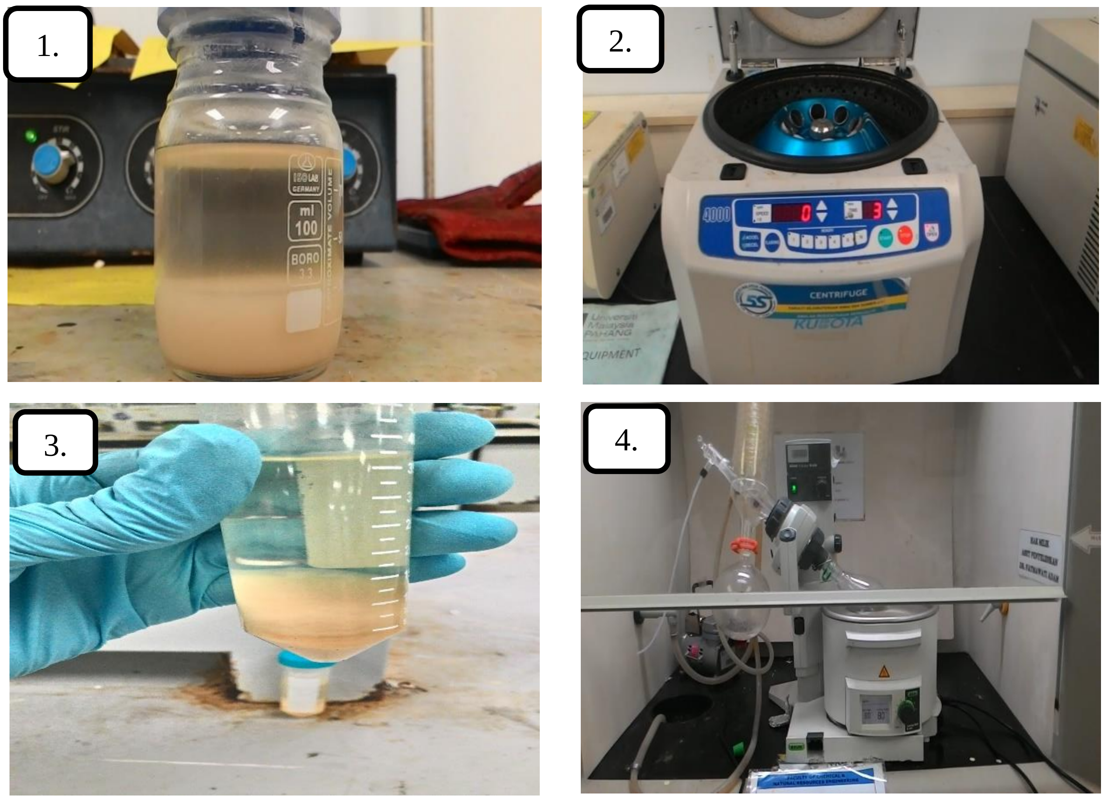


Figure 3.2 (a): Metathesis steps

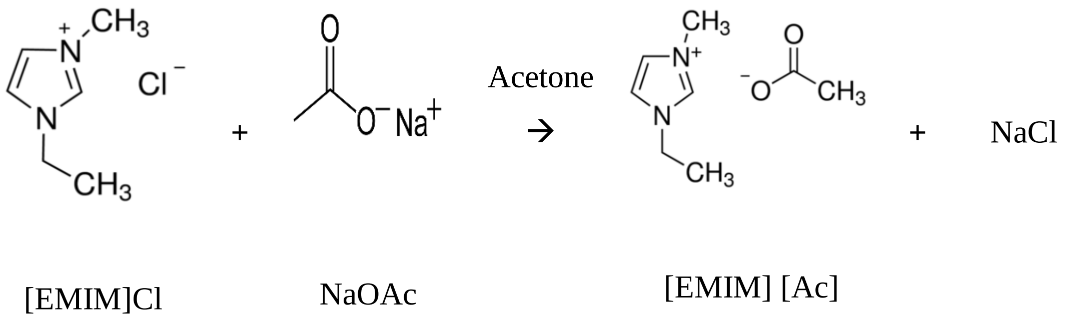


Figure 3.2 (b): Chemical reaction in metathesis process

Equimolar amounts (0.5 M) of sodium acetate (NaOAc) and 1-ethyl-3-methylimidazolium chloride, [EMIM] Cl were mixed by using 100mL of acetone as solvent. The solution was stirred for 24 hours. The mixture will appeared into two layer where the bottom is sodium chloride while the top are [EMIM] Ac and acetone. Then, the mixture was separated by using centrifuge for 5 minutes with 5000rpm speed. The acetone was separated by using rotary evaporator to obtain the [EMIM] [Ac].

ii. *Alkylation*

Alkylation is the transfer of an alkyl group from one molecule to another. The alkyl group may be transferred as an alkyl carbocation, a free radical, a carbanion or a carbene (or their equivalents) (Smith & March, 2001).


1.


2.

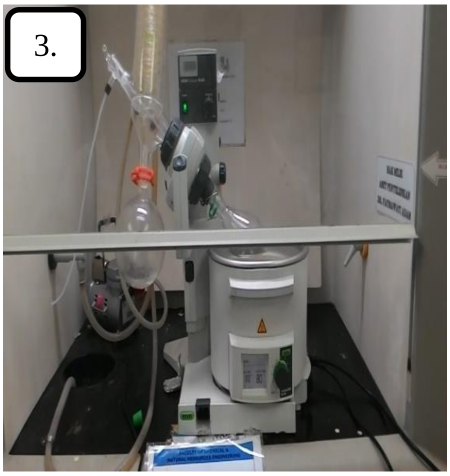

3.

Figure 3.3 (a): Alkylation steps

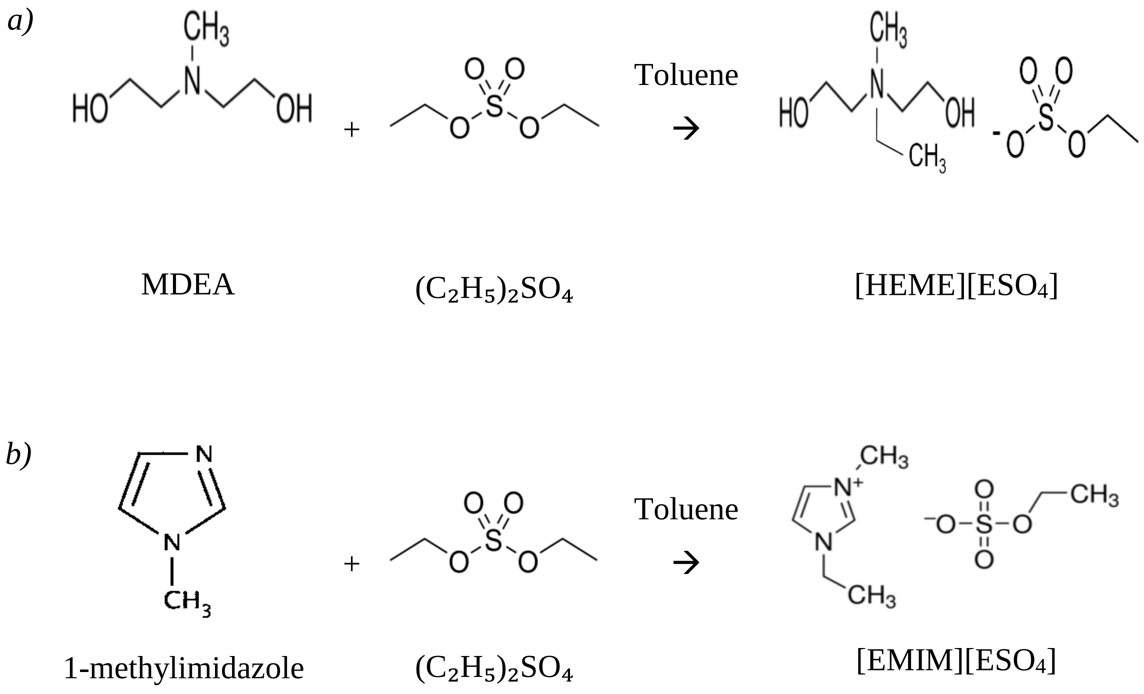


Figure 3.3 (b): Chemical reaction in alkylation process

This method is to produce ethylammonium sulphate [HEME][ESO_4] and 1-ethyl-3-methylimidazolium ethyl sulphate . Equimolar amounts (0.3 M) of selected cation (methyl-diethanolamine/1-methylimidazole) were mixed with diethyl sulphate slowly into the three neck bottom flask with 50mL of toluene as the medium of the reaction. This procedure also supplied with the nitrogen and water to stabilize the reaction. The reaction was stirred until two layers formed for 3 hours. Then, the toluene was separated by using rotary evaporator to obtain [HEME][ESO_4] and [EMIM] [ESO_4].

iii. *Neutralization*

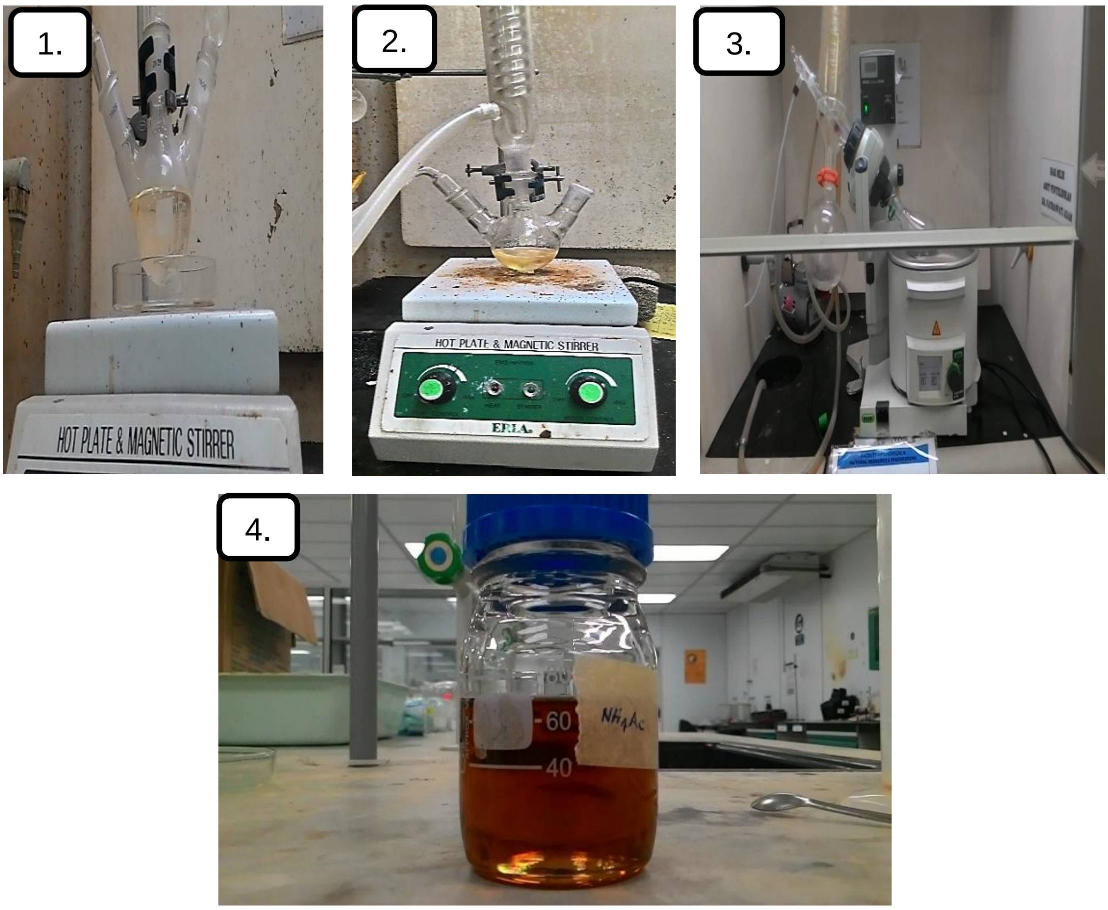


Figure 3.4 (a): Neutralization steps

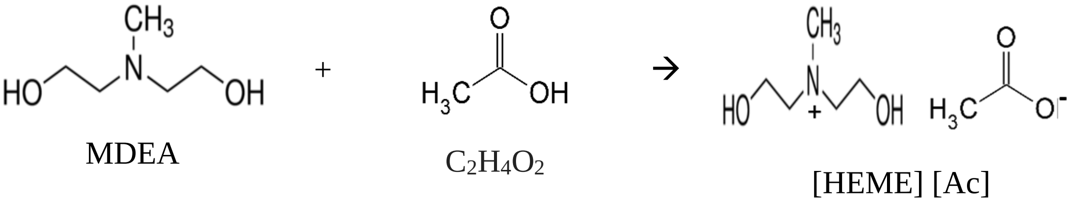


Figure 3.4 (b): Chemical reaction in neutralization process

0.3 mol of MDEA was stirred for half an hour at room temperature. Then, 0.3 mol acetic acid was mixed and stirred into the MDEA for 3 hours at room temperature with supplied of nitrogen and water. After 3 hours, the temperature was changed to 60°C under glycerol as the medium of heat supplied. The reaction was left for 24 hours to produce [HEME][Ac].

3.3-3 Ionic liquids characterization

i. pH test

Figure 3.5: Mettler Toledo pH meter

The determination of pH values is measured by using Mettler Toledo pH meter. Firstly, the pH meter was calibrated using the calibration buffer to improve the accuracy of measurements. Then, the 10 ml for each pure ILs were prepared in 50 ml beaker. The sensor of the pH meter was rinsed with distilled water and dried before dipped into the samples. After a while, the pH value appeared in the screen.

ii. Density

Figure 3.6: AccuPyc II 1340 Micromeritics

Figure 3.6 show an AccuPyc II 1340 Micromeritics to determine the density for each ILs. 10 cycles were set to obtain the average value of density. About 10mL for each ILs will put into the 10cm^3 nominal cell volume before being put into the AccuPyc II 1340 Micromeritics. The weight of each sample were collected as the data required before the analysis started. The calibration by using water to improve the accuracy of the measurement before attempting with another samples.

iii. Viscosity

Figure 3.7: Brookfield viscometer (DV-II+ Pro)

Viscosity is measured using a Brookfield viscometer (DV-II+ Pro). The principle of operation of the DV-II+Pro is a rotating spindle by immersed in the test fluid attached to a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. The measurement range of a DV-II+Pro (in centipoise or milliPascal seconds) is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full scale torque of the calibrated spring.

iv. Fourier Transform Infra-Red (FTIR) analysis

Figure 3.8: FT-IR Spectrometer Nicolet iS10 model

FT-IR Spectrometer Nicolet iS10 model was used to collect the data for each ILs. A few drop of sample was put on the silver plate and the analysis were collected. The data will compared before and after adding Fe_2O_3 in the ILs.

3.3-4 Solubility study

All four ILs will be tested by adding Fe_2O_3 to determine their solubility potential. Each ILs will be added with 0.0015g of Fe_2O_3 into 1.5mL ILs and left for 24 hours by using Grant-bio Multifunction Rotators, 360º Vertical.

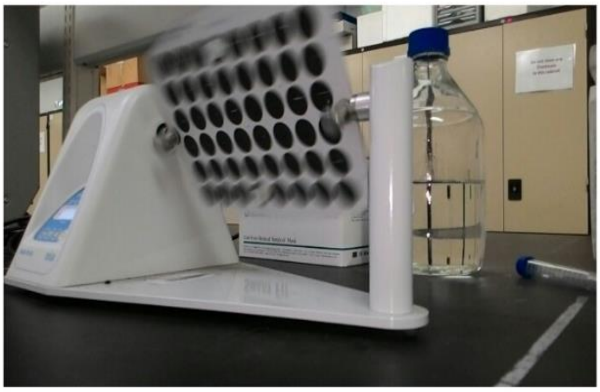


Figure 3.9: Grant-bio Multifunction Rotators, 360º Vertical

4 RESULTS AND DISCUSSIONS

4.0 Overview

This chapter presents the results and discussion for the solubility study on ILs. In this part, a manual calculation were done to determine the value of solubility parameter by using both methods which is Fedors' and Small group contribution method. The data analysis from density, viscosity, pH value and FTIR for characterization have been compared for each ILs. Finally, the solubility potential for each ILs have been observed and determined as a better solvent to Fe_2O_3.

In order to determine the solubility parameter of ionic liquids, the molecular structure of the molecules was identified. There are various type of cation and anion for ILs with different structure. ILs screening show the result obtained after the calculation part and summarized as table below. The selected ILs was synthesized and characterized in order to identify which ILs will dissolve Fe_2O_3.

4.1 Ionic liquids screening

Table 4.1 and 4.2 below shows the result that obtained from the calculation by using Fedors' and Small group contribution method.

Table 4.1: Solubility parameter of cation ILs based on Fedors' and Small contribution method.

Cation	Fedors	Small
Ammonium	19.14	-
Pyrolidinium	19.66	17.6
Pyridinium	21.41	-
Imidazolium	25.70	-

Table 4.2: Solubility parameter of anion ILs based on Fedors' and Small group contribution method.

Anion	Fedors	Small
Lactate	-	14.35
Acetate	16.49	16.66
Tosylate	19.61	20.27
Triflate	27.54	-
Sulphate	37.12	31.83
Bicarbonate	-	33.08
Thiocyanate	72.98	-

Based on the Table 4.1 and 4.2, ammonium show the lower solubility parameter value while imidazole is the highest among the cation. Some data obtained from the Small method is not fully provided as the values for the method to determine the solubility parameter cannot be calculated. Then, ammonia and imidazole were selected in order to test the solubility potential for the better solvent to dissolve Fe_2O_3.

For anion, lactate have the lower SP value while thiocyanate is the highest among the anion list. From the data recorded, acetate and sulphate (second highest) were selected for the lower and highest anion.

4.2 Ionic liquids synthesis

Table 4.3 below shows the selection of ILs based on the estimation solubility parameter.

Table 4.3: Type of selected ILs

Cation	Anion	ILs type
Ammonium	Acetate	Lower-lower
Ammonium	Sulphate	Lower-higher
Imidazolium	Acetate	Higher-lower
Imidazolium	Sulphate	Higher-higher

The selection of cation and anion were mixed from lower-lower to higher-higher. Then, 2-hydroxy-N-(2-hydroxyethyl)-N-methylethanolammonium acetate, [HEME][Ac], 2-ethyl-N-(2-hydroxyethyl)-N-methylethanolammonium ethyl sulphate, [HEME][ESO_4], 1-ethyl-3-metylimidazolium ethyl sulphate, [EMIM][ESO_4] and 1-ethyl-3-methylimidazolium acetate [EMIM][Ac] were produced by the ILs synthesis.

Figure 4.1 (a): [HEME][Ac]

Figure 4.1 (b): [HEME][ESO_4]

Figure 4.1(c): [EMIM][Ac]

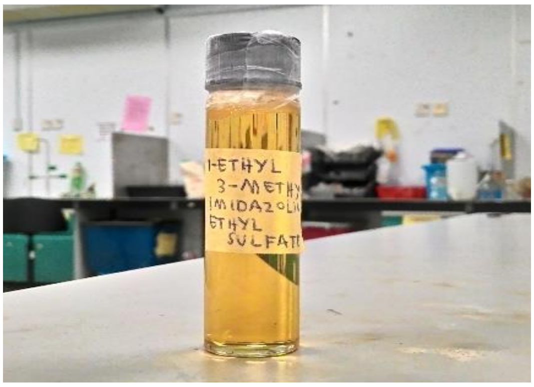


Figure 4.1 (d): [EMIM][ESO_4]

Table 4.4 below shows the yield for each ILs by using the formula:

$$percent\ yield = \frac{actual\ mass}{theoritical\ mass}\ x\ 100\% \qquad \text{(Eq.11)}$$

Table 4.4: Yield obtained for each ILs

ILs	**Yield (%)**
[EMIM][Ac]	91.65
[HEME] Ac	88.75
[EMIM] [ESO_4]	86.05
[HEME] [ESO_4]	76.15

From the Table 4.4 above, yield for each ILs is above 70% from the actual value. It shows that the [EMIM][Ac] has the highest yield obtained from the synthesized.

4.3 Ionic liquids characterizations

4.3.1 pH test

Table 4.5 above show the pH value by pH meter for each ILs.

Table 4.5: pH value for each ILs

ILs	pH
[EMIM][Ac]	8.95
[HEME] [ESO_4]	8.42
[HEME][Ac]	7.82
[EMIM] [ESO_4]	6.39

Other characterizations which should be considered is pH value. Table 4.5 above show the pH value by pH meter for each ILs. [HEME][ESO_4] and [EMIM][Ac] are in alkaline category while [HEME][Ac] nearest to neutral type and [EMIM][ESO_4] is in the range of acidic.

4.3.2 Density

Figure 4.2 and Table 4.6 below show the summary of density after 10 cycles for each ILs.

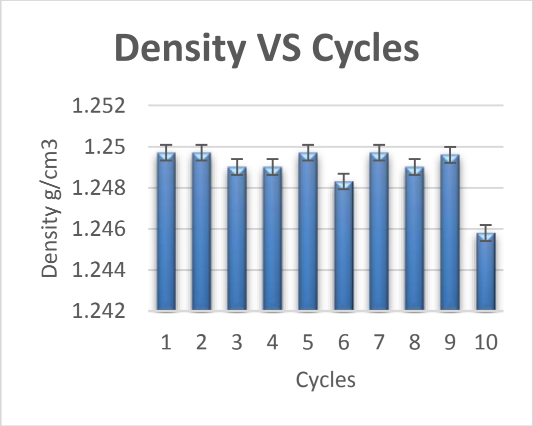


Figure 4.2 (a): [HEME][Ac]

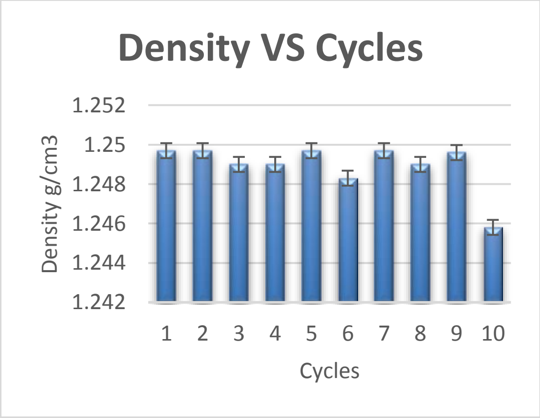


Figure 4.2 (b): [HEME][ESO_4]

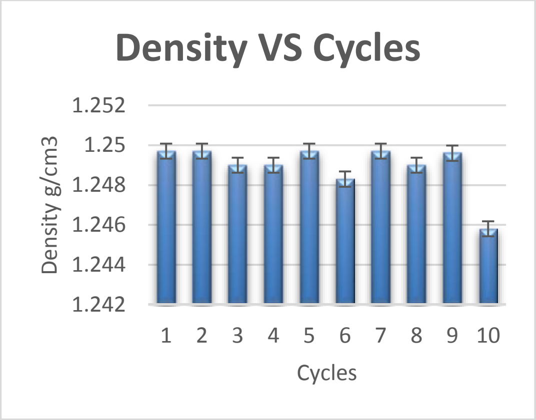


Figure 4.2 (c): [EMIM][Ac]

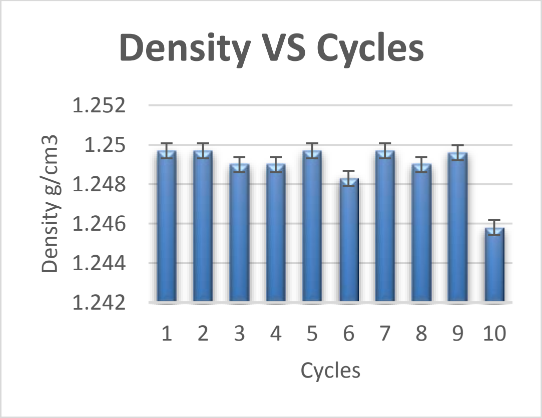


Figure 4.2 (d): [EMIM][ESO$_4$]

Table 4.6: Summary of density for each ILs

ILs	**Density (g/cm^3)**
[EMIM] [ESO$_4$]	1.2849
[HEME] [ESO$_4$]	1.2422
[HEME][Ac]	1.1245
[EMIM][Ac]	1.0324

From the Table 4.6 above, [EMIM] [ESO$_4$] has a higher density with 1.2849g/cm^3 followed by [HEME][ESO$_4$] 1.2422g/cm^3. [EMIM][Ac] is the lowest density compared to the other three ILs with 1.0324g/cm^3.

4.3.3 Viscosity

Table 4.7 below shows the summary of viscosity for each ILs.

Table 4.7: Summary of viscosity for each ILs

ILs	**Viscosity (mPa.s)**
[HEME][Ac]	104.8
[HEME] [ESO$_4$]	150.43
[EMIM][Ac]	15.8
[EMIM] [ESO$_4$]	51.6

Viscosity has been tried with varying speeds which is 25, 50 and 100 RPM as in appendix C. The range of value for different speed is not much different. The average for 3 different speed was calculated and summarized as in the Table 4.7 above.

[HEME]$[ESO_4]$ has a higher viscosity which is 150.43 mPa.s followed by [HEME][Ac] 104.8 mPa.s. The lowest is [EMIM]$[ESO_4]$ as much as 15.8 mPa.s.

4.3.4 Fourier Transform Infra-Red (FTIR) analysis

By using FTIR, each chemical bonds in a molecule can be identified by producing an infrared absorption spectrum. The result obtained from each pure ILs after synthesized process as shown in figure below.

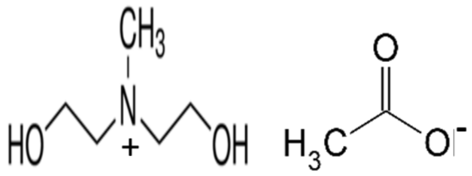


Figure 4.3 (a): [HEME][Ac] molecular structure

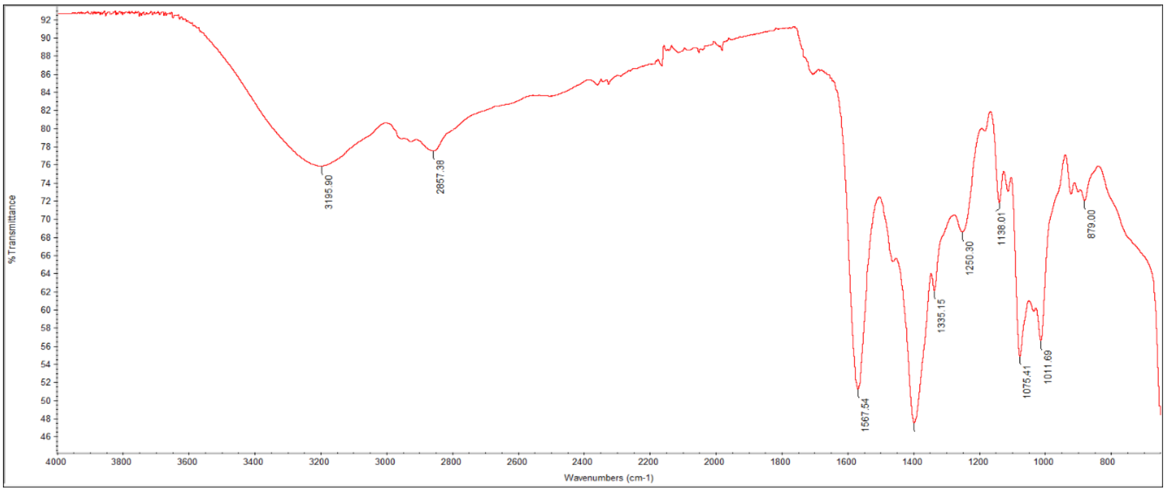


Figure 4.3 (b): [HEME][Ac] FTIR analysis

Table 4.8 (a): FTIR peak analysis for [HEME][Ac]

Wavenumber (cm^{-1})	**Bond**	**Functional group**
3195.90	O–H	Carboxylic acids
2857.38	H–C=O: C–H	Aldehydes
1250.30	C-N	Aliphatic amines
1011.69	C-O	Alcohols, carboxylic acid, esters, ethers

From the Table 4.8 (a) above, almost all the funtional group of [HEME][Ac] were determined by peak analysis of FTIR.

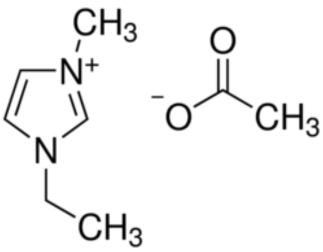


Figure 4.4 (a): [EMIM][Ac] molecular structure

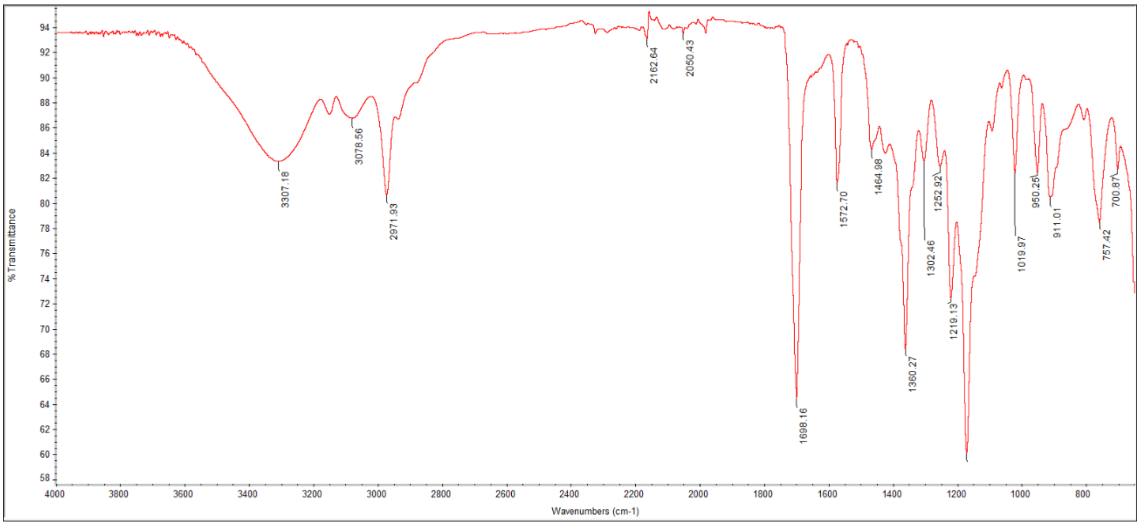


Figure 4.4 (b): [EMIM][Ac] FTIR analysis

Table 4.8 (b): FTIR peak analysis for [EMIM][Ac]

Wavenumber (cm^{-1})	**Bond**	**Functional group**
3307.16	-C≡ C-H : C-H stretch	alkynes
3078.56	=C–H stretch	alkenes
2971.93	C–H	alkanes
1688.16	C=O skretch	α , β –unsaturated aldehydes, ketones
1360.27	N–O symmetric stretch	nitro compounds
1302.27	C-O stretch	Alcohols, carboxylic acids, esters, ethers
1219.13	C-N stretch	Aliphatic amines

From the Table 4.8 (b), almost all the functional group in [EMIM][Ac] can be identified based on the peak from FTIR analysis.

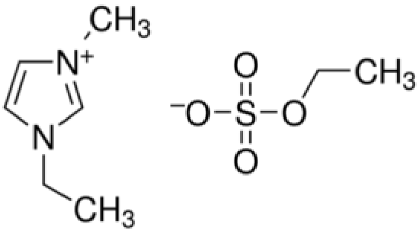


Figure 4.5 (a): [EMIM][ESO_4] molecular structure

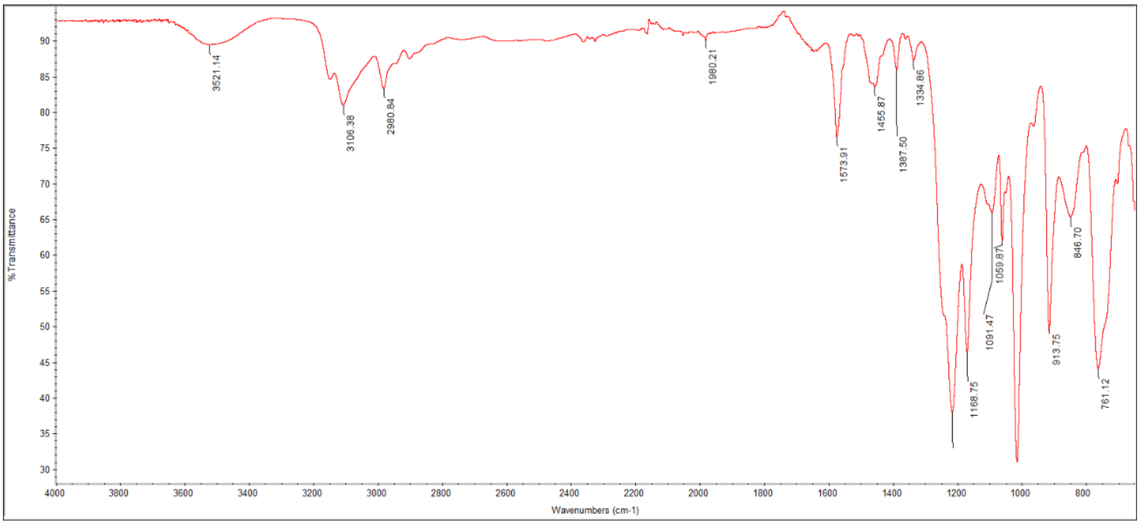


Figure 4.5 (b): [EMIM][ESO_4] FTIR analysis

Table 4.8 (c): FTIR peak analysis for [EMIM][ESO_4]

Wavenumber (cm^{-1})	**Bond**	**Functional group**
3106.38	C-H skretch	aromatics
2980.64	C-H skretch	Alkanes
1455.87	C–H bend	Alkanes
1334.86	N–O symmetric stretch	nitro compounds
1020-1250	C–N stretch	aliphatic amines

From Table 4.8 (c), there is another peak that formed in the [EMIM] [ESO_4] that is not represent functional group in the [EMIM][ESO_4]. From the molecular structure of [EMIM][ESO_4] as shown in Figure 4.5 (a), also shows that some functional group cannot be analysed from the FTIR.

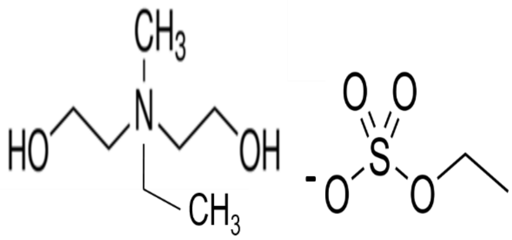


Figure 4.6 (a): [HEME][ESO4] molecular structure

Figure 4.6 (b): [HEME][ESO4] FTIR analysis

Table 4.8 (d): FTIR peak analysis for [HEME] [ESO4]

Wavenumber (cm^{-1})	**Bond**	**Functional group**
3365.11	N–H stretch	1˚, 2˚ amines, amides
2981.87	C–H stretch	alkanes
1463.73	C–H bend	alkanes
1020-1250	C–N stretch	aliphatic amines

From the Table 4.8 (d) above, almost all functional group in [HEME][ESO4] were determined after FTIR peak analysis towards this ILs.

4.4 Solubility study

Each ILs will be tested by adding 0.0015g of Fe_2O_3. All the figure below shows the observation after 24 hours using Rotators, 360º Vertical.

Before	After	Observation
		The black spots of Fe_2O_3 at the bottom in the [HEME][Ac] have started to disappear and decreased.

Figure 4.7 (a): [HEME][Ac] before and after 24 hours by using Rotators, 360º Vertical.

[HEME][Ac] is the ILs with the lower cation and lower anion type. From the Figure 4.7 (a) above, the amount of Fe_2O_3 has been reduced after 24 hours. The black spots of Fe_2O_3 in the [HEME][Ac] have started to disappear and decreased.

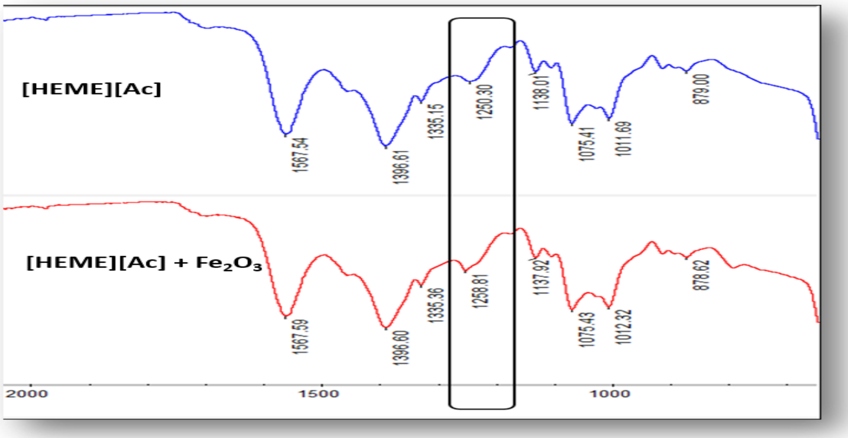


Figure 4.7 (b): Comparison FTIR analysis data of [HEME][Ac]

From Figure 4.7 (b) above shows that there was interaction at the C-N funtional group in the pure [HEME][Ac] and after adding Fe_2O_3. The shifting of the peak to the left was happened as shown at the mixture of [HEME][Ac] and Fe_2O_3.

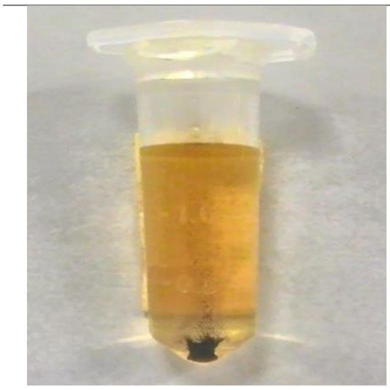
Before	After	Observation
		Reducing of Fe_2O_3 inside the [EMIM][Ac].

Figure 4.8 (a): [EMIM][Ac] before and after 24 hours by using Rotators, 360º Vertical.

[EMIM][Ac] is the ILs with higher cation and lower anion type. From the Figure 4.8 (a) above, it significantly changes with the reduced of Fe_2O_3 inside the vial tube. But still looks fraction of Fe_2O_3 inside the ILs.

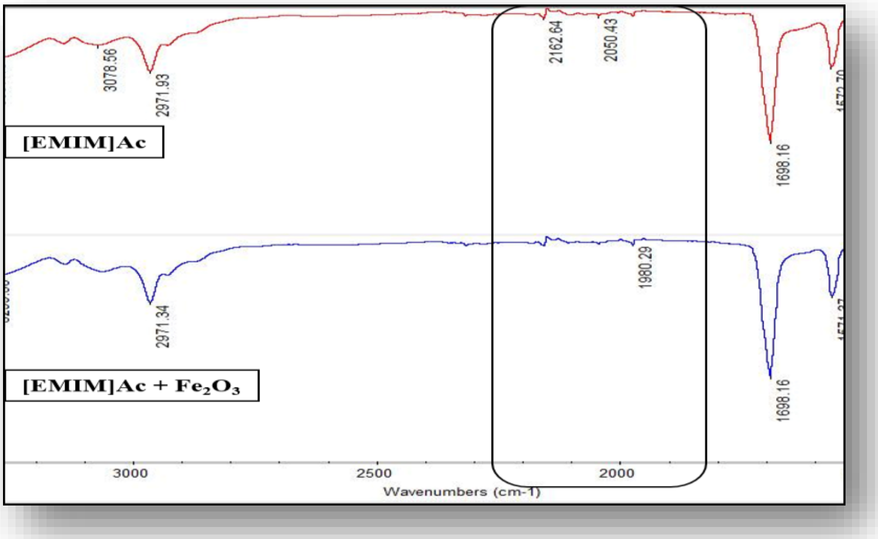


Figure 4.8 (b): Comparison FTIR analysis data of [EMIM][Ac]

For [EMIM][Ac] FTIR analysis, two peak have been disappeared with addition of another peak as highlighted in Figure 4.8 (b) above. The interaction was happened at the alkynes and alkenes funtional group in the [EMIM][Ac].

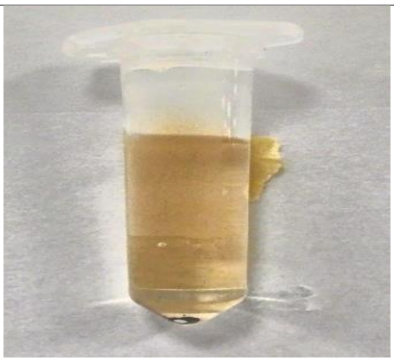
Before	After	Observation
		Slightly decreased

Figure 4.9 (a): [HEME][ESO_4] before and after 1 day using Rotators, 360° Vertical.

[HEME][ESO_4] is the ILs with the lower cation and higher anion type. From the Figure 4.9 (a) above, the Fe_2O_3 still visible at the vial tube. It accumulates on the bottom surface of ILs. But the number was reduced slightly from the original.

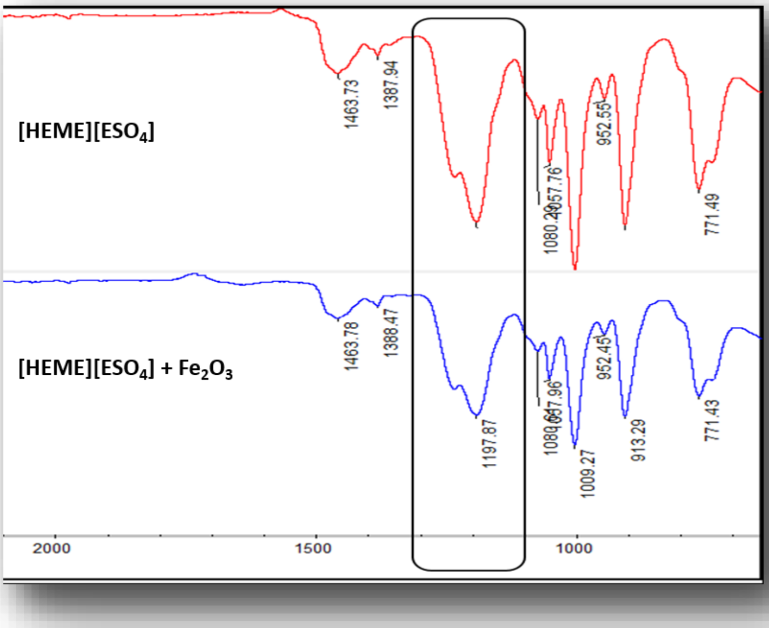


Figure 4.9 (b): Comparison FTIR analysis data of [HEME][ESO_4]

From the Figure 4.9 (b) above, the peak value was appeared at the aliphatic amines C-N functional group. The interaction was happened after adding Fe_2O_3 in [HEME][ESO_4] FTIR results.

Before	After	Observation
		Not dissolved

Figure 5 (a): [EMIM][ESO_4] before and after 24 hours by using Rotators, 360° Vertical.

[EMIM][ESO_4] is the ILs with higher cation and higher anion type. From the Figure 5 (a) observed, iron is still visible despite being shaken in a day. The Fe_2O_3 is insoluble in the [EMIM][ESO_4]. The amount of Fe_2O_3 also seems like not reduced.

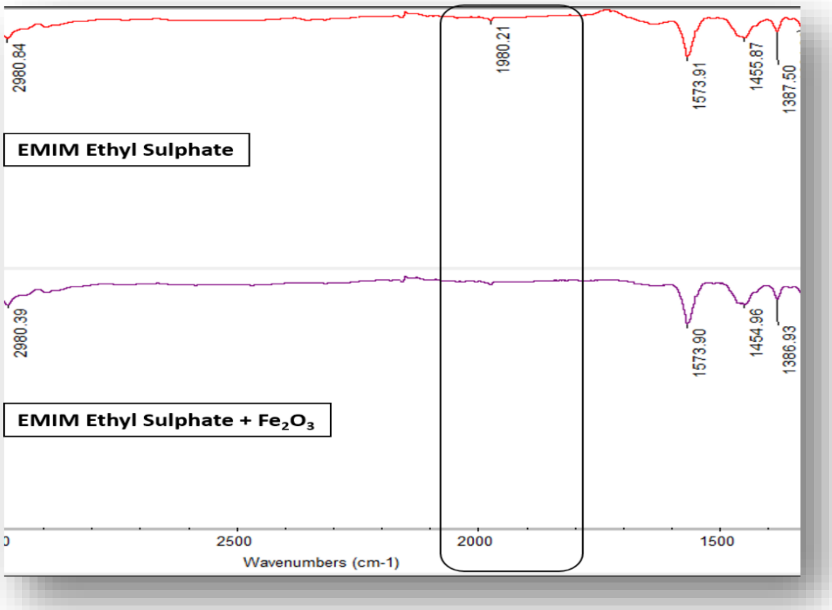


Figure 5 (b): Comparison FTIR analysis data of [EMIM][ESO_4]

The comparison of FTIR analysis for pure [EMIM] [ESO_4] and after adding Fe_2O_3 can be observed at the peak shown in Figure 5 (b) above. The peak was disappeared at the alkenes functional group in the adding Fe_2O_3 data.

Table 4.9: Summary of solubility study towards Fe_2O_3

ILs	Solubility Potential	Type of ILs
[HEME][Ac]	High	Lower-Lower
[EMIM][Ac]	Intermediate	Higher-Lower
[HEME] [ESO_4]	Intermediate	Lower-Higher
[EMIM] [ESO_4]	Low	Higher-Higher

From the Table 4.9 above, the observation of ILs after 24 hours proved that [HEME][Ac] has the ability to dissolve Fe_2O_3 better than the other ILs. Based on the estimation method by using Fedors and Small group contribution method, [HEME][Ac] is the lower-lower type of ILs with lower solubility parameter value of both cation and anion. From the investigation, Fe_2O_3 was possible to dissolve in the ILs with either lower solubility of cation or anion. ILs of [EMIM][Ac] and [HEME][ESO_4] also proved that either there have low cation or anion, the ILs have the potential to reduce the amount of Fe_2O_3 even not fully dissolve. Lastly, the higher-higher type of ILs which is [EMIM][ESO_4] shows that it is not dissolving even reducing the amount of Fe_2O_3.

Another factor that can be related in solubility potential by comparing pH value, the potential of Fe_2O_3 to soluble in four different ILs is in the range from neutral to alkaline types. [HEME][Ac][emim which is a better solvency potential within range near to neutral type can dissolve Fe_2O_3. For the acidic type ILs which is [EMIM][ESO_4] is difficult to dissolve the Fe_2O_3.

From the observation on density, all other three ILs stated have lower density that are dissolved Fe_2O_3 well compared to [EMIM][ESO_4] which has higher density that shown poor in dissolving Fe_2O_3.

5 CONCLUSION

5.1 *Conclusion*

[HEME][Ac] is a better solvent of tested ILs in dissolving Fe_2O_3 which having lower cation and lower anion followed by [EMIM][Ac] with higher cation and lower anion solubility parameter. From the observation, ILs which consists of ammonia and acetate will show a little change against the amount of Fe_2O_3. Lower value in terms of solubility parameter of cation and anion can give a better solubility potential with the characteristic of neutral type of solvent and lower density.

5.2 *Recommendation*

The estimation method of Fedors and Small must be compared with any different methods to determine the solubility parameter of ILs. Besides, a lot of ILs must be considered in order to identify a better solvent towards Fe_2O_3. The observation of solubility study is inadequate but need to improve by using other equipment such as Atomic Absorption Spectrophotometer (AAS) to determine the concentration of Fe_2O_3 in ILs.

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APPENDICES

Appendix A

A.1. Table of Small group contribution. (Robeson, 2007)

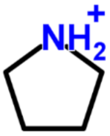
Groups	$\boldsymbol{F_i}$**($J^{1/2}cm^{3/2}mol^{-1}$)**	**V_g $(cm)^3mol^{-1}$**
$-CH_3-$	438	23.9
$-CH_2-$	272	15.85
-CH<	47	4.6
-CH=	227	-
>C=	39	-
Phenyl	1504	72.7
Phenylene	1346	65.5
-O-	143	10.0
-CO-	563	13.4
-COO- (general)	634	23.0
-COO- acrylic	634	18.25
-Cl	532	19.9
-CN	839	-
$-CF_2-$	307	-
$-CF_3$	560	-
$-NH_2$	-	-
>NH	-	-
-S-	460	17.8

A.2. Table of Fedors' group contribution.

Groups	**E_i (J/mol)**	**V_i (cm^3/mol)**
>NH	8370	4.5
Phenylene (o, m, p)	31940	52.4
-O-	3350	3.8
-CONH-	33490	9.5
=CH-	4310	13.5
=N-	11720	5.0
$-CH_2-$	4940	16.1
$-CH_3-$	4710	33.5
=C<	4310	-5.5
-N=N-	4190	*
>C<	1470	-19.2
Ring closure 5 or more atoms	1050	16
$-NO_2$ (aromatic)	15360	32
$-N^+H_2$ ($-NH_2$)	12560	19.2
-OH-	21850	13

Appendix B

B.1. Calculation of solubility parameter by Small group contribution method

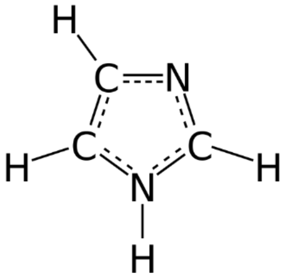


Pyrolidinium

Small Method

Groups	#units	F_i ($J^{1/2}cm^{3/2}mol^{-1}$)	v_g $(cm)^3mol^{-1}$
$-NH_2$	1	-	-
$-CH_2$	4	4 x 272	4 x 15.85
$\sum =$		1088	63.4
		δ_P =17.16 $(MPa)^{1/2}$	

B.2. Calculation of solubility parameter by Fedors' group contribution method



Imidazole

Fedors Method

Groups	No. Of Fragment	E_i (J/mol)	V_i (cm^3/mol)	Ecoh (Sum)	V (Sum)
= N -	1	11720	5	11720	5
= CH -	3	4310	13.5	12930	40.5
> NH	1	8370	4.5	8370	4.5
			Total	33020	50
				δ = 25.7 $J^{1/2}$ $cm^{3/2}$	

$1\ (MPa)^{1/2} = 1\ J^{1/2}\ cm^{3/2}$

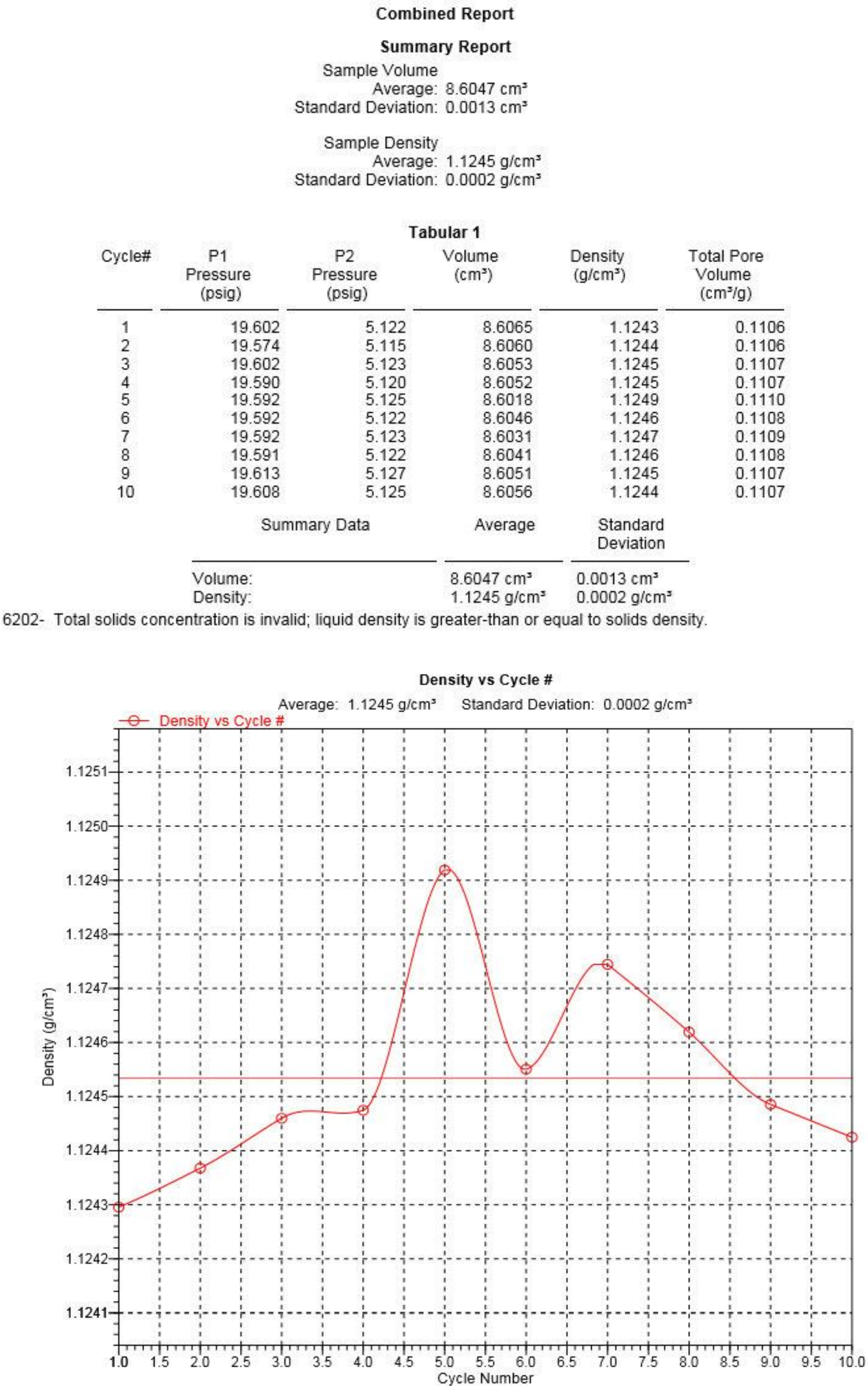
Appendix C

C.1. Table of yield ILs

ILs	**Molecular weight (g/mol)**	**Mol**	**Theoritical (g)**	**Actual (g)**	**Yield (%)**
[HEME][Ac]	77.08	0.3	23.12	20.52	88.75
[HEME]ESO$_4$]	188.25	0.3	56.47	43.0	76.15
[EMIM][Ac]	170.21	0.5	85.11	78.0	91.65
[EMIM][ESO$_4$]	236.29	0.3	70.89	61.0	86.05

Appendix D

D.1. Density of [HEME][Ac]



Combined Report

Summary Report

Sample Volume
Average: 8.6047 cm³
Standard Deviation: 0.0013 cm³

Sample Density
Average: 1.1245 g/cm³
Standard Deviation: 0.0002 g/cm³

Tabular 1

Cycle#	P1 Pressure (psig)	P2 Pressure (psig)	Volume (cm³)	Density (g/cm³)	Total Pore Volume (cm³/g)
1	19.602	5.122	8.6065	1.1243	0.1106
2	19.574	5.115	8.6060	1.1244	0.1106
3	19.602	5.123	8.6053	1.1245	0.1107
4	19.590	5.120	8.6052	1.1245	0.1107
5	19.592	5.125	8.6018	1.1249	0.1110
6	19.592	5.122	8.6046	1.1246	0.1108
7	19.592	5.123	8.6031	1.1247	0.1109
8	19.591	5.122	8.6041	1.1246	0.1108
9	19.613	5.127	8.6051	1.1245	0.1107
10	19.608	5.125	8.6056	1.1244	0.1107

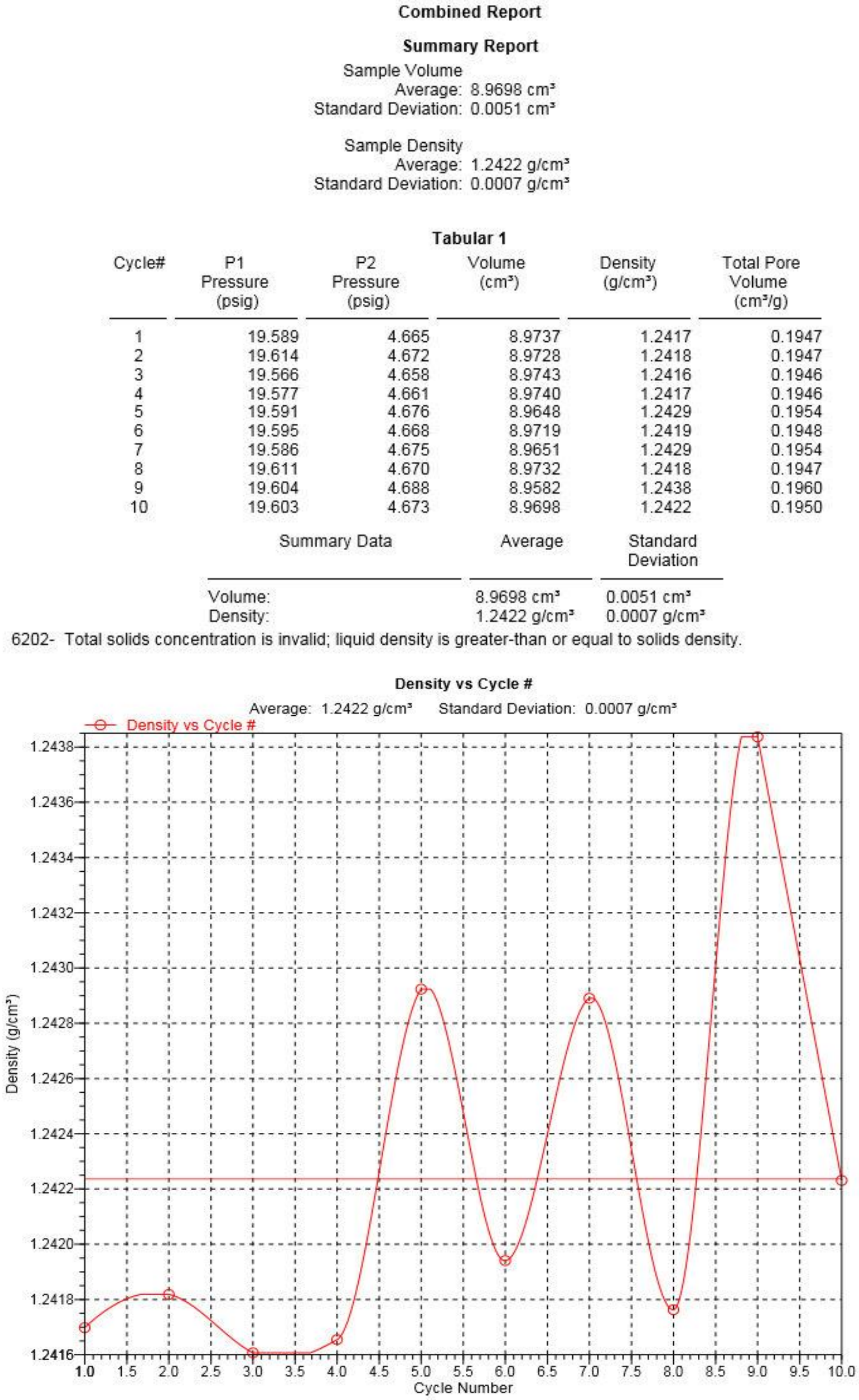
Summary Data	Average	Standard Deviation
Volume:	8.6047 cm³	0.0013 cm³
Density:	1.1245 g/cm³	0.0002 g/cm³

6202- Total solids concentration is invalid; liquid density is greater-than or equal to solids density.

Density vs Cycle #

Average: 1.1245 g/cm³ Standard Deviation: 0.0002 g/cm³

D.2. Density of [HEME][ESO_4]



Combined Report

Summary Report

Sample Volume
Average: 8.9698 cm³
Standard Deviation: 0.0051 cm³

Sample Density
Average: 1.2422 g/cm³
Standard Deviation: 0.0007 g/cm³

Tabular 1

Cycle#	P1 Pressure (psig)	P2 Pressure (psig)	Volume (cm³)	Density (g/cm³)	Total Pore Volume (cm³/g)
1	19.589	4.665	8.9737	1.2417	0.1947
2	19.614	4.672	8.9728	1.2418	0.1947
3	19.566	4.658	8.9743	1.2416	0.1946
4	19.577	4.661	8.9740	1.2417	0.1946
5	19.591	4.676	8.9648	1.2429	0.1954
6	19.595	4.668	8.9719	1.2419	0.1948
7	19.586	4.675	8.9651	1.2429	0.1954
8	19.611	4.670	8.9732	1.2418	0.1947
9	19.604	4.688	8.9582	1.2438	0.1960
10	19.603	4.673	8.9698	1.2422	0.1950

Summary Data	Average	Standard Deviation
Volume:	8.9698 cm³	0.0051 cm³
Density:	1.2422 g/cm³	0.0007 g/cm³

6202- Total solids concentration is invalid; liquid density is greater-than or equal to solids density.

Density vs Cycle #

Average: 1.2422 g/cm³ Standard Deviation: 0.0007 g/cm³

D.3. Density of [EMIM][Ac]

Combined Report

Summary Report

Sample Volume
Average: 7.9001 cm³
Standard Deviation: 0.0040 cm³

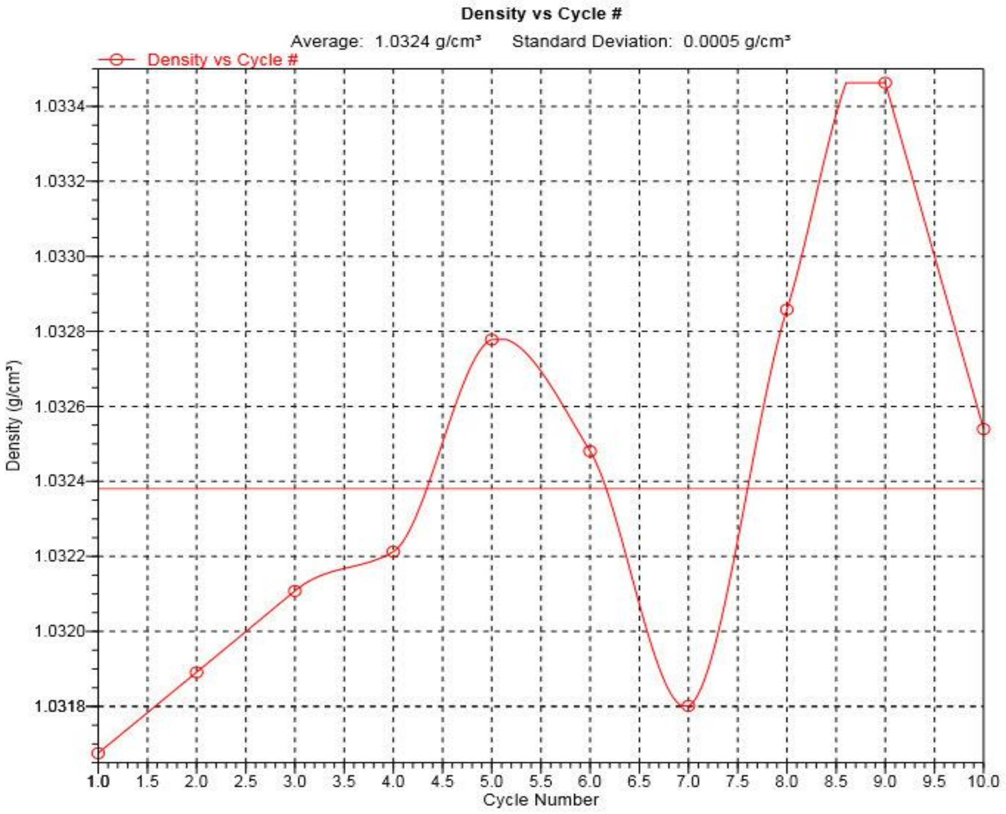
Sample Density
Average: 1.0324 g/cm³
Standard Deviation: 0.0005 g/cm³

Tabular 1

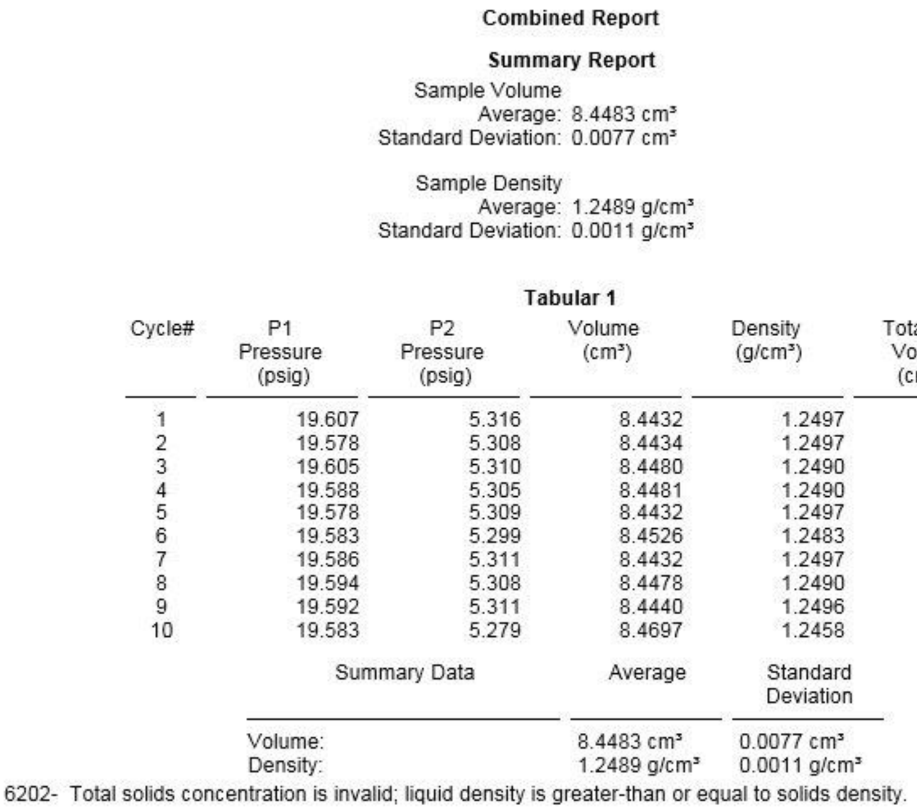
Cycle#	P1 Pressure (psig)	P2 Pressure (psig)	Volume (cm³)	Density (g/cm³)	Total Pore Volume (cm³/g)
1	19.595	5.914	7.9055	1.0317	0.0307
2	19.597	5.917	7.9038	1.0319	0.0309
3	19.587	5.915	7.9022	1.0321	0.0311
4	19.600	5.920	7.9014	1.0322	0.0312
5	19.577	5.918	7.8971	1.0328	0.0317
6	19.585	5.918	7.8993	1.0325	0.0315
7	19.567	5.907	7.9045	1.0318	0.0308
8	19.579	5.919	7.8964	1.0329	0.0318
9	19.561	5.919	7.8918	1.0335	0.0324
10	19.569	5.914	7.8989	1.0325	0.0315

Summary Data	Average	Standard Deviation
Volume:	7.9001 cm³	0.0040 cm³
Density:	1.0324 g/cm³	0.0005 g/cm³

6202- Total solids concentration is invalid; liquid density is greater-than or equal to solids density.



D.4. Density of [EMIM][ESO_4]



Combined Report

Summary Report

Sample Volume
Average: 8.4483 cm^3
Standard Deviation: 0.0077 cm^3

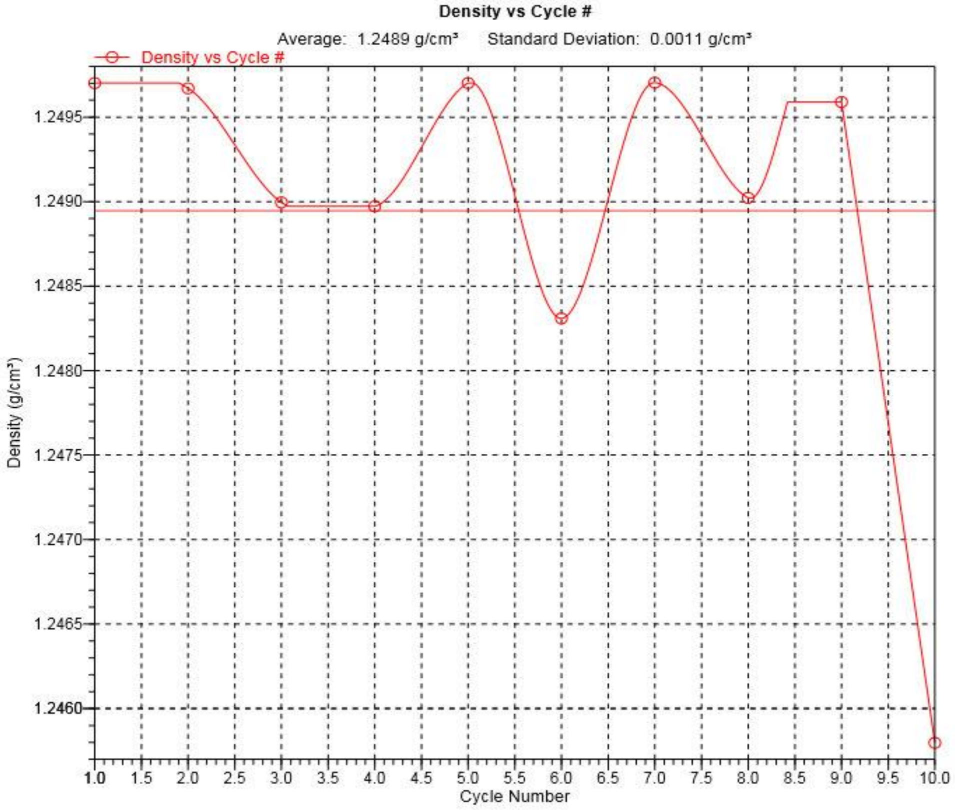
Sample Density
Average: 1.2489 g/cm^3
Standard Deviation: 0.0011 g/cm^3

Tabular 1

Cycle#	P1 Pressure (psig)	P2 Pressure (psig)	Volume (cm^3)	Density (g/cm^3)	Total Pore Volume (cm^3/g)
1	19.607	5.316	8.4432	1.2497	0.1998
2	19.578	5.308	8.4434	1.2497	0.1998
3	19.605	5.310	8.4480	1.2490	0.1994
4	19.588	5.305	8.4481	1.2490	0.1993
5	19.578	5.309	8.4432	1.2497	0.1998
6	19.583	5.299	8.4526	1.2483	0.1989
7	19.586	5.311	8.4432	1.2497	0.1998
8	19.594	5.308	8.4478	1.2490	0.1994
9	19.592	5.311	8.4440	1.2496	0.1997
10	19.583	5.279	8.4697	1.2458	0.1973

Summary Data	Average	Standard Deviation
Volume:	8.4483 cm^3	0.0077 cm^3
Density:	1.2489 g/cm^3	0.0011 g/cm^3

6202- Total solids concentration is invalid; liquid density is greater-than or equal to solids density.



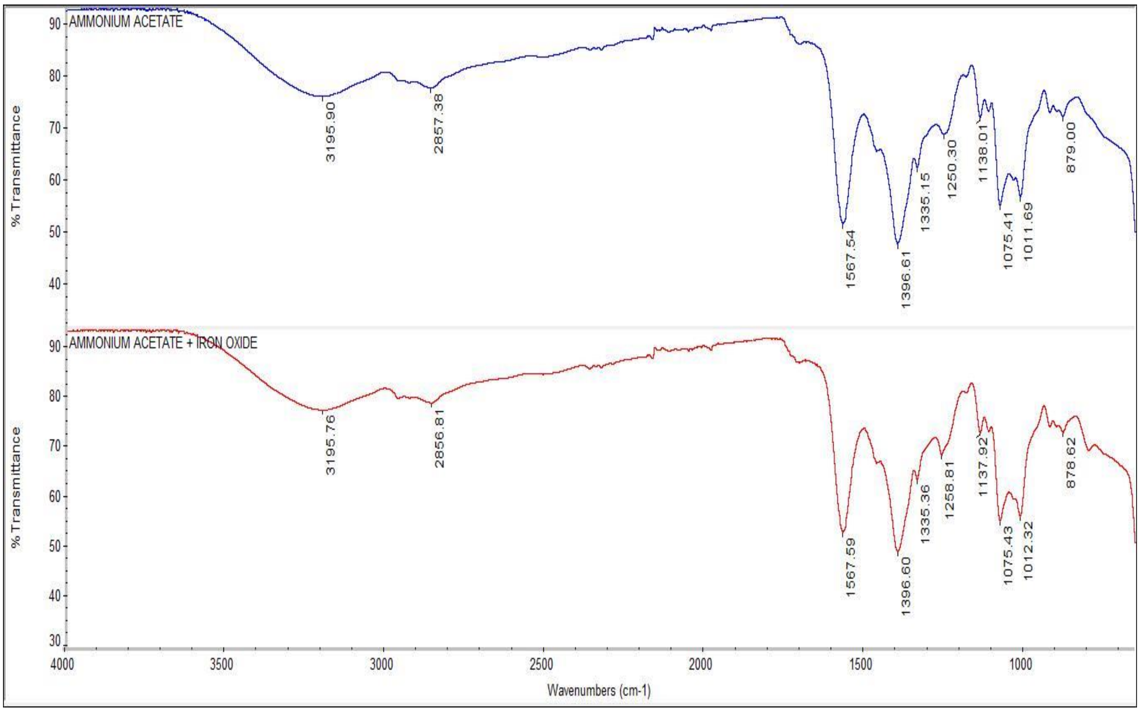
Appendix E

E.1 Table of viscosity for each ILs

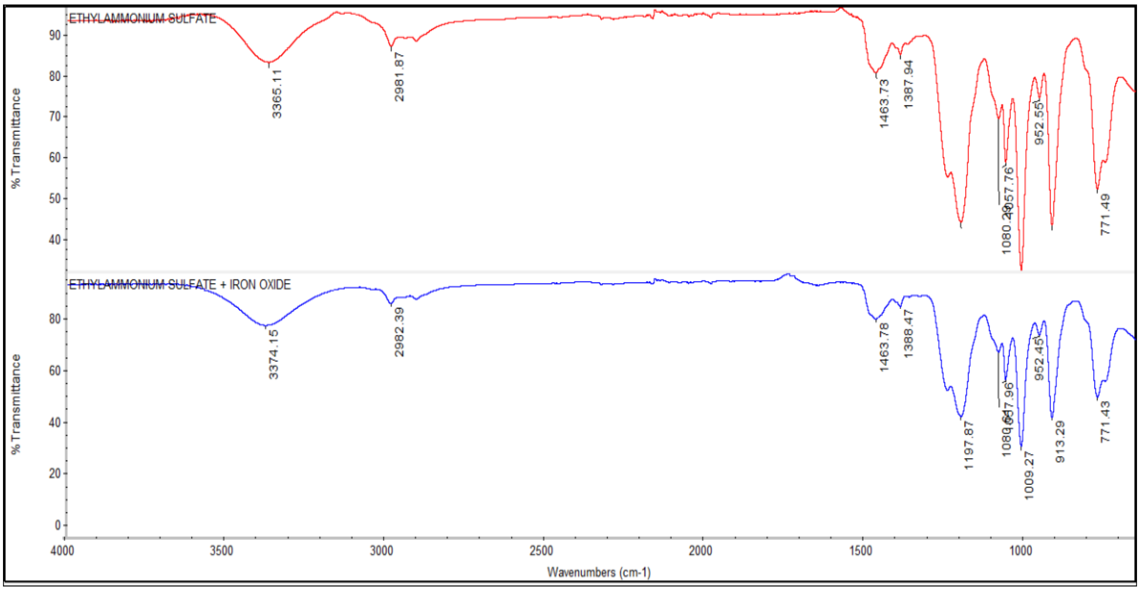
ILs		**[HEME][Ac]**	**[HEME] $[ESO_4]$**	**[EMIM][Ac]**	**[EMIM] $[ESO_4]$**
RPM 25	Viscosity (mPas)	91.2	106.8	15.6	40.8
	SSTR (N/m^2)	0.74	0.91	0.15	0.35
	SRATE (1/sec)	8.5	8.5	8.5	8.5
RPM 50	Viscosity(mPas)	109.2	159.4	15.6	56.4
	SSTR (N/m^2)	1.83	2.66	0.27	0.96
	SRATE (1/sec)	17	17	17	17
RPM 100	Viscosity (mPas)	114.0	185.1	16.2	57.6
	SSTR (N/m^2)	3.88	6.2	0.56	1.96
	SRATE (1/sec)	34	34.0	34	34
MEAN VIS		104.8	150.43	15.8	51.6

Appendix F

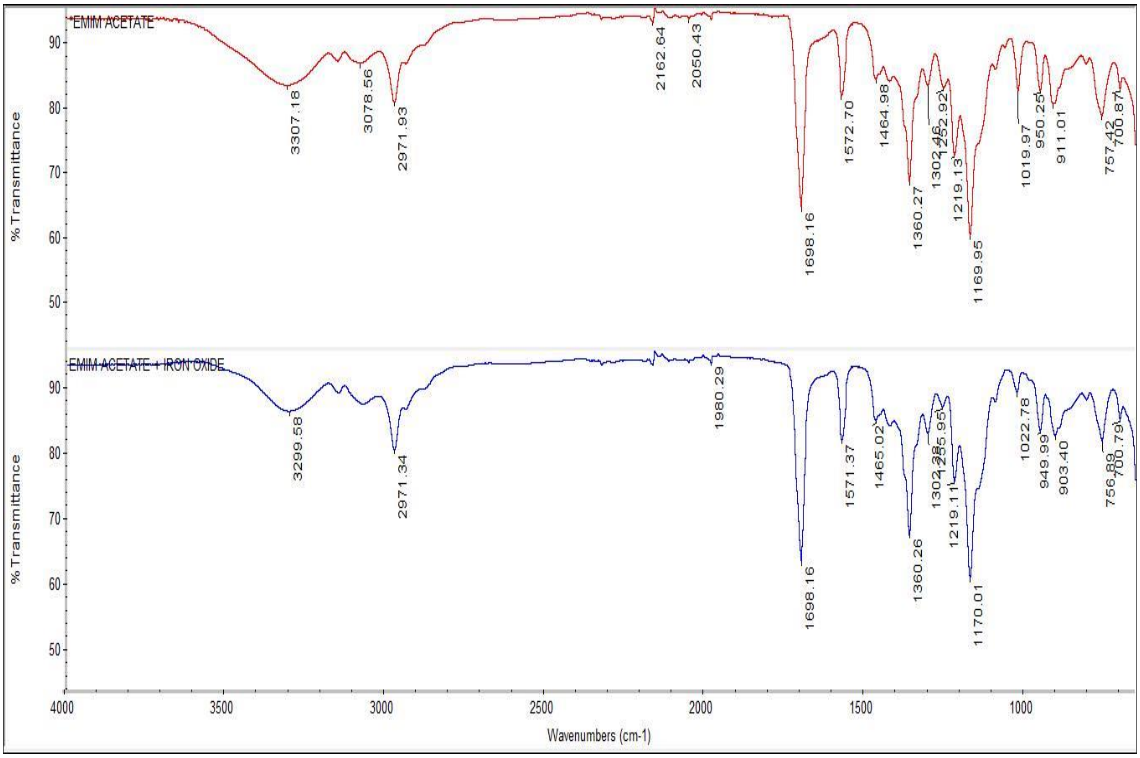
F.1 [HEME][Ac] FTIR analysis



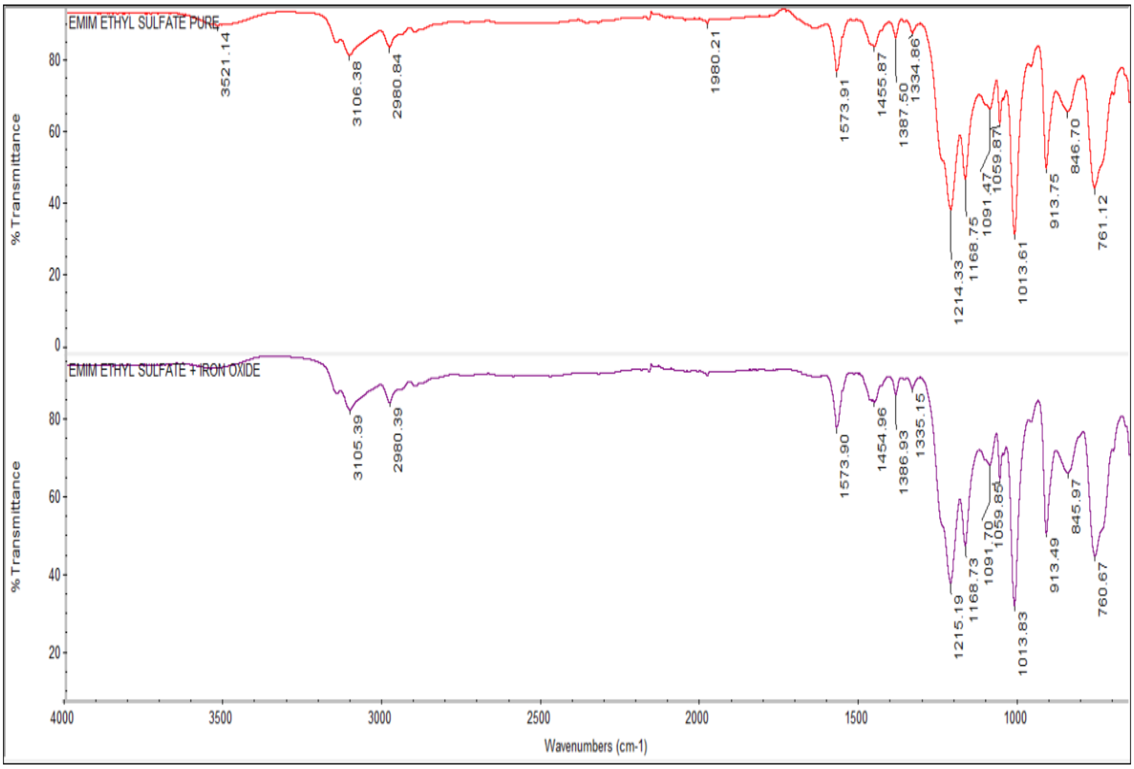
F.2 [HEME][ESO_4] FTIR nalysis



F.3 [EMIM][Ac] FTIR analysis



F.3 [EMIM][ESO$_4$] FTIR analysis



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