# Binary Mixtures' Thermophysical Properties Study of Novel Ionic Liquids Incorporating Thiosalicylate Anion

by

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Dissertation submitted in partial fulfillment of

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(Chemical Engineering)

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## CERTIFICATION OF APPROVAL

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Approved by,

(AP. DR. Cecilia Devi Wilfred)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

DECEMBER 2010

## CERTICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is own except as specified in the references and acknowledgements and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(FADWA BABIKER MUSTAFA)

#### Abstract

Ionic liquids are a class of organic molten salts "designer solvents" that are composed totally of anions (inorganic poly-atomic parts e.g., tetrafluoroborate [BF<sub>4</sub>]) and organic cations (e.g., 1-butyl-3-methylimidazolium - [BMIM]. Among the several aspects of green chemistry, the reduction/replacement of volatile organic solvents from the reaction medium is of utmost importance since the use of a large excess of conventional volatile solvents required to conduct a chemical reaction creates ecological and economic concerns. This research looks at producing a new cluster of ionic liquids which have the same anion part of thiosalicylate  $[C_6H_4SHCOO]^-$  with various cations of choline, tetramethylamonium, methylimidazolium and pyridinium which the latter two differ on the chain length. The chemical and physical properties such as the thermophysical properties of density, viscosity and refractive index for the pure ionic liquids and chiefly the density and viscosity for their binary systems with water are examined.

From experimental data the molecular volume ( $V_m$ ), thermal expansion coefficient ( $\alpha_P$ ), standard entropy (S<sup>o</sup>) and crystal energy ( $U_{POT}$ ) which are considered as derived thermophysical properties are studied for the pure ionic liquids particularly room temperature ionic liquids (RTILs).

From the Thermal Gravimetric Analysis (TGA) the decomposition temperature for 1octyl-3-methylimidazolium thiosalicylate, 1-butyl-3-methylimidazolium thiosalicylate, choline thiosalicylate, tetra-methylammonium thiosalicylate and 1-octylpyridinium thiosalicylate as 212.02 °C, 253.2 °C, 195.34°C, 225.05 °C and 235.1 °C respectively.

Based on the experiemental data the crystal energy for 1-octyl-3-methylimidazolium thiosalicylate, 1-octylpyridinium thiosalicylate and choline thiosalicylate were calculated in respect to their densities at 25  $^{\circ}$ C to be 399.6, 396.9 and 450.2 kJ correspondingly.

The dissertation included the synthesis methodology for thiosalicylate ionic liquids, characterization of the pure ionic liquids and their binary mixtures such as densities and viscosities, proton Nuclear Magnetic Resonance analysis (<sup>1</sup>HNMR) and the derived thermo physical properties data for pure ionic liquids.

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## DEDICATION

To My Father's Soul

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#### **CHAPTER 1**

## INTRODUCTION

#### 1.1 Background study

Up to now, the majority of chemical reactions are taking place in molecular solvents and our understanding of chemistry is rooted in the molecules behavior of the solution phase in molecular solvents. Recently, a new class of solvent has emerged in the chemistry planet, it is called ionic liquid with abbreviation form of (IL). These organic molten salts are often fluid at room temperature, and compose entirely of ionic species. They have numerous attractive properties for green synthesis which makes them of interest to all chemists and chemical engineers in terms of the thermodynamics and kinetics of reactions.

What is amazing about ionic liquids that they have no measurable vapor pressure; thus, they can emit no volatile organic compounds (VOCs) [1]. They consist of at least two components which determined as the organic or inorganic anion and organic cation, these ionic species differ in size and can be either hydrophobic or hydropic [2,3]. Another attractive behavior of ILs is they can be designed with a particular end use in mind to possess a particular set of properties that is why sometimes they are called as "designer solvents"[4].

The history of ionic liquids was recorded with the first initiation of ethylammonium nitrate -  $(C_2H_5)$  NH<sub>3</sub>·NO<sub>3</sub> (m.p. 12 °C) - synthesized in 1914 by Paul Walden. It is done by the addition of concentrated nitric acid to ethylamine, in order to get the pure salt which was liquid at room temperature water was removed by distillation [5].

In general, ionic liquids' cation has a low degree of symmetry which have a tendency to reduce the lattice energy of the crystalline form of the salt, and thus lower the melting point, in fact most ionic liquids have melting point below 100 °C [5].

In the past, there was a conflict between ionic liquids and molten salts, accepting the idea of ionic liquids have the same characteristics of these salts. Fortunately, much

literature on low melting salts have clarified the difference and the term "Ionic liquid" was used accordingly as early as 1943 [6]. As mentioned above ionic liquids now can be identified as a category of organic molten salts that are totally composed of anions inorganic poly-atomic parts and organic cations.[4]

In the 1970s and 1980s there was interest in ionic liquids based on alkyl-substituted imidazolium and pyridinium cations, with halide or trihalogenoaluminate anions, initially developed for use as electrolytes in battery applications. An important property of the imidazolium halogenoaluminate salts was that their physical properties — viscosity, melting point, and acidity — could be adjusted by changing the alkyl substituents and the imidazolium/pyridinium and halide/halogenoaluminate ratios [6].

Synthesis of ionic liquids can be classified into two sections: first the formation of the desired cation and anion to make the exchange to form the desired product. Second the formation of the anion where the cation is available at reasonable cost [6]. A large number of ionic liquids have organic cations that do not hold acidic protons and inorganic poly-atomic anion. The most common classes of cations and anions are illustrated in the two figures below [7].



Imidazolium

Pyridinium Tetraalkylphosphonium Tetraalkylammonium

Figure 1.1: Cations of ionic liquids



Figure 1.2: Anions used for the formation of Ionic Liquids

In this study thermophysical and derived thermophysical properties of six new thiosalicylate Ionic Liquids (each has *different cation base of imidazolium, pyridinium, choline hydroxide and tetra-methyl ammonium hydroxide*) will be studied pure as well with water as binary mixtures. Bear in mind each of the imidazolium and pyridinum cation has two different alky chain-length.

#### **1.2Problem Statement**

- 1. Most of ionic liquids are known to be highly viscous which limit their transportation such as reaction occurrence or transfer through pipes.
- 2. Water soluble ILs are necessary for certain industrial applications like extraction.
- 3. Thermophysical properties data of the imidazolium/pyridinium-based ILs incorporating the thiosalicylate anion have not yet been reported.

#### 1.3 Objectives

- 1. To synthesize imidazolium/pyridinium/choline/tetramethylammoniun-based ILs incorporating thiosalicylate anion.
- 2. To study the thermophysical properties if the pure ILs.
- 3. To study the thermophysical properties of density and viscosity for the binary systems (ILs with water)
- 4. To study the thermophysical and derived thermophysical properties for the pure ILs which include: density, viscosity, refractive index, standard entropy, thermal expansion coefficient and crystal energy.

#### 1.4 Scope of the study

The TGA, DSC, Ion Chromatography, refractive index and NMR tests were used throughout to verify the structures and purity of these compounds after anion metathesis. Binary systems' thermophysical properties (density, viscosity and refractive index) were measured while; thermal expansion coefficient, molar volume, standard entropy and crystal energy were estimated using the experimental values of density and refractive index.

No.	IL ME	TATHESIS	NEW IONIC LIQUID	
	Ionic Anion Liquid exchange with		Metathesis of IL with	BINARY
			Thiosalicylate (TS) anion to measure all thermophysical	SYSTEM
			properties	
1.	[BMIM]Cl	Sodium thiosalicylate	[BMIM]TS; (TS06)	
2.	[OMIM]Br	Sodium thiosalicylate	[OMIM]TS; (TS01)	Study
3.	[OPy]Br	Sodium thiosalicylate	[OPy]TS; (TS02)	densities, viscosities in
4.	[BPy]Cl	Sodium thiosalicylate	[BPy]TS; (TS03)	different molar
5.	Neutralization	1	[Tetramethyl ammonium]TS; (MT05)	ranons
6.	Neutralization	1	[Choline]TS; (TS04)	

Table 1.1: Scope of the study

## 1.5 The relevancy of the project

- 1. Most of the chemical and technological applications of ILs take place in mixtures not in single phase.
- 2. Binary mixtures data are used as fundamental data for the chemical design and optimizations.
- 3. Thiosalicylate anion is usually used as extraction of heavy metals from aqueous solution media and hence, it can be latter verified in ILs application as extraction of hazardous metals from waste water.

#### 1.6 Significance of the project

- 1. High ILs viscosity not desirable. However most of low viscous contain anion that have fluorine which is known to be quite unstable against hydrolysis and produces toxic and corrosive HF or fluorides and the disposal of these fluorous compounds is expensive and problematic. Therefore thiosalicylate is used to give low viscous ILs by producing binary mixtures of thiosalicylate with water.
- Thiosalicylate ILs contains no fluorine and is absolutely stable to any hydrolysis. It therefore does not release HF or fluorides, is not corrosive and much easier to dispose.
- 3. Thermophysical properties of the binary mixtures are required and of importance for industrial applications since more industries used binary or tertiary systems (extraction and absorption).
- 4. The purities of ILs have gained attention as their physical and chemical properties, specially towards their performance as solvents.

# CHAPTER 2 LITERATURE REVIEW

Numerous journals' and conferences' papers published about the use of *thiosalicylate* acid in synthesizing some ionic liquids, such as the following:

The synthesis of *Trioctylmethylammonium thiosalicylate* known as TOMATS which is a novel task specific ionic liquid and contains no fluorine and is absolutely stable to any hydrolysis with Melting Point less than 30°C and Refractive index  $n_D^{20}$  of 1,5185. [8]



Figure 2.1: TOMATS ionic liquid

#### **Application of TOMATS:**

It is used in the extraction of copper out of a blue coloured aqueous  $Cu^{2+}$ -tetramine phase as shown in the figure below. After addition of the TOMATS ionic liquid and before shaking the test tube, nice diffusion zones can be seen (second test tube) showing a copper free,uncoloured region and a dark copper containing upper region. After shaking for some seconds andwaiting for the separation of the phases, all the copper is extracted into the upper phase, forming an organic, dark coloured copper compound (third test tube).

Phase separation sometimes takes quite long, due to the relative high viscosity of TOMATS of 1500 mPa.s at 20°C. This drawback can be overcome by making its binary mixture since it is soluble in water or immiscible organic solvent like ethyl acetate or dichloromethane (or by heating it up).



Figure 2.2: Extraction of copper by TOMATS

### **Characterization of TOMATS:**

Appearance: olive green, viscous liquid

Relative molecular mass: 521,89 g/mol; empirical formula: C32H59NO2S

Solubility: Soluble in alcohols, ethyl acetate, THF, acetonitrile, acetone, dichloromethane,

DMSO; insoluble in water, hexane

Nernst distribution coeffizients3:  $Cd^{2+} > 50000$ ;  $Cu^{2+} > 50000$ ;  $Pb^{2+}$  and  $Hg^{2+} > 100000$ 

Melting Point: <30°C

Refractive index: nD20 = 1,5185

Leaching into aqueous phase: < 100 ppm

Viscosity and density as shown in the table below:

Table 2.1: TOMATS IL relative density and viscosity as pure and binary

Tirci	TOMATS 100% d [g/cm <sup>2</sup> ]	n imPasi	TOMATS 95% (5° d [g/cm³]	% ethyl acetate) η [mPas]
20	0,9556	1.500	0,9534	509
40	0,9445	352	0,9424	158
60	0,9325	119	0,9300	63
80	0,9213	50	0,9185	30

mixture

High efficiency and selectivity were reached for the extraction of cadmium from a natural river matrix with *tricaprylmethylammonium thiodsalicylate* (Daniel Kogelnig, 2008).

In 1996 some researchers mentioned the use of sodium-thiosalisylate in synthesis of ionic liquids. It was reacted with (RNC)AuCl [R= tert-butyl or mesityl isocyanide] in the two-phase system water/dichloromethane and gave high yields of the corresponding (isocyanide)gold(I) thiosalicylates. The products are set to be colorless, crystalline compounds stable to air and moisture and with high melting points (above 100 °C). The solid-state structure of the ILs latter has been determined by X-ray diffraction studies [9]. The reactions detail are as follows:

- (dimethyl sulfide)gold(I) chloride has been reacted with tert-butyl or mesityl isocyanide, both choices has provided high yields of the corresponding (RNC)AuCl.
- o These precursors were readily converted into the thiosalicylates by reaction with sodium thiosalicylate in the two-phase system water/dichloromethane:
  (RNC)AuCl + 2-(NaS)C<sub>6</sub>H<sub>4</sub>COOH →2-[(RNC)AuS]C<sub>6</sub>H<sub>4</sub>COOH + NaCl

t-Butyl o-(p-Chloropheny1thio)perbenzoate. The synthesis of o-(p-chloropheny1thio)benzoic acid was carried out by a procedure similar to that for the preparation of o-(9anisy1thio)-benzoic acid. The addition of a slurry of 4,4'-dichlorodiphenyliodonium bromide in methanol to a stirred solution of the sodium salt of methyl thiosalicylate under nitrogen, followed by saponification of the ester produced a 40% yield of the acid, m.p. 236-237°C [10].

Thus clarification on the characterization of Choline/RMIM/RPy-based thiosalicylate and their binary systems and the factors influence their quality will be discussed in this chapter.

#### 2.1 Imidazolium binary systems

Several properties of 1-alkyl-3-methylimidazolium-based ILs have been reported in the literature. However, the later has never reported imidazolium-based ILs incorporating with thiosalicylate anion:

- Densities and viscosities of (1-butyl-3-methylimidazolium tetrafluroborates + water) binary mixtures were measured over the whole range of compositions from (303.15 to 353.15) K. the excess molar volume and viscosity deviations of this system were correlated using Redlish-Kister polynomial equation [11].
- For the binary mixture of (1-ethyl-3-methyl-imidazolium diethyleneglycol monomethylethersulphate + water) the excess molar volume values increased with an increase in temperature in the water rich region (x > 0.5) whereas the values decrease in the ionic liquid rich region [4]. This is because in the water rich region, breakdown of hydrogen bonding between water molecules is greater than intermolecular hydrogen bonding between water and the anion of the ionic liquid.
- Densities and excess molar volume of binary mixtures of the ionic liquid 1butyl-3-methylimidazolium hexafluorophosphate with aromatic compounds of benzyl alcohol or benzaldehyde were measured over the whole range of compositions from (298.15 to 313.15) K. [12]. The excess molar volume values for benzaldehyde mixtures are more negative than those for the alcohol mixtures, which imply that in the benzaldehyde solutions there are stronger ion-dipole interactions and packing effects than in the benzyl alcohol solutions.

#### 2.2 Imidazolium and Pyridinium substituent alkyl chain length

[RMIM]<sup>+</sup> and [RPy]<sup>+</sup> salts with asymmetric *N*-substitution have no rotation or reflection symmetry operations. Alteration in the alkyl chain such as octyl- or butyl- substitution on one of the rings does not change the symmetry of the cation. However, manipulation of the alkyl chain can produce major changes in the melting points, and also in the tendency of the ILs to form glasses rather than crystalline solids on cooling due to the changing on the efficiency of ion packing [13].

The following discussion concerns the thermal liquidus ranges available in different pyridinium and imidazolium ILs, as functions of cation and anion structure and composition such as melting points and sizes of cations and anions as well the effect of size on the melting points.

#### 2.3 Determination of Liquidus Ranges

The liquidus rages exhibited by pyridinium and imidazolium ILs can be much greater that those found in common molecular solvents. Dichloromethane, for example, has liquidus range of -95 to 40 °C.

#### 2.3.1 Melting points

The thermal behavior of many ILs is somehow complex. For a typical IL cooling from the liquid state causes glass formation at low temperatures because cooling the liquid at low-temperature region is not usually bounded by phase diagram liquidus line, but rather is extended down to a lower temperature limit imposed by the glass transition temperature [6] since the structure of an IL directly impacts upon its properties, in particular the melting point and liquidus ranges. Thus crystallization is often not favored.

#### 2.3.1.1 Effect of Ion Sizes on Salt Melting Points

The charge, size and distribution of charge on the ions are the main factors that influence the melting points of the salts, however, within a similar series of salts small changes in the shape of ions uncharged regions can have an important influence on the melting points of the salts.

Coulombic attraction between ions which is the main force in ILs given by the following equation:

## $E_c = MZ^+ Z^- / 4 \pi \epsilon_0 r$

Where  $Z^+$  and  $Z^-$  are the ion charges, and r is the inter-ion separation.

As the size of the anion increases, the melting point of the salt decreases, reflecting the weaker Coulombic interactions in the crystal lattice.

#### 2.3.2 Anion size

As mentioned above, reduction in melting points can, simplistically, be achieved by increasing the size of anion through reduction of the Coulombic attraction contribution to the lattice energy of the crystal and increasing covalency of the ions. Generally in ionic liquids, increasing anion size results in lower melting points, as can be seen for a selection of [EMIM]X salts in the table below [6].

Anion [X]	Melting Point (°C)
Cl-	87
Br	81
Ι-	79-81
[BF <sub>4</sub> ] <sup>-</sup>	15

Table 2.2: [EMIM]X salts and melting points, illustrating anion effects

#### 2.3.3 Cation size

From synthesis and temperature dependence of physical properties of four pyridiniumbased ionic liquids (1,2-diethylpyridinium ethylsulfate, 1-methylpyridinium methylsulfate, 1,3-dimethylpyridinium methylsulfate and 2-ethyl-1-methylpyridinium methylsulfate). It was found that an increase in length and number of the cation alkyl chain means a decrease in density and an increase in refractive index and dynamic viscosity. This behavior is because an increase in length of the cation chain length means an increase in the values of molar refractions [1].

#### 2.3.4 Hydrophopicity

The degree of polarity can be varied by adapting the length of the 1-alkyl chain as in 1,3-substituted imidazolium cations. Long chain IL salts have attracted some interest due to their liquid crystalline (LC) properties. As mentioned above the anion chemistry has a large influence on the IL properties even if it has the same cation, the actual differences can be dramatic. For example, [BMIM]PF<sub>6</sub><sup>-</sup> is immiscible with water, whereas [BMIM]BF<sub>4</sub><sup>-</sup> is water soluble. [14].

#### 2.3.5 Hydrophicity:

The water content has an influence on the viscosity of the ionic liquids. Viscosity measurement indicates that ionic liquids became less viscous with increasing water content. [14].

#### 2.4 Quality Aspects of commercial IL production

Commercial producers try to make ILs in the highest quality that can be achieved at a reasonable cost. For some ILs they can guarantee purity greater than 99% for others perhaps only 95%. The following subsections attempt to comment upon common impurities in commercial IL products and their significance for their application [6].

#### 2.4.1 Color

ILs are all colorless and look almost like water. However most researchers who start IL synthesis will probably get a highly colored product at first. The chemical nature of the colored impurities in ILs is still not very clear, but it is probably a mixture of traces of compounds derived from the starting materials, oxidation products, and thermal degradation products of the starting materials. Based on this research synthesis pyridinium salts tend to form colored impurities more easily than imidazolium salts do as shown in below figures.



Figure 2.3: [BMIM]Cl color



Figure 2.4: [BPy]Cl color

#### 2.4.2 Organic starting materials and volatiles

Volatile impurities in ILs may result from solvents used in the extraction steps during the synthesis or starting materials from the alkylation reaction or even from any volatile organic compound previously dissolved in the IL. However, these impurities can easily be removed from the nonvolatile IL by simple evaporation when one considers the able time. Factors that influence the time required for the removal of all volatiles from an IL are:

- a) The amount of volatiles
- b) Their boiling points
- c) The interaction with the IL
- d) Viscosity of IL
- e) Surface tension of IL

#### 2.4.3 Halide Impurities

Halide exchange reactions may cause greater or lesser quantities of halide impurities in the final product. The choice of the best procedure to obtain complete exchange depends mainly on the nature of the IL that is being produced. Unfortunately, there is no general method to obtain a halide-free IL that can be used for all types of ILs. However, the common method is to monitor the reaction by the physical approach of Thin Layer Chromatography (TLC) to ensure whether the reaction has finished or not.

#### 2.5 Cost of Ionic Liquids

The price of ionic liquids is determined by many parameters, such as production costs. On a large-scale, the material cost should become more important and mainly determine the price of an ionic liquid. This means that the price of a large-scale commercial ionic liquid should be dictated by the price of the cation and anion source [6].

It is noteworthy that the efficiency of the recycling process for various ionic liquids varies from quite poor to very good. This scenario could be interesting from an economic point of view for truly commercial application on a large scale [6].

#### **CHAPTER 3**

### METHODOLOGY

Towards the completion of this project the following steps must be followed:

#### 1. SYNTHESIS

In order to produce thiosalicyalte ILs synthesis of halide ILs of imidazolium and pyridinium comes at the first place. An example here is taken based on the synthesis of 1-octyl-3-methylimidazolium thiosalicylate [OMIM]TS. Choline thiosalicylate IL and tetramethyl ammonium thiosalicylate IL were synthesized based on normal neutralization procedure (thiosalicylate acid with choline hydroxide) and (tetra-methyl ammonium hydroxide with thiosalicylate acid). Both reactions took place in closed round bottom flasks under ambient conditions (25 °C and 1 atm) and stirring for 24 hours where produced water (by product) was removed by evaporation before the final drying under vacuum at 70–80°C.

#### A. 1-methylimidazole + 1-Bromooctane

Methylimidazole,, acetonitrile and bromooctane were added to a three neck round bottom flask as shown in figure 3.2. The system was flushed with nitrogen gas before reactants addition to ensure the reaction is not under ambient air [15]. The amount of reactant used is 0.2436 mol methylimidazole, 0.3654 mol bromooctane. The reactants were stirred in the round bottom flask at 80 °C and 185 rpm for 96 hours.



Figure 3.1: Experimental Set-up for synthesis of the ionic liquids

In order to ensure the reaction is completed Thin Layer Chromatography (TLC) test is always used during ILs synthesis as physical procedure to monitor the reaction yield before shifting the product to next stage. The test was conducted during [OMIM]Br synthesis, small amount (2 drops) of the starting materials as well the synthesized mixture was diluted in sample bottle by acetone nitrile (stationary phase). Clean pipettes were used for each material to spot on TLC paper and then the paper is converted into covered beaker having 5-6 ml of acetonenirtile (mobile phase). After it dried visually the amount of starting material in the IL was detected by the distance calculation as follows:

 $R_f$  = distance moved by the molecule (location of the spot) / Distance moved by the mobile phase (solvent front).

Where R<sub>f</sub> is the solvent front

 $R_{f,MIM} = 5.7 \text{ cm}/8.1 = 0.703$ 

 $R_{f,Mix} = 1.2 \text{ cm} / 8.1 \text{ cm} = 0.15$ 



Figure 3.2: TLC test for [OMIM]Br

#### **B.** Purification

The main three steps involved in this step before anion exchange with sodiumthiosalicyalte are:

#### a. Extraction of residue

Residues (if any) were separated from the IL by washing with ethyl acetate three times using 20ml of ethylacetate in the separation funnel as shown in the figure below.



Figure 3.3: washing of 1-bromooctane from [OMIM]Br

#### b. Removal of acetonenitrile in the rotary evaporator

The liquid is put into the set-up with water bath temperature of 80°C for 8 hours to remove the solvents.



Figure 3.4: solvent removal in the rotary-evaporator

#### c. Drying the ILs in vacuum oven

The oven temperature was set to 70  $^{\circ}$ C for 48 hours. The obtained product is viscous yellow IL of 32.9441 g with average water content result of 7483.212 ppm or 0.75 wt% which indicates the product is highly hydropic.

### C. Anion Exchange (Thiosalicylate ionic liquids synthesis)

## C. Anion Exchange (Thiosalicylate ionic liquids synthesis)

ILs namely, 1-butyl-3-methylimidazolium thiosalicylate [BMIM]TS, 1-octyl-3methylimidazolium thiosalicylate [OMIM]TS, 1-butyl pyridinium thiosalicylate [BPy]TS, 1-octyl pyridinium thiosalicylate [OPy]TS, choline thiosalicylate and tetramethylammonium thiosalicylate have been produced using the following general procedures of ILs synthesis:

First:



Methylimidazolium Alkyl halide [RMIM]X ionic Liquid

The reaction conditions for both imidazolium ILs were conducted at 80 °C. R represents the alkyl group which is either octyl or butyl and X is Br<sup>-</sup> for 1-bromooctane or Cl- for 1-chlorobutane.

Sodium thiosalicylate was synthesized based on neutralization reaction under stirring and ambient conditions of equal molar ratios of thiosalicyalte acid and NaOH while this base is in access since it is highly hydropic.

Methylimidazolium ionic liquid metathesis with sodium thiosalicylate:



[RMIM]X sodium thiosalicylate [RMIM] thiosalicylate IL

The metathesis for all imidazolium and pyridinium ionic liquids took place at room temperature and pressure for 72 hours in distilled-water as reaction medium, since both synthesized ILs and sodium thiosalicylate are soluble in water. The water was removed each compound was removed by filtration after addition of 150 ml dichloromethane (DCM) at 60 °C. DCM was chosen because both salts are non-soluble in this solvent and the salt can be easily detected visually [16]. For pyridinium-based thiosalicylate ILs the use of methanol instead DCM led to better NACl and NaBr removal. Solvent removal was also required in order to get the new pure thiosalicylate ILs through evaporation and before drying under vacuum at 80 °C for 72 hours.



Figure 3.5: NaBr removal from [OMIM]TS

Second:



Pyridinium Alkyl halide [RPy]X ionic Liquid

The reaction conditions for both pyridinium ILs were conducted at 60 C° for 120 to 240 hours. R represents the alkyl group which is either octyl or butyl and X is Br<sup>-</sup> for 1-bromooctane or Cl- for 1-chlorobutane.

Pyridinium ionic liquid metathesis with sodium thiosalicylate



[RPy]X sodium thiosalicylate [RPy] thiosalicylate ionic Liquid

It is of importance to draw the final product full chemical structure that indicates the molecular weight of each compound which initially needed for the characterization and the thermophysical properties study of the pure ILs as well their binary mixtures. The chemical structure of each IL is shown below:



Figure 3.6: Structure of 1-butyl-3-methylimidazolium thiosalicylate [BMIM]TS (TS06)



Figure 3.7: Structure of 1-octyl-3-methylimidazolium thiosalicylate [OMIM]TS (TS01)



**Figure 3.8:** Structure of 1-octylpyridinium thiosalisylate [OPY]TS (TS02)



**3.9:** Structure of 1-butylpyridinium thiosalisylate [BPY]TS (TS03)







Figure 3.11: Structure of choline thiosalicylate (TS04)

#### 2. CHARACTERIZATION

Characterization, when used in materials science, refers to the use of external techniques to probe into the internal structure and properties of a material. Characterization can take the form of actual materials testing, or analysis, for example refractive index which is the optical analysis to show the speed of light on the substance.

Analysis techniques are used simply to magnify the specimen, to visualize its internal structure, and to gain knowledge as to the distribution of elements within the specimen and their interactions. Tests and analysis to be conducted for this research completion are:

- 1- TGA: thermogravimetric analysis study has to be investigated to check the decomposition temperature for all synthesized pure ionic liquids by heating the sample at a rate of 10 °C/min.
- 2- <sup>1</sup>HNMR: Nuclear magnetic resonance is to analyze weather ionic liquid is pure or not by viewing the protons 'hydrogen atoms' position in the spectrum and the number of these atoms through peaks' integration.
- **3- Water content:** using Karl-Fisher equipment for all pure ILs due to its high effect on the density and viscosity analysis.
- 4- CHNS: analytical analysis to measure the exact weight percentage of Carbon, Hydrogen, Nitrogen and Sulfur in each one of the six ILs.
- 5- Ion Chromotography: to measure the thiosalicylate ionic liquid halide content existence of either chloride or bromide.

- 6- DSC: Deferential Scanning Calorimetry is to examine the heat capacity or the enthalpy of the pure IL. A second scan will be performed by heating the sample up to 200 at rate of °C/min and quick cooling followed by heating at a rat of °C/min up to 300 °C.
- 7- **Refractive Index:** to measure the speed of light for the sake of molar refraction indication.

### 3. PREPERATION OF BINARY MIXTURES (IL+ Water)

Based on the following ratios, the density and viscosity of each binary mixture for the five mentioned IL accept tetra-methyl ammonium thiosalicylate will be studied. The IL was excluded from the measurements due to its solid state.

Table	3.1:	Mixing	Ratios
-------	------	--------	--------

Binary	IL	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	08	0.9	0.95
mixture												
	H <sub>2</sub> O	0.95	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.05

Table 3.2: Molecular Weight of pure IL (g/mol)

Label	TS01	TS02	TS03	TS04	MT05	TS06
MW (g/mol)	349.507	346.51	290.35	227.36	227.33	292.35

# 4. THERMOPHYSICAL AND THERMODYNAMIC PROERTIES MEASUREMENTS

Using Stabinger viscometer (SVM 3000) the pure ionic liquid and its binary mixtures dynamic viscosity and density will be measured. Acetone was used for washing the equipment before the new measurement and amost 55 mins/measurement is needed. For optical analysis, refractive index equipment will be used to measure the speed of light on the pure ionic liquids at ambient temperature.



Figure 3.12: Stabinger ANTON PAAR- (SVM 3000)- viscometer

# CHAPTER 4 RESULTS AND DISCUSSION

# 4.1 <sup>1</sup>HNMR:

For the five listed proton NMR results below the experimental outcomes were already compared with the predicted analysis on ACD LAB –  $H^1$ NMR software to ensure the hydrogen atoms position in each of the IL in the same spectrum with prediction analysis or in an acceptable chemical shift. And the number of these atoms matches with the prediction value based on the peaks integration of the ionic liquid.



Figure 4.1: Choline thiosalicylate (TS04) <sup>1</sup>HNMR



Figure 4.2: 1-octyl pyridinium thiosalicylate (TS01) <sup>1</sup>HNMR



Figure 4.3: 1-octyl-3-methylimidazolium thiosalicylate (TS02) <sup>1</sup>HNMR


Figure 4.4: 1-butyl-3-methylimidazolium thiosalicylate (TS06)<sup>1</sup>HNMR



Figure 4.5: tetra-methyl ammonium thiosalicylatev (MT05) <sup>1</sup>HNMR

#### 2. Density and Viscosity:

The comparison first was done based on the pure ionic liquids which are Room Temperature Ionic Liquids: choline thiosalicylate (TS04), 1-octyl-3-methylimidazolium thiosalicylate (TS01) and 1-octylpyridinium thiosalicylate (TS02). As ionic liquids viscosity is a major concern in green chemistry; its concern was derived here based on the RTILs and it is observed that only long chain cations (octyl) of imidazolium- and pyrdinium ILs give room temperature ionic liquids.

Obviously the figures below show the cation type effect on the viscosity. Thus TS01 has viscosity of 69559 [mPa] while TS01 and TS04 have a viscosity of 55477 [mPa] and 8566.2 [mPa] respectively. Density of these ILs has slight decrease with temperature if compared with the viscosity due to the slight increase in the volume while viscosity is highly effected with temperature due to the big change occurs on the molecular and atomic attraction force as well the intermolecular arrangement.



Figure 4.6: Density of pure ILs



Figure 4.7: Viscosity of pure ILs

#### 3. Density and viscosity for binary Mixtures:

Desnsity and viscosity are not measured for 1-butyl-3-methylimidazolium thiosalicylate (TS06) and 1-butyl pyridinium thiosalicylate (TS03) pure ionic liquids, simply because they are not RTIL and hence; their melting points are above 100 °C. Therefore, the binary mixture of these ionic liquids could be measured only from (0.05 to 0.6 IL molar ratios) and (0.05 to 0.5 molar ratios) respectively. Any measurement ran above the mentioned ratios for both ILs the viscometer equipment displayed an error of (out of range).



Figure 4.8: Densities for TS03 binary mixtures



Figure 4.9: Viscosities for TS03 binary mixtures



Figure 4.10: Densities for TS06 binary mixtures



Figure 4.11: Viscosities for TS06 binary mixtures

For all ionic liquids it is realized that a great decrease will occur on the viscosity starting from 0.95 ionic liquid and onwards, although 0.95 IL with 0.05 water is about one drop of water. This is due to the following factors:

- 1- Complete dilution (Likes dissolved likes)
- 2- Decrease on the atomic force attraction (rearrangement of atoms in the molecules as well bonds rearrangement between molecules which is known as intermolecular forces).
- 3- in the water rich region, breakdown of hydrogen bonding between water molecules is greater than intermolecular hydrogen bonding between water and the anion of the ionic liquid.
- 4- Perfect mixing and hydropicity behavior of these ionic liquids.



Figure 4.12: Densities for TS01 binary mixtures



Figure 4.13: viscosities for TS01 binary mixtures



Figure 4.14: Densities for TS04 binary mixtures



Figure 4.15: Viscosities for TS04 binary mixtures



Figure 4.16: Densities for TS02 binary mixtures



Figure 4.17: Viscosities for TS02 binary mixtures

#### 4. TGA results:

Thermal analysis was conducted to identify the decomposition temperature of the pure ionic liquids. The results differences are mainly based on cation effect, from the figure below it is clear that the longer cation chain length of octyl in TS01 and TS02 ILs showed less decomposition temperature compared to butyl-cations as in TS06 and TS03 ILs because when any organic compound is exposed to high temperature longer chain has the potential to degrade and leave the compound before shorter chain does [6]. tetramethyl ammonium thiosalicylate IL has the highest decomposition temperature of 227.85 °C since it is solid by nature and this shows it has high thermal stability while choline thiosalicylate exhibits the lowest decomposition temperature of 200 °C since it is room temperature ionic liquid with longer cation chain length at one bond and among the rest of ionic liquids it has the lowest thermal stability.



The thermal stability can be compared for all ionic liquids as follows: Choline TS < [OPy]TS< [OMIM]TS < [BMIM]TS < [BPy]TS <[TMA]TS

#### 4.5 DSC results:

The result of this experiment is a curve of heat flux versus temperature. This curve can be used to calculate heat of enthalpy as shown below by integrating the peak corresponding to a given transition.

Glass transition temperature of  $T_g$  which is of importance to be determined is also calculated as peak temperature because it shows the reversible transition in amorphous materials from a hard and relatively brittle state into a molten or rubber-like state.

SAMPLE	PEAK T(°C) or Tg	DELTA H (J/g)
[BMIM]Ts	201.48	0.2086
[OMIM]Ts	55.94	0.0269
[OPy]Ts	214.66	0.1003
[BPy]Ts	185.20	0.1420
Choline Ts	154.08	0.229

Table 4.1: DSC results

#### 4.6 Refractive Index (nD):

The refractive index can afford useful information about the behavior of the molecules in the solution and the forces between these molecules using its relation with the electronic polarizability of the molecule (this relation can be expressed in terms of molar polarizability or molar refraction) which is known as Lorenz-Lorentz equation [5].

The Lorenz-Lorentz equation can provide important information concerning the

performance of a liquid as a solvent media since it represents the effect of the dispersion forces in the cohesion of the liquid The molar refractions are often considered as a measure of the hard-core molecular volumes, consequently was used to calculate the molar free volume (unoccupied part of the molar volume of a substance) of the present room temperature ionic liquids (RTILs).

the results were taken based on automatic digital refractometer which managed to get the results only at room temperature for [OMIM]TS and [OPy]TS as 1.4384 1.5088 respectively and therefore the molar refraction affect has not been studied for both of ionic liquids.

#### 4.7 Water content:

Karl-Fisher titration technique was used for water content determination of below ionic liquids. The results showed these materials are hydrophic and sensitive to moisture even though all RTILs were dried for 72 hours before the measurement.

- [OPy]Ts: 7.46 wt% or 74561.15 ppm
- Choline Ts: 2.97 wt% or 29704.9 ppm
- [OMIM]Ts: 4.53 wt% or 45292.67 ppm

#### 4.8 Halide content:

Ion chromatography was used in order to determine the halide content of RTILs. the procedure was to dilute 0.1 g of the ionic liquid in 10 ml deionized water since it is pure of mineral salts. In this measurement the bromide content was the target in both ionic liquids.

- [OMIM]Ts: 0.194 ppm
- [OPy]Ts : 0.0006 ppm

#### 4.9 Thermodynamic, volumetric and surface properties of ILs:

The thermal expansion coefficients (The thermal expansion coefficients ( $\alpha$ ), also known as volume expansivity) as a function of temperature at atmospheric pressure was estimated using the following equations [15]:

$$\rho / (g.cm^{-1}) = A_0 + A_1 T$$

$$\alpha_p / (K^{-1}) = -(1/\rho) (\partial \rho / \partial T)_p$$

$$= -(A_1) / (A_0 + A_1 T)$$
(2)

Where,  $\rho$  is density; *T* is the absolute temperature;  $A_0$  and  $A_1$  are fitting parameters and  $\alpha$  is thermal expansion coefficient in K<sup>-1</sup>. The fitting parameters are estimated using the method of least squares. The estimated thermal expansion coefficient values are reported in Table 4.1. These values indicate that an increase in the alkyl chain length of the cation tends to decrease the thermal expansion coefficient. The ionic liquids in the present work show weak temperature dependence for the thermal expansion coefficient,  $\alpha_p = (4.62 \times 10^{-4} \text{ to } 5.84 \times 10^{-4}) \text{ K}^{-1}$  in the present studied temperature range (293.15 to 353.15) K. These range of values are high compare with those reported for imidazolium-, pyridinium-, phosphonium- and ammonium – based ILs ( $\alpha_p = (5.0 \times 10^{-4} \text{ to } 5.8 \times 10^{-4}) \text{ K}^{-1}$ ).

**Table 4.2:** Thermal expansion coefficients  $\alpha_p$  as a function of temperature.

<b>T</b> (K)	10 <sup>4</sup> α <sub>p</sub> /(K	-1)	
	TS 01	TS 02	TS 04
293.15	5.69	5.39	4.62
298.15	5.70	5.40	4.63
303.15	5.72	5.41	4.65
308.15	5.74	5.43	4.66
313.15	5.75	5.44	4.67
318.15	5.77	5.46	4.68
323.15	5.79	5.47	4.69
328.15	5.80	5.49	4.70
333.15	5.82	5.50	4.71
338.15	5.84	5.52	4.72
343.15	5.85	5.53	4.73
348.15	5.87	5.55	4.74
353.15	5.89	5.57	4.76

The experimental density values were used to calculate molecular volumes  $(V_m)$  at 298.15 K and atmospheric pressure using the following equation [14]:

$$V_m = M/(N_A \rho) \tag{3}$$

where *M* is the molecular weight in g.mol<sup>-1</sup>,  $N_A$  is the Avogadro's number in mol<sup>-1</sup>,  $\rho$  is the density in g.cm<sup>-3</sup> and  $V_m$  is molecular volume in cm<sup>3</sup>. The results are shown in Table 2.

The standard entropy for ionic liquids using molecular volume was estimated as suggested by Glasser and Jenkins [17,18].

$$S^{0} = 1246.5(V_{m}) + 29.5 \tag{4}$$

where  $S^0$  is the standard entropy at 298.15 K in J,K<sup>-1</sup>.mol<sup>-1</sup> and  $V_m$  is the molecular volume in nm<sup>3</sup>. The standard entropies for the nitrile-functionalized ILs were estimated using equation (4) and the results are presented in Table 4.2. The results show a good agreement with the other ILs; for [C<sub>n</sub>Mim]alanine and [C<sub>n</sub>Mim]glycine; where n=2-6, the standard entropy ranges from 396.9 to 535.8 J.K<sup>-1</sup>.mol<sup>-1</sup> and from 360.2 to 498.8 J.K<sup>-1</sup>.mol<sup>-1</sup> respectively [17,18].

Crystal energy of IL is the surface excess energy which is reliant on interaction energy between ions. The low crystal energy is the underlying reason for forming the IL at room temperature. Crystal energies of ionic liquids were estimated according to Glasser theory [17] using the following equation:

$$U_{POT} = 1981.2(\rho/M)^{1/3} + 103.8$$
<sup>(5)</sup>

where  $U_{POT}$  is the crystal energy in kJ.mol<sup>-1</sup>. The results presented in Table 4.2 show that crystal energies of ILs are much less than that of inorganic fused salts; the minimal crystal energy (U<sub>POT</sub>) among alkali chlorides is 602.5 kJ.mol<sup>-</sup>. The results indicate that the crystal energies for the nitrile – functionalized ILs are in good agreements with that

of the other ILs (for  $[C_nMim]$ alanine and  $[C_nMim]$ glycine (where n=2-6), ranging from 421 to 456 and 429 to 469 kJ.mol<sup>-1</sup> respectively [17].

Properties and a second	TS 01	TS 02	TS 04
Crystal energy (Upor/kJ.mol <sup>-1</sup> )	399.6	396.4	450.2
Molecular volume ( $V_m$ /cm <sup>3</sup> )	5.02E-22	5.18E-22	3.12E-22
Standard entropy(S <sup>0</sup> / J.K <sup>-1</sup> .mol <sup>-1</sup> )	654.8	675.7	419.0

Table 4.3: Crystal energy, molecular volume and standard entropy at 298.15 K

### **CHAPTER 5**

# **CONCLUSIONS AND RECOMMENDATIONS**

In this project the synthesis of the six novel ionic liquids was achieved and that has been shown in all <sup>1</sup>HNMR results. There was a tremendous reduction of viscosity by adding small amount of water, this is because in the water rich region, breakdown of hydrogen bonding between water molecules is greater than intermolecular hydrogen bonding between water and the anion of the ionic liquid.

Chain-length of the IL's cation has great effect on the viscosity and melting point. Meaning [OMIM]TS and [OPy]TS gave RTIL while [BMIM]TS and [BPy]TS gave non RTIL.

Effect of molar ratio on viscosity of these Ionic Liquids is greater than temperature. This proves that for industrial applications the use of binary mixtures is better than heating the pure ionic liquids and this will contribute on saving the operating cost.

As a finding on the study an effective salt removal procedure for imidazolium ILs was achieved by using dichloromethane (DCM) followed by acetone while for pyridinium ILs methanol followed by acetone was favorable and evidently heating must be involved in both cases to enhance the salt removal.

It is recommended the use of these green solvents or their binary mixtures for demetalization application such as removal of mercury or any other heavy metal from aqueous solution will be useful for the industrial application such as waste water treatment.

The binary systems may also be applied for desulfurization purposes in crude oil by altering the thiosalicylate anion chain length to be hydrophobic but dissolves in crude oil.

Among best five final year projects in chemical engineering department this project won a silver medal during Engineering Design Exhibition (EDX-26).

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# 1. Mixing ratios calculations:

8

		Frank and the second second						
- IL	$-\Pi$	wt(g)	factor	water		Wt(g)	IL(wt)	water(wt
290.35	0.05	14.5175	10	18	0.95	17.1	1.45175	1.71
290.35	0.1	29.035	15	18	0.9	16.2	1.9357	1.0800
290.35	0.2	58.07	25	18	0.8	14.4	2.3228	0.5760
290.35	0.3	87.105	35	18	0.7	12.6	2.4887	0.3600
290.35	0.4	116.14	42	18	0.6	10.8	2.7652	0.2571
290.35	0.5	145,175	52.63	18	0.5	9	2.7584	0.1710
290.35	0.6	174.21	41	18	0.4	7.2	4.2490	0.1756
290.35	0.7	203.245	46	18	0.3	5.4	4,4184	0.1174
290.35	0.8	232.28	50	18	0.2	3.6	4.6456	0.0720
290.35	0.9	261.315	55	18	0.1	1.8	4,7512	0.0327
290.35	0.95	275.832	100	18	0.05	0.9	2.7583	0.0090

					-			Norocas or south the south sector
- IL-	IL (møl%)	wt(g)	factor	water	water (mol%)	Wt(g)	IL(wt)	water(wt)
346.51	0.05	17.3255	10.39	18	0.95	17.1	1.667517	1.645813
346.51	0.1	34.651	23.1	18	0.9	16.2	1.5000	0.7013
346.51	0.2	69.302	45.366	18	0.8	14.4	1.5276	0.3174
346.51	0.3	103.953	62.774	18	0.7	12.6	1.6560	0.2007
346.51	0.4	138.604	72.83	18	0.6	10.8	1.9031	0.1483
346.51	0.5	173.255	78.595	18	0.5	9	2.2044	0.1145
346.51	0.6	207.906	100	18	0.4	7.2	2.0791	0.0720
346.51	0.7	242.557	110	18		5,4	2.2051	0.0491
346.51	0.8	277.208	130	18	0.2	3.6	2,1324	0.0277
346.51	0.9	311.859	120	18	0.1	1.8	2.5988	0.0150
346.51	0.95	329.1845	124.48	18	0.05	0.9	2.6445	0.0072

dina ta							•	
IL.	IL (mol%)	wt(g)	factor	water	water (mol%)	Wt(g)	IL(wt)	water(wt)
349,507	0.05	17.47535	15	18	0.95	17.1	1.1650	1.1400
349.507	0.1	34.9507	28	18	0.9	16.2	1.2482	0.5786
349.507	0.2	69.9014	35	18	0.8	14.4	1.9972	0.4114
349.507	0.3	104.8521	50	18	0.7	12.6	2.0970	0.2520
349.507	0.4	139.8028	83.85	18	0.6	10.8	1.6673	0,1288
349.507	0.5	174.7535	87,302	18	0.5	9	2.0017	0,1031
349.507	0.6	209,7042	99.86	18	0.4	7.2	2.1000	0.0721
349.507	0.7	244.6549	105.23	18	0.3	5.4	2.3250	0.0513
349.507	0.8	279.6056	140	18	0.2	3.6	1.9972	0.0257
349.507	0.9	314.5563	155	18	0.1	1.8	2.0294	0.0116
349.507	0.95	332.0317	160	18	0.05	0.9	2.0752	0.0056

n tea Securation								
IL.	正 (mol%)	wt(g)	factor	water	water (mol%)	Wi(g)	IL(wt)	water(wt)
293.35	0.05	14.6675	12.9	18	0.95	17.1	1.137016	1.325581
293.35	0.1	29.335	15	18	0.9	16.2	1.9557	1.0800
293.35	0.2	58.67	27	18	0.8	14.4	2,1730	0.5333
293.35	0.3	88.005	35	18	0.7	12.6	2.5144	0,3600
293.35	0.4	117.34	48	18	0.6	10.8	2.4446	0.2250
293.35	0.5	146.675	57	18	0.5	9	2.5732	0.1579
293.35	0.6	176.01	80	18	0.4	7.2	2.2001	0.0900
293.35	0.7	205.345	80	18	0.3	5.4	2.5668	0.0675
293.35	0.8	234.68	90	18	0.2	3.6	2.6076	0.0400
293.35	0.9	264.015	100	18	0.1	1.8	2.6402	0.0180
293.35	0.95	278.6825	110	18	0.05	0.9	2.5335	0.0082

• - IL	L (mol%)	wt(g)	factor	water	water (mol%)	Wt(g)	IL(wt)	water(wt)
227,36	0.05	11.368	the grand from the second	18	0.95	17.1	1.624	2.442857
227.36	0.1	22.736	10	18	0.9	16.2	2.2736	1.6200
227.36	0.2	45.472	16	18	0.8	14.4	2.8420	0.9000
227.36	0.3	68.208	24	18	0.7	12.6	2.8420	0.5250
227.36	0.4	90.944	31	18	0.6	10.8	2.9337	0.3484
227.36	0.5	113.68	37	18	0.5	· 9	3.0724	0.2432
227.36	0.6	136.416	44	18	0.4	7.2	3.1004	0.1636
227.36	0.7	159.152	50	18	0.3	5.4	3.1830	0.1080
227.36	0.8	181.888	57	18	0.2	3.6	3.1910	0.0632
227.36	0.9	204.624	<b>55</b> 📀	18	0.1	1.8	3.7204	0.0327
227.36	0.95	215.992	55	18	0.05	0.9	3.9271	0.0164

# 2. Data of density and viscosity for pure ionic liquids and its binary mixtures:

# Figure1: TS04 at 20°C

fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.2114	69559	57422
0.95	1.2009	5238.2	4362
0.9	1.1984	2433.9	2030.9
0.8	1.1982	1907.1	1591.6
0.7	1.1969	1326.5	1108.3
0.6	1.1948	733.69	614.06
0.5	1.1902	345.95	290.66
0.4	1.1833	174.26	147.26
0.3	1.1748	77.672	66.117
0.2	1.1624	32.042	27.566
0.1	1.1268	8.9927	7.9811
0.05	1.0852	3.5282	3.2512

#### Figure2: TS04 at 25°C

TL mole	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.2084	36106	29878
0.95	1.1979	3299.6	2754.5
0.9	1.1953	1465.1	1225.7
0.8	1.1951	1215.7	1017.3
0.7	1.1937	865.24	724.82
0.6	1.1915	494.84	415.3
0.5	1.1869	242.42	204.24
0.4	1.1819	126.51	107.04
0.3	1.1714	58.536	49.971
0.2	1.159	25.113	21.668
0.1	1.1235	7.4794	6.6572
0.05	1.0824	3.0367	2.8056

Figure3: TS04 at 30°C

IL mole	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.2056	19722	16358
0.95	1.1945	2099.4	1757.6
0.9	1.1923	954.48	800.53
0.8	1.1921	806.43	676.49
0.7	1.1906	584.56	490.96
0.6	1.1884	344.16	289.59
0.5	1.1838	174.55	147.44
0.4	1.1788	93.987	79.73
0.3	1,1682	45.037	38.553
0.2	0.2 1.1557		17.345
0.1	1,1203	6.2772	5.603
0.05	1.0796	2.634	2.4397

Figure 4: TS04 at 35°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.2028	11269	9369.5
0.95	1.1915	1312.9	1101.9
0.9	1.1892	643.62	541.22
0.8	1.189	551.52	463.86
0.7	1.1875	406.51	342.33
0.6	1.1854	245.97	207.5
0.5	1.1808	128.88	109.14
0.4	1.1757	71.415	60.74
0.3	1.165	35.339	30.335
0.2	1.1524	16.261	14.11
0.1	1.1172	5.3303	4.7713
0.05	1.0768	2.3054	2.141

Figure5: TS04 at 40°C

IL mole	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1999	6693.4	5578.1
0.95	1.1886	880.65	740.93
0.9	1.186	447.83	377.58
0.8	1,1858	387.97	327.16
0.7	1.1844	290.48	245.25
0.6	1.1824	180.29	152.48
0.5	1.1778	97.257	82.574
0.4	1.1726	55.246	47.113
0.3	1.1618	28.12	24.204
0.2	1.1491	13.346	11.614
0.1	1.1139	4.5159	4.0539
0.05	1.0739	2.0237	1.8845

Figure	6:	<b>TS04</b>	at	45°C	1
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IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1971	4131.1	3450.8
0.95	1.1856	607.87	512.72
0.9	1.183	320.04	270.52
0.8	1.1829	279.98	236.69
0.7	1.1815	212.73	180.06
0.6	1.1795	135.12	114.56
0.5	1.1748	75.01	63.85
0.4	1.1695	43.682	37.351
0.3	1.1585	22.923	19.786
0.2	1.1458	11.171	9.7496
0.1	1.1107	3.9665	3.5711
0.05	1.0709	1.8108	1.6909

Figure 7: TS04 at 50°C

ole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1943	2648.5	2217.5
0.95	1.1826	430.69	364.19
0.9	1.1801	234.28	198.52
0.8	1.1799	206.76	175.24
0.7	1.1785	159.25	135.13
0.6	1.1765	103.4	87.883
0.5	1.1718	58.894	50.261
0.4	1.1664	35.076	30.072
0.3	1.1554	18.878	16.34
0.2	1.1425	9.4361	8.2589
0.1	1.1074	3.4686	3.1321
0.05	1.0678	1.621	1.5181

# Figure 8: TS04 at 55°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1916	1753.6	1471.7
0.95	1.1797	312.79	265.14
0.9	1.1772	175.86	149.38
0.8	1.177	156.03	132.56
0.7	1.1757	121.66	103.48
0.6	1.1736	80.605	68.679
0.5	1.1688	47.03	40.239
0.4	1,1633	28.62	24.603
0.3	1.1521	15.782	13.698
0.2	1.1392	8.0664	7.0805
0.1	1.1041	3.0608	2.7722
0.05	1.0647	1.4605	1.3717

Figure 9: TS04 at 60°C

L mole	Density	Viscosity (mPa)	Kinetic
1 action =	1.1888	1193.5	1003.9
0.95	1.1769	232.29	197.38
0.9	1.1744	134.61	114.62
0.8	1.1742	120.23	102.39
0.7	1.1728	94,928	80.94
0.6	1.1708	63.677	54.389
0.5	1.1658	38.202	32.769
0.4	1.1602	23.452	20.214
0.3	1.1489	13.343	11.613
0.2	1.136	6.9788	6.1435
0.1	1.1007	2.7306	2.4807
0.05	1.0615	1.3351	1.2578

# Figure 10: TS04 at 65°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.186	830.95	700.61
0.95	1.1743	173.5	147.74
0.9	1.1716	104.8	89.45
0.8	1.1713	93.779	80.062
0.7	1.1699	75.135	64.221
0.6	1.1678	51.146	43.795
0.5	1.1628	31.398	27.004
0.4	1.1571	19.573	16.915
0.3	1.1457	11.381	9.9333
-0.2	1.1326	6.0721	5.3611
0.1	1.0973	2.4355	2.2194
0.05	1.0582	1.218	1.151

Figure 11: TS04 at 70°C

IL mole	Density (g/om 3)	Viscosity	Kinetic
1 IFACTION	1.1832	592.74	500.95
0.95	1.1707	134.93	115.25
.0.9	1.1688	82.983	71.001
0.8	1.1685	74.575	63.822
0.7	1.1671	60.403	51.757
0.6	1.1649	41.77	35.857
0.5	1.1597	26.139	22.539
0.4	1.1539	16.564	14.355
0.3	1.1425	9.8064	8.5834
0.2	1.1293	5.3272	4.7174
0.1	1.0939	2.1959	2.0074
0.05	1.0549	1.1295	1.0707

# Figure 12: TS04 at 75°C

		C.A	
IL mole	Density	Viscosity	Kinetic
гасион	(g/ciiis)	(mr a)	23 HI III 275 [12]
1	1.1804	437.84	370.92
0.95	1.1686	107.43	<b>91.93</b> 1
0.9	1.1659	66.704	57.211
0.8	1.1656	60.229	51.67
0.7	1.1642	49.243	42.298
0.6	1.162	34.865	30.004
0.5	1.1567	22.012	19.029
0.4	1.1509	14.334	12.455
0.3	1,1393	8.5255	7.4834
0.2	1.1259	4.7106	4.1839
0.1	1.0904	1.9863	1.8216
0.05	1.0515	1.025	0.97477

Figure 13: TS04 at 80°C

IL mole	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1.0000	1.1778	325.9800	276.7700
0.9500	1.1659	85.2180	73.0910
0.9000	1.1631	54.3680	46.7430
0.8000	1.1628	49.4250	42.5050
0.7000	1.1613	40.6920	35.0390
0.6000	1.1591	29.1930	25.1860
0.5000	1.1537	18.7160	16.2220
0.4000	1.1478	12.3570	10.7660
0.3000	1.1360	7.4598	6.5665
0.2000	1.1225	4.1899	3.7325
0.1000	1.0870	1.7842	1.6415
0.0500	1.0480	0.9458	0.9026

mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1491	96215	<b>876</b> 41
0.95	1.1467	71674	62558
0.9	1.1434	22773	19878
0.8	1.1424	6873.9	6017.3
0.7	1.1399	4557.4	3974.4
0.6	1.1371	3830.2	3360.1
0.5	1.1334	1992.5	1742.7
0.4	1.1299	787.48	691.2
0.3	1.1286	136.27	120.75
0.2	1.1188	64.386	57.55
0.1	1.0959	42.223	38.529
0.05	1.0718	12.85	11.989

Figure 14: TS-01 at 20°C

Figure 15: TS-01 at 25°C

IL mole	Density	Viscosity	Kinetic 🚽
fraction	(g/em3)	(mPa)	[mm2/s]
1	1.1457	66802	59342
0.95	1.1424	25313	22157
0.9	1.1423	10995	1256
0.8	1.1401	4128.2	3624
0.7	1.1391	2823.2	2475.2
0.6	1.1367	2358	2073.3
0.5	1.1353	1245.3	1092
0.4	1.133	532.76	468.85
0.3	1.125	100.81	89.608
0.2	1.1152	49.341	44.245
0.1	1.0926	33.006	30.209
0.05	1.0688	10.44	9.7679

# Figure 16: TS-01 at 30 °C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1425	33648	29977
0.95	1.1392	13012	11422
0.9	1.1391	7299.4	6408
0.8	1.1376	2619.1	2305.5
0.7	1.1371	1787.5	1571.3
0.6	1.1366	1547	1364.5
0.5	1.1337	831.8	731.49
0.4	1.1322	371.18	327.54
0.3	1.1216	76.216	67.953
0.2	1.1118	38.469	34.601
0.1	1.0893	26.184	24.036
0.05	1.066	8.5826	8.0513

Figure 17: TS-01 at 35 °C

- IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1403	18136	16204
0.95	1.136	7520.9	6620.3
0.9	1.1359	4447	3914.8
0.8	1.1347	1717	1515.5
0.7	1.1334	1171	1032
0.6	1.1329	1043.5	922.91
0.5	1.1318	570.47	503.08
0.4	1.1255	265.46	234.87
0.3	1.1182	58.803	52,587
0.2	1.1083	30.504	27.521
0.1	1.0861	21.016	19.35
0.05	1.0629	7.1502	6.7271

Figure	18:	TS-01	at 40	°C
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IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1361	10389	9308.6
0.95	1.1329	4384.7	3870.3
0.9	1.1327	2807.1	2478.1
0.8	1.1317	1154.9	1022.1
0.7	1.1308	791.77	699.6
0.6	1.1299	726.82	644.62
0.5	1.1275	401.46	355.03
0.4	1.1253	194.41	172.47
0.3	1.1147	46.073	41.331
0.2	1.1049	24.453	22.132
0.1	1.0829	17.022	15.718
0.05	1.0598	5.9619	5.6254

Figure 19: TS-01 at 45 °C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1342	6228.4	5596
0.95	1.1298	2663.6	2357.6
0.9	1.1296	1831.8	1621.6
0.8	1.1287	799.04	709.13
0.7	1.1277	550.84	488.01
0.6	1.1244	513.65	456.82
0.5	1.1213	289.25	256.5
0.4	1.12	145.44	129.37
0.3	1.1113	36.915	33.218
0.2	1.1014	20.054	18.208
0.1	1.0797	14.118	13.076
0.05	1.0567	5.1339	4.8586

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1312	3863.4	3480.8
0.95	1.1266	1697.9	1507.1
0.9	1.1264	1231.9	1093.6
0.8	1.1258	565.73	503.48
0.7	1.1246	392.37	348.86
0.6	1.1236	373.37	332.97
0.5	1.1213	213.17	189.55
0.4	1.112	110.83	98.846
0.3	1.1079	29.933	27.018
0.2	1.0979	16.677	15.19
0.1	1.0766	11.805	10.965
0.05	1.0535	4.4129	4.1888

Figure 20: TS-01 at 50 °C

Figure 21: TS-01 at 55 °C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1268	2477.9	2238.8
0.95	1.1235	1122	998.63
0.9	1.1233	851.22	757.81
0.8	1.1229	409.74	365.69
0.7	1.1216	285.03	253.85
0.6	1.1205	277.15	247.86
0.5	1.1183	160.31	142.93
0.4	1.1172	86.031	76.927
0.3	1.1045	24.606	22.279
0.2	1.0943	13.995	12.788
0.1	1.0734	10.031	9.3458
0.05	1.0502	3.8263	3.6435

IL mole	Density	Viscosity	Kinetic
fraction	(g/cm3)	(mPa)	[mm2/s]
1	1.1237	1640.1	1486
0.95	1.1204	720.39	642.99
0.9	1.1201	602.61	538.02
0.8	1.12	302.37	270.61
0.7	1.1186	212.18	189.44
0.6	1.1173	208.6	187.06
0.5	1.1154	122.64	109.64
0.4	1.1132	67.86	60.839
0.3	1.1011	20.532	18.647
0.2	1.0988	11.806	10.823
0.1	1.0703	8.6293	8.0628
0.05	1.0469	3.3611	3.2104

Figure 22: TS-01 at 60 °C

Figure 23: TS-01 at 65 °C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1186	1117.7	1015.6
0.95	1.1172	489.24	437.93
0.9	1.1168	436.14	390.52
0.8	1.1156	227.75	204.39
0.7	1.1143	161.44	143.99
0.6	1.1121	160.14	143.99
0.5	1.1113	95.672	85.761
0.4	1.099	54.323	48.835
0.3	1.0976	17.28	15.743
0.2	1.0873	10.078	9.2692
0.1	1.067	7.4654	6.9963
0.05	1.0435	2.9559	2.8326

# Figure 24: TS-01 at 70 °C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1163	785.49	715.72
0.95	1.1144	348.75	313.04
0.9	1.1141	322.28	289.38
0.8	1.1137	174.6	157.13
0.7	1.1126	124.98	112.69
0.6	1.1112	124.36	111.59
0.5	1.1093	75.668	<b>68</b> .01
0.4	1.1071	44.093	39.747
0.3	1.0941	14.663	13.401
0.2	1.0837	8.7303	8.0558
0.1	1.0637	6.425	6.04
0.05	1.04	2.618	2.5172

Figure 25: TS-01 at 75 °C

IL-mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1143	562.34	513.87
0.95	1.1116	259.65	233.71
0.9	1.111	242.69	218.52
0.8	1.1106	135.96	122.7
0.7	1.1091	98.92	89.437
0.6	1.1081	97.473	87.686
0.5	1.1063	60.667	54.674
0.4	1.1033	36.202	32.724
0.3	1.0907	12.527	11.485
0.2	1.0802	7.578	7.0156
0.1	1.0603	5.6012	5.2827
0.05	1.0365	2.3356	2.2533
Figure 26: TS-	01 at	80	°C
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IL mole	Density (g/cm3)	Viscosity	Kinetic
1.0000	1.1112	410.9000	376.5600
0.9500	1.1089	200.9100	181.3400
0.9000	1.1079	185.9800	167.9300
0.8000	1.1075	107.4500	97.2350
0.7000	1.1066	79.3660	71.9560
0.6000	1.1032	77.5430	69.9310
0.5000	1.0872	49.3060	44.5560
0.4000	1.0766	30.0970	27.2810
0.3000	1.0568	10.8600	9.9888
0.2000	1.0500	6.6152	6.1443
0.1000	1.0329	4.9245	4.6596
0.0500	1.0300	2.0723	2.0063

Figure 27: TS-06 at 20°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2392	5990.6	5414.5
0.5	1.222	1520.5	1244.2
0.4	1.2188	686.32	563.12
0.3	1.2179	308.4	253.21
0.2	1.2051	104.36	86.598
0.1	1.1788	28.889	24.508
0.05	1.0357	3.5778	3.4545

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2357	1763.19	1617.63
0.5	1.2184	953.27	782.39
0.4	1.215	448.99	369.55
0.3	1.2141	211.3	174.04
0.2	1.2012	75.456	62.818
0.1	1.1748	22.497	19.15
0.05	1.0324	3.0946	2.9974

### Figure 28: TS-06 at 25 °C

Figure 29: TS-06 at 30°C

IL mole	Density	Viscosity	Kinetic
пасноп	(g/cms)	(mra)	2
1			
0.95	-		
0.9			
0.8			
0.7			
0.6	1.2322	831.8	731.49
0.5	1.2149	626.21	515.45
0.4	1.2114	302.38	249.62
0.3	1.2105	148.26	122.48
0.2	1.1975	56.045	46.802
0.1	1.1711	17.858	15.249
0.05	1.0294	2.666	2.59

Figure 30:	TS-06	at 35	°C
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IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2289	549.33	384.27
0.5	1.2113	426.43	352.05
0.4	1.2078	210.88	174.6
0.3	1.207	107.23	88.844
0.2	1.1938	42.69	35.759
0.1	1.1673	14.425	12.357
0.05	1.0263	2.32	2.2606

Figure 31: TS-06 at 40°C

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IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2256	448.35	402.63
0.5	1.2078	300.14	248.51
0.4	1.2044	151.66	125.92
0.3	1.2035	79.602	66.141
0.2	1.1901	33.119	27.828
0.1	1.1637	11.811	10.15
0.05	1.0231	2.0253	1.9795

Figure	32:	TS-06	at 45°C

IL mole	Density	Viscosity	Kinetic
fraction	(g/cm3)	(mPa)	[mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0,6	1.2224	281.77	248.7
0.5	1.2044	217.58	180.66
0.4	1.2009	112.03	93.286
0.3	1.2	60.748	50.625
0.2	1,1864	26.415	22.266
0.1	1.1599	10	8.501
0.05	1.0198	1.8075	1.7723

Figure 33: TS-06 at 50°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2193	236.72	212.13
0.5	1.201	161.86	134.77
0.4	1.1975	84.873	70.873
0.3	1.1965	47.249	39.491
0.2	1.1827	21.368	18.067
0.1	1.1561	8.3215	7.1977
0.05	1.0165	1.6142	1.5879

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2165	206.33	102.9
0.5	1.1977	123.25	97.406
0.4	1.1941	65.698	55.018
0.3	1.1895	30.492	25.635
0.2	1.1789	17.556	14.892
0.1	1.1524	7.1038	6.1646
0.05	1.0131	1.449	1.4302

Figure 34: TS-06 at 55°C

Figure 35: TS-06 at 60°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2137	122.64	109.64
0.5	1.1944	95.573	80.016
0.4	1.907	51.838	43.536
0.3	1.1895	30,492	25.635
0.2	1.1752	14.628	12.447
0.1	1.1486	6.1413	5.3469
0.05	1.0097	1.3118	1.2993

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2104	86.366	71.159
0.5	1.1912	75.934	63.746
0.4	1.1872	41.636	35.07
0.3	1.1861	25.083	21.148
0.2	1.1716	12.366	10.555
0.1	1.1448	5.3476	4.6713
0.05	1.0066	1.1705	1 1629

Figure 37: TS-06 at 70°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.206	65.011	55.614
0.5	1.188	61.146	51.471
0.4	1.1838	33.96	28.687
0.3	1.1827	20.66	17.468
0.2	1.1678	10.635	9.1066
0.1	1.1418	4.6775	4.0996
0.05	1.0029	1.0675	1.0644

1 igure 50. 15-00 dt 75 C	Figure	38:	TS-06	at	75	°C
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IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6	1.2034	51.783	44.72
0.5	1.1847	49.936	42.149
0.4	1.1803	28.089	23.797
0.3	1.1795	17.471	14.812
0.2	1.1642	9.145	7.8554
0.1	1.1371	4.1326	3.6342
0.05	0.999	1.0002	1.0011

Figure 39: TS-06 at 80°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1.0000			
0.9500			
0.9000			-
0.8000			
0.7000			
0.6000	1.2011	43.6630	38.0270
0.5000	1.1815	40.9460	34.6550
0.4000	1.1769	23.5310	19.9940
0.3000	1.1767	14.9430	12.6990
0.2000	1.1605	7.9374	6.8399
0.1000	1.1333	3.6718	3.2398
0.0500	0.9956	0.9072	0.9113

### Figure 40: TS-02 at 20°C

<b>IL mole</b> fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.113	55477	49847
0.95	1.1063	7965.3	7199.8
0.9	1.1046	7426.9	6723.6
0.8	1.1106	6597.3	5940.1
0.7	1.1064	5990.6	5414.5
0.6	1.1069	3506.1	3167.6
0.5	1.1036	1783.8	1616.3
0.4	1.1019	694.38	630.18
0.3	1.1021	433.64	393.47
0.2	1.0952	201.09	183.61
0.1	1.0733	47.735	44.474
0.05	1.0565	16.62	15.731

Figure 41: TS-02 at 25°C

IL mole	Density	Viscosity (mPa)	Kinetic
1	1.1099	28039	25264
0.95	1.1035	4575.6	4146.7
0.9	1.1017	4327.8	3928.3
0.8	1.1075	4017.4	3627.5
0.7	1.1036	3585.8	3249.3
0.6	1.1039	2151.6	1949.1
0.5	1.1007	1169.8	1062.8
0.4	1.0993	479.74	436.42
0.3	1.0987	307.86	280.2
0.2	1.0919	147.15	134.77
0.1	1.07	37.475	35.024
0.05	1.0541	13.418	12.729

# Figure 42: TS-02 at 30°C

IL mole	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1068	14994	13547
0.95	1.1006	2851.8	2591
0.9	1.0987	2717.8	2473.5
0.8	1.1044	2534.9	2295.3
0.7	1.1008	2307.5	2096.3
0.6	1.101	1412.8	1283.2
0.5	1.0978	795.41	724.54
0.4	1.0965	340.98	310.96
0.3	1.0955	223.1	203.65
0.2	1.0887	197	100.79
0.1	1.0669	29.59	27.735
0.05	1.0519	11.12	10.572

Figure 43: TS-02 at 35°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1038	8542.3	7739.1
0.95	1.0979	1844.7	1680.2
0.9	1.0959	1769.3	1614.5
0.8	1.1013	1646	1494.5
0.7	1.0979	1498.7	1365
0.6	1.098	957.07	871.66
0.5	1.0949	554.85	506.77
0.4	1.0937	247.76	226.54
0.3	1.0923	164.86	150.92
0.2	1.0855	83.31	76.745
0.1	1.0638	23.669	22.25
0.05	1.0498	9.2877	8.8471

Figure 44:	TS-02	at 40°C
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IL mole	Density	Viscosity	Kinetic
fraction	(g/cm3)	(mPa)	mm2/s
1	1.1007	5126.3	4657.1
0.95	1.0952	1230.5	1123.6
0.9	1.0931	1187.1	1086
0.8	1.0983	1100.2	1001.7
0.7	1.0951	1014.1	926.01
0.6	1.095	666.25	608.47
0.5	1.0919	397.09	363.66
0.4	1.0908	183.71	168.43
0.3	124.16	124.16	114
0.2	1.0823	64.305	59.415
0.1	1.0606	19.117	18.025
0.05	1.0477	7.7833	7.4289

Figure 45: TS-02 at 45°C

IL mole	Density (e/em3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.0977	3201.6	2916.6
0.95	1.0925	843.87	772.44
0.9	1.0903	818.62	750.83
0.8	1.0953	756.74	690.92
0.7	1.0922	675.61	618.6
0.6	1.0919	474.96	434.98
0.5	1.089	290.58	266.83
0.4	1.0878	138.6	127.41
0.3	1.086	95.19	87.65
0.2	1.0791	50.51	46.808
0.1	1.0574	15.765	14.909
0.05	1.0456	6.7522	6.4574

# Figure 46: TS-02 at 50°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.0947	2056.6	1 <b>878.7</b>
0.95	1.0897	593.45	544,58
0.9	1.0876	578.83	532.22
0.8	1.0923	534.16	489.04
0.7	1.0892	482.25	442.75
0.6	1.0889	346.28	318.01
0.5	1.0861	216.87	199.67
0.4	1.0848	106.33	98.023
0.3	1.0828	74.029	68.365
0.2	1.0785	40.038	37.216
0.1	1.0542	13.051	12.38
0.05	1.0435	5.8154	5.5729

Figure 47: TS-02 at 55°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.0917	1368.4	1253.4
0.95	1.0869	427.22	393.07
0.9	1.0848	417.93	385.25
0.8	1.0893	386.08	354.44
0.7	1.0863	352.18	324.21
0.6	1.0859	275.32	236.96
0.5	1.0833	164.79	152.12
0.4	1.0817	82.927	76.661
0.3	1.0797	58.487	54.172
0.2	1.0726	32.19	30.012
0.1	1.051	10.898	10.369
0.05	1.0413	5.0613	4.8604

# Figure 48: TS-02 at 60°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.0887	933.46	857.39
0.95	1.0841	314.4	290.01
0.9	1.0821	307.78	284.44
0.8	1.0864	285.22	262.55
0.7	1.0834	262.42	242.22
0.6	1.083	194.57	179.66
0.5	1.0806	127.63	118.11
0.4	1.0787	65.6	60.816
0.3	1.0765	46.869	43.539
0.2	1.0693	26.232	24.532
0.1	1.0477	9.1954	8.7765
0.05	1.0392	4.4278	4.2608

Figure 49: TS-02 at 65°C

mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.0857	651.77	600.33
0.95	1.0814	236.03	218.27
0.9	1.0793	231.88	214.85
0.8	1.0834	214.76	198.22
0.7	1,0805	199.2	184.36
0.6	1.0801	149.6	138.5
0.5	1.0778	99.881	92.67
0.4	1.0756	52.604	48.908
0.3	1.0733	38.076	35.475
0.2	1.066	21.719	20.374
0.1	1.0445	7.8527	7.5182
0.05	1.0371	3.8616	3.7236

# Figure 50: TS-02 at 70°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.0826	465.72	430.18
0.95	1.0787	1 <b>80.</b> 77	167.58
0.9	1.0766	177.33	164.71
0.8	1.0805	165.23	152.92
0.7	1.0776	153.69	142.62
0.6	1.0772	116.87	108.49
0.5	1.075	79.415	73.873
0.4	1.0725	42.717	39.831
0.3	1.0701	31.276	29.227
0.2	1.0627	18.067	17.001
0.1	1.0413	6.74600	6.4787
0.05	1.03470	3.3722	3.259

Figure 51: TS-02 at 75°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.0797	341.44	316.25
0.95	1.0761	140.45	130.52
0.9	1.074	137.97	128.46
0.8	1.0776	128.85	119.57
0.7	1.0748	120.44	112.06
0.6	1.0743	92.666	86.254
0.5	1.0721	63.967	59.664
0.4	1.0693	35.097	32,821
0.3	1.0669	25.872	24.25
0.2	1.0594	15.172	14.321
0.1	1.038	5.8368	5.6229
0.05	1.0322	2.9567	2.8646

Figure 52: TS-02 at 80°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1.0000	1.0767	255.5800	237.3700
0.9500	1.0735	110.5300	102.9600
0.9000	1.0716	109.0300	101.7400
0.8000	1.0747	101.8100	94.7390
0.7000	1.0720	95.7200	89.2950
0.6000	1.0714	74.4570	69.4910
0.5000	1.0692	52.1630	48.7860
0.4000	1.0662	29.1460	27.3350
0.3000	1.0637	21.6620	20.3650
0.2000	1.0561	12.8430	12.1610
0.1000	1.0348	5.0783	4.9074
0.0500	1.0292	2.6115	2.5375

Figure 53: TS-03 at 20°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7	·····		
0.6			
0.5	1.1998	3509.2	2924.8
0.4	1.1993	2117.3	1760.3
0.3	1.1878	481.84	405.66
0.2	1.1853	234.26	197.65
0.1	1.1477	37.56	32.725
0.05	1.0987	7.2507	6.5991

### Figure 54: TS-03 at 25°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6			
0.5	1.1964	2079.7	1738.4
0.4	1,1958	1307.6	1090.3
0.3	1.1842	326.15	275.43
0.2	1.1818	164.59	139.28
0.1	1.1441	28.898	25.259
0.05	1.0955	6.0332	5.507

Figure 55: TS-03 at 30°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6			
0.5	1.1931	1296.9	1087
0.4	1.1924	835.6	698.72
0.3	1.1807	226.04	191.44
0.2	1.1785	116.94	99.229
0.1	1.1407	22.583	19.797
0.05	1.10926	5.0625	4.6333

Figure	56:	TS-03	at	35°	C
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IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			;
0.7			
0.6			
0.5	1.1897	842.07	707.77
0.4	1.1889	554.85	465.34
0.3	1.1773	161.13	136.86
0.2	1.175	86.366	73.503
0.1	1.1377	17.854	15.693
0.05	1.0896	4.3005	3.9468

Figure 57: TS-03 at 40°C

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IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95		1.1 Martin	
0.9			
0.8			
0.7			
0.6			
0.5	1.1863	566.75	477.73
0.4	1.1853	380.91	320.41
0.3	1.1739	117.96	100.48
0.2	1.1715	65.071	55.543
0.1	1.1343	14.402	12.697
0.05	1.0865	3.6443	3.3543

# Figure 58: TS-03 at 45°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6			
0.5	1.1829	393.97	333.06
0.4	1.1819	269.49	227.34
0.3	1.1705	88.443	75.559
0.2	1.168	50.301	43.065
0.1	1.1303	11.942	10.566
0.05	1.0833	3.2029	2.9566

Figure 59: TS-03 at 50°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6			
0.5	1.1795	281.95	239.04
0.4	1.1785	195.79	165.64
0.3	1.1671	67.756	58.054
0.2	1.1645	39.258	33.713
0.1	1.1267	9.9356	8.8181
0.05	1.0801	2.8017	2.594

H. mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6			
0.5	1.1764	206.85	175.84
0.4	1.1752	145.75	123.65
0.3	1.1637	52.933	45.486
0.2	1.161	31.274	26.938
0.1	1,1232	8.3588	7.4417
0.05	1.0768	2.4704	2.2942

Figure 61: TS-03 at 60°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9	· ·		
0.8			
0.7			
0.6			
0.5	1.1732	155.1	132.2
0.4	1.1719	110.89	94.338
0.3	1.1603	42.093	36.278
0.2	1.1574	25.53	22.058
0.1	1.1196	7.0914	6.3337
0.05	1.0734	2.1961	2.0459

### Figure 62: TS-03 at 65°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6			
0.5	1.1699	118.53	101.31
0.4	1.1686	86.07	73.431
0.3	1.1569	34.027	29.412
0.2	1.1538	20.947	18.154
0.1	1.1164	6.0467	5.4163
0.05	1.0699	1.9694	1.8407

Figure 63: TS-03 at 70°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1	1.1629	9440.7	8118.2
0.95			
0.9			
0.8			
0.7			
0.6			
0.5	1.1665	92.802	79.554
0.4	1.1653	67.993	58.172
0.3	1.1535	27.923	24.2
0.2	1.1501	17.46	15.18
0.1	1.1128	5.2364	4.7075
0.05	1.0665	1.774	1.6642

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1			
0.95			
0.9			
0.8			
0.7			
0.6			
0.5	1.1631	73.419	63.123
0.4	1.162	54.724	46.952
0.3	1.15	27.923	24.208
0.2	1.1448	14.664	12.809
0.1	1,1086	na	4.1598
0.05	1.0629	1.5902	1.4962

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Figure 64: TS-03 at 75°C

Figure 65: TS-03 at 80°C

IL mole fraction	Density (g/cm3)	Viscosity (mPa)	Kinetic [mm2/s]
1.0000			
0.9500			·
0.9000			
0.8000			
0.7000			
0.6000			
0.5000	1.1596	59.0180	50.8950
0.4000	1.1587	44.5070	38.2940
0.3000	1,1466	19.4500	16.9630
0.2000	1.1426	12.6090	11.0350
0.1000	1.1049	4.0513	3.6667
0.0500	1.0592	1.4237	1.3441