

Physical Properties of Alcohol Based Deep Eutectic Solvents

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by

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ABSTRACT

The physical properties, viscosity, conductivity, surface tension and density were measured for a series of alcohol based Deep Eutectic Solvents (DES) as a function of choline chloride (ChCl) concentration. The point at which the system becomes a saturated salt solution in the diol systems is at 20 mol% ChCl, because at higher concentrations the conductivity decreases despite the increase in number of charge carrying species. The addition of ChCl to glycerol results in a decrease in the viscosity of the system by interrupting the intermolecular hydrogen bonding of the glycerol molecules, whereas the addition of ChCl to the diols results in an increase in viscosity. The mono-alcohol phenol has been shown to form a DES in a ratio of 4:1 phenol: ChCl. Stable DES's have also been formed using sugars, D-(-) fructose, D-glucose, xylitol and *meso*-erythritol.

Determination of solvent-solute interactions is key to the understanding of solvent properties in liquids therefore the Kamlet-Taft parameters α , β , π^* and $E_T(30)$ parameter were determined for a series of alcohol based DES using three solvatochromic dyes, 4-nitroaniline, N,N-dimethyl-4-nitroaniline and Reichardt's dye $E_T(30)$. It is shown that they are similar to RNH_3^+X^- , $\text{R}_2\text{NH}_2^+\text{X}^-$ and imidazolium ionic liquids. The effect of ChCl on the Kamlet-Taft parameters is not uniform across the systems and is dependant upon the hydrogen bond donor.

The solventless esterification of glycerol and lauric was carried out using ChCl with the intention of using its hydrogen bonding interaction with glycerol to behave a potential site inhibitor as to selectively form mono- or di-ester products. The work has shown that the addition of ChCl to the system, initially slows the rate of the mono-ester formation, but actually encourages the reaction to progress further towards the di-ester product, when compared to the pure glycerol system encouraging only mono-ester formation.

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CHAPTER 1

Introduction

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1. Introduction

Ionic liquids are salts that have a very low melting temperature.¹ By definition they are molten salts that are required to melt below 100 °C.^{1,2} Ambient melting requires that the melting point of the ionic liquid occur at a temperature that is not very far from the glass temperature.³ The majority of ionic liquids have melting points in the range of;⁴

$$T_g - 1.5T_g \quad (1.1)$$

Structurally, at least one of the ionic components is an organic compound, most commonly the cation.⁵ The ions in ionic liquids are both large and bulky with the cationic component tending to have a very low degree of symmetry. By carefully considering these components it is possible to prepare ionic liquids that are liquid around and below room temperature.^{1,2,5}

In recent years, a lot of interest has been generated in ionic liquids for their potential use as a solvent media. This is attributed to the unique combination of properties they possess. Firstly, they are good solvents for a wide range of both organic and inorganic materials.^{1,2,5} As a consequence, it is possible to bring unusual combinations of reagents into the same phase.^{1,5} As ionic liquids are composed mainly of poorly coordinating ions and so as a result have the potential to be highly polar^{1,2,5} yet non-coordinating solvents.¹ They are also immiscible with a large number of organic solvents, thus provide a non-aqueous, polar alternative for two-phase systems.¹ They are considered to be generally non-volatile and so have the potential to be used in high vacuum systems, although it has been reported that some ionic liquids do have significant vapour pressure.^{1,2,5-8}

1.1 History of Ionic Liquids

Ionic liquids, although have only gained much interest relatively recently, have actually been documented as early as 1914.⁹ This ionic liquid was made from [EtNH₃][NO₃], and had a melting point of 12 °C. In 1948 at the Rice Institute in Texas, the first ionic liquids containing chloroaluminate ions were developed and were used as bath solutions for electroplating aluminium.¹⁰ By the 1980's chloroaluminate melts began to be used as non-aqueous, polar solvents for the investigation of transition metal complexes.¹¹⁻¹³ This work mainly began with the study of the electrochemical aspects of

transition metal complexes and was soon followed by investigations into spectroscopic and complex chemistry.¹⁴ It was towards the end of the 1980's that ionic liquids started to be used as both a new reaction media and as catalysts. Various Friedel-Crafts reactions were carried out using acidic ionic liquids with chloroaluminate ions.¹⁵ In addition phosphonium halides melts were used to successfully perform aromatic substitution reactions.¹⁶ During the 1990's, weakly acidic chloroaluminate melts were used for the first time in transition metal catalysis. By dissolving nickel catalysts in the chloroaluminate melt, ionic catalyst solutions were formed and used for propene dimerization.¹⁷ Ethylene polymerizations using the Ziegler-Natta catalyst were carried out in the weakly acidic chloroaluminate melts.¹⁸ In 1992, the concept of ionic liquids received a substantial boost to their potential when low melting tetrafluoroborate melts were first described.¹⁹ These systems showed a significant improvement in the stability of the solvent against hydrolysis. Tetrafluoroborate melts have a much higher tolerance versus functional groups, resulting in a much larger range of potential applications, especially for transition metal catalysis.⁵ For example, the rhodium catalysed hydroformylation of olefins have been used successfully with tetrafluoroborate melts.²⁰

More recent publications show that the focus of ionic liquid research has shifted toward the design of the ionic liquid itself.²¹⁻²⁷ Systematically, both the physical and chemical properties of the ionic liquids have been investigated.²⁷⁻³⁰ Further applications as solvents and catalysts were then investigated as a result.³¹⁻⁴⁰

1.2 Common Components of Ionic Liquids

The scope for making ionic liquids is currently believed to be of the order of 10^{30} compounds. These compounds are mainly made from four groups of compounds. Four common cationic groups that have been used for making ionic liquids are shown in Figure 1.1

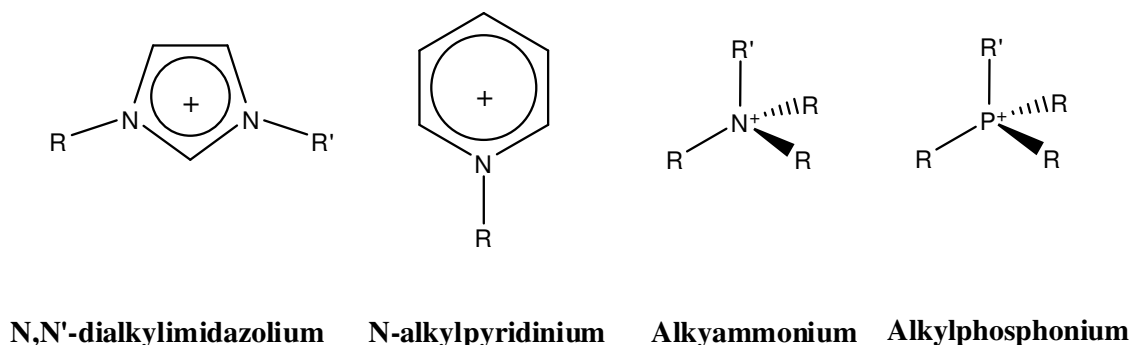


Figure 1.1: Common structures of cations used in ionic liquids

In recent years, N,N'-dialkylimidazolium has become the most widely used cationic type to make ionic liquids. Two of the most widely studied N,N'-dialkylimidazolium species are 1-butyl-3-methylimidazolium (BMIM) and 1-ethyl-3-methylimidazolium (EMIM) cations (Figure 1.2).

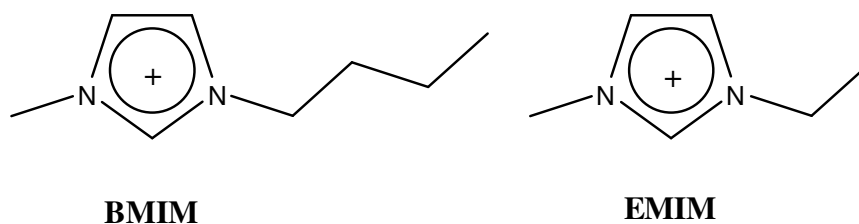


Figure 1.2: Structures of 1-butyl-3-methylimidazolium (BMIM) and 1-ethyl-3-methylimidazolium (EMIM)

The anionic components commonly used in ionic liquids tend not to be as asymmetric as the cationic components, if at all. However, like their cationic counterparts they are still bulky. Common anionic components range from inorganic anions such as $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{AlCl}_3]^-$ to simple acids such as $[\text{HNO}_3]$ which form by the neutralization of the amine by the acid. Hagiwara et al. showed that fluorohydrogenate anions can be used to form room temperature liquids with N,N'-dialkylimidazolium cations.²⁴ The anion is in the form $(\text{HF})_{2.3}\text{F}^-$ and is composed of a mixture of $(\text{HF})_2\text{F}^-$ and $(\text{HF})_3\text{F}^-$ anions. Ionic liquids containing a combination of sulfonyl and fluorine groups such as bis(trifluoromethanesulfonyl)amide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ has been shown to offer large depressions in the freezing points of systems.⁴¹

Zwitterionic liquids have generated much interest in recent times due to the component ions not being able to migrate along a potential gradient.⁴²⁻⁴⁴ They show some ionic conductivity when metal salts are added and so can be used as ion conductors.

There has also been some work that has made ionic liquids by using poly-ionic species. Whilst it would appear that ionic liquids are made up of the general formula A^+B^- , it has been shown that polycationic ionic liquids which incorporate a series of polyammonium halide salts and phosphate ions, resulting in ionic liquids with the basic formula $A^{n+}B^{n-}$ can be formed.⁴⁵

1.3 Synthesis of Ionic Liquids

The synthesis of ionic liquids usually begins with the quaternisation of an imidazole or amine, for example, to produce the cationic component.⁴⁶ The quaternisation is carried out using an alkylating agent, which is commonly a halogenoalkane. The anionic component is dependent on the form of the alkylating reagent. The alkylating agent is often a halogenoalkane. It is possible to produce salts that melt below 100 °C by this process.^{1,5} Ionic liquids that can be formed by direct quaternisation for example are [BMIM]Cl and [EMIM]CF₃SO₃ etc.⁵ It is however not always possible to form the desired anion directly by this process. An additional step is required. Two possible steps to generating the anionic component can be seen in Figure 1.3.

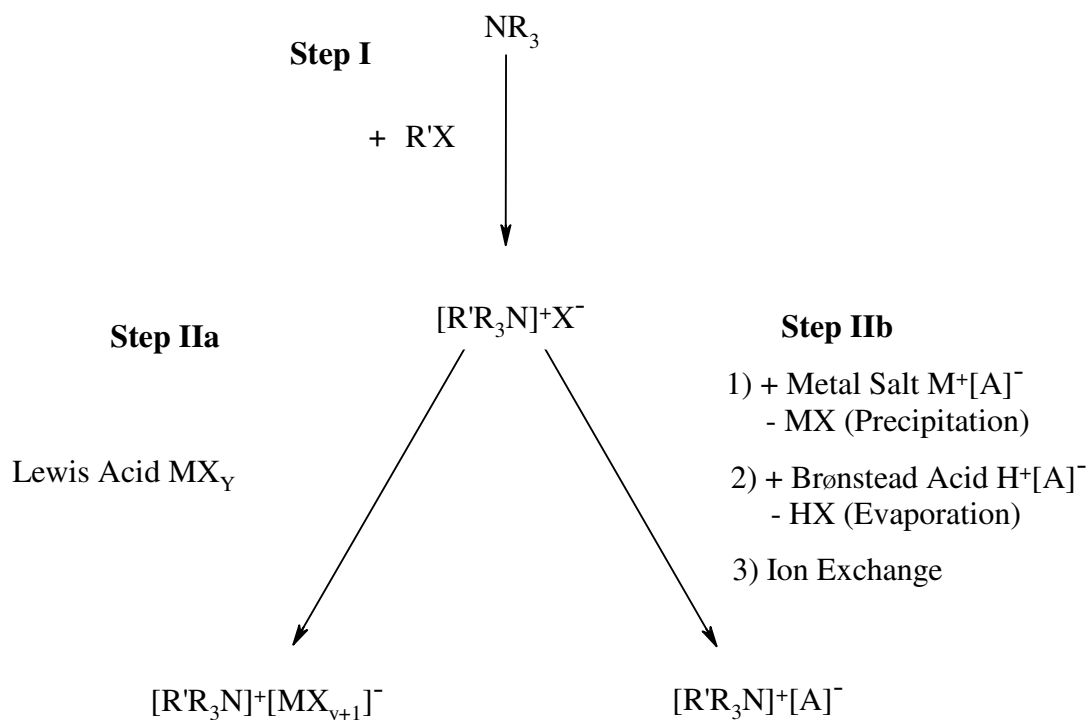
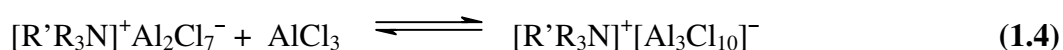


Figure 1.3: Synthetic pathway for the preparation of ionic liquids, exemplified for an ammonium salt⁵

Step I in Figure 1.3 describes the synthesis of an ammonium halide, $[\text{R}'\text{R}_3\text{N}]^+\text{X}^-$. From this point the ammonium halide can be treated with a Lewis acid MX_y , leading to an ionic liquid that is of the form $[\text{R}'\text{R}_3\text{N}]^+[\text{MX}_{y+1}]^-$ as is shown in Step IIa and equation (1.2). In this process several anion species are observed in equilibrium. The ratio of species present depends upon the ratio of the two components, in this case $[\text{R}'\text{R}_3\text{N}]^+\text{X}^-$ and MX_y . A good example of this is displayed by the chloroaluminate melts. As the ratio of chloride to AlCl_3 ratio changes, so does the anionic species. When the ratio of $\text{Cl}:\text{AlCl}_3$ the only anionic species observed is AlCl_4^- . When the molar fraction of AlCl_3 is at $x(\text{AlCl}_3) > 0.5$ the chloroaluminate anions become multi-nuclear. The various species can be seen in equations (1.3) and (1.4).⁵



Although, chloroaluminates are perhaps the best known ionic liquids that are formed by the use of a Lewis acid, ionic liquids containing SnCl_2 , CuCl , BCl_4 etc. as the Lewis acid have been reported.⁵

Step IIb in Figure 1.3 also describes the production of an ionic liquid by the addition of a metal salt $\text{M}^+[\text{A}]^-$ or by displacing it with a strong acid $\text{H}^+[\text{A}]^-$. This route will only produce one anion species unlike the Lewis acid method described by Step IIa. Anion exchange methods however tend to result in impurities from residual halide species. These halide ions may attack solute materials and so it is important to remove them. Unlike conventional solvents, purification cannot occur by distillation. Purification of the ionic liquid is achieved by the use of an anion exchange resin.⁵

1.4 Physical Properties of Ionic Liquids

By careful selection of suitable cations and anions, it is possible to vary the physical properties of ionic liquids and so systems can be tailored to meet the criteria of a specific application. This has led to them being termed 'designer solvents'.⁴⁷

1.4.1 Melting Point

Since ionic liquids are defined as molten salts that melt below 100 °C, the melting point is a defining feature of ionic liquids. The structure and chemical composition of an ionic liquid is related to its melting point. By comparing various chloride salts, the influence of the cationic component becomes obvious. Alkali metal chlorides such as NaCl and KCl have extremely high melting points (801 °C and 772 °C respectively). By replacing the cation with a suitable organic cation for example $[\text{EMIM}]^+$ or $[\text{BMIM}]^+$, the melting point decreases drastically (87 °C and 65 °C respectively).^{46,48} Factors which result in lower melting ionic liquids are cations with low symmetry, weak intermolecular bonding, for example the avoidance of hydrogen bonding^{49,50} and a good distribution of charge in the cation.⁴⁸⁻⁵¹

The cationic component is not the only deciding factor in the melting point of the system. The anion also plays a role. By keeping the cation constant, in this case $[\text{EMIM}]^+$ it can be seen that altering the size of the anion whilst maintaining the same charge alters the melting point for example $[\text{EMIM}]\text{Cl}$ has a melting point of 87 °C, but the melting point lowers when the Cl anion is replaced with for example NO_3 (38 °C)⁴⁶,

AlCl_3 (7 °C)⁵², CF_3CO_2 (-14 °C).²¹ As anion size is increased there is a further decrease in the melting point of the system. Also the presence of several anionic species have also been shown to reduce the melting point of the system.⁵² As discussed in Section 1.3, the molar ratio of Lewis acid species added to the halide salt can alter the anionic species. This mixture of anionic species results in a decrease in the melting point of the system.

1.4.2 Vapour Pressure and Thermal Stability

It has been widely reported that ionic liquids have no measurable vapour pressure. This property means that it is possible to separate the reaction mixture by distillation effectively. There is no azeotropic effect between the ionic liquid and the product.^{1,5} The thermal stability of an ionic liquid is directly related to the strength of the heteroatom-carbon and heteroatom-hydrogen bonds. Ionic liquids formed from either protonation of amines or phosphanes show significantly restricted thermal stability.⁵ Many of these denature at 80 °C in vacuo.⁵ Ionic liquids formed from alkylation of amines or phosphanes show higher thermal stability but do show a tendency to undergo retro-quaternization at temperatures nearer 150 °C. It has been shown that certain ionic liquid however show very high thermal stability for example [EMIM][BF₄] has a liquid stability range of 300 °C⁵³ and [EMIM][(CF₃SO₂)₂N] has been shown to have a liquid range of 400 °C.²¹

The non-volatility so often referred to in ionic liquid literature has been shown to be somewhat of an over assumption. Seddon *et al.* has shown that some ionic liquids are in fact distillable under vacuum and at high temperatures.⁶ It has been shown that [EMIM][(CF₃SO₂)₂N] (1-ethyl-3-methylimidazolium bistriflamide) and [DMIM][(CF₃SO₂)₂N] (1-decyl-3-methylimidazolium bistriflamide) can be distilled at a rate of 0.120 g h⁻¹ and 0.070 g h⁻¹, at 300 °C and at 0.1 mbar pressure. Negligible decomposition was seen in the distillate. It has also been reported that several distillable ionic liquids have been developed based on N,N-dialkylammonium N',N'-dialkylcarbamate melts, (dialcarbs). Dialcarbs are mixtures of CO₂ and dialkylamines.^{7,8} By mixing MeNH₂ with CO₂ in a ratio of 1.8:1, dimethylammonium dimethyl carbamate, (DIMCARB), is formed and is a stable liquid at room temperature. During the distillation process, the ionic liquid decomposes into its constituent elements at temperatures greater than 60 °C, but can be condensed and reassociated easily, with no

decomposition of the ionic liquid. This ionic liquid has been used in both electrochemical applications and organic synthetic applications.⁶⁻⁸

1.4.3 Density

The density of an ionic liquid is related to its ionic components. By taking a series of chloroaluminate melts and only changing the cation, Wilkes *et al.* showed that there is an almost linear relationship between the length of the *N*-alkyl chain on the imidazolium cation and the density was observed.⁵² The density decreased as the *N*-alkyl chain increased. As a general rule, the bulkier the cation the lower the density tends to be. Some slight structural changes allow for finer adjustments to the density. It has also been shown that the anionic effects are greater than the cationic effects. A classic example of this is to compare the [EMIM]AlBr₄ and [EMIM]AlCl₄ ionic liquids.⁵¹ The density for the bromoaluminates is much higher than that of the chloroaluminates, ranging from approximately 0.5 gcm⁻³ – 0.8 gcm⁻³.⁵⁴

1.4.4 Viscosity

The strength of van der Waals interactions and tendency to form hydrogen bonds are the major factors which contribute to the viscosity of an ionic liquid.²¹ Hydrogen bonding plays a large part in the viscosity of the chloroaluminate systems. High viscosity at low AlCl₃ molar composition due to greater hydrogen bonding between the cation and basic chloride ion.⁵² At higher AlCl₃ molar compositions the species AlCl₄⁻ and Al₂Cl₇⁻ are present, resulting in a more acidic environment. The negative charge is more widely distributed through these species which results in decreasing the strength of the hydrogen bonds. The effect of van der Waals forces on viscosity is obvious in some of the hydrophobic ionic liquids containing fluorinated anions. The ionic liquid [BMIM][CF₃SO₃] has a viscosity of 90 cP at 20 °C.²¹ By changing the triflate anion to [*n*-C₄F₉SO₃]⁻ there is a significant increase in viscosity to 373 cP. A similar trend is observed with the use of a trifluoroacetate ion. For example [BMIM][CF₃COO] has a viscosity of 73 cP, [BMIM][*n*-C₃F₇COO] has a viscosity of 182 cP. In each case the rise in viscosity is due to an increase in van der Waals interactions for the longer chain anions. There is however an exception to this observation of stronger van der Waals interactions resulting in greater viscosity. By using the

bis(trifluoromethanesulfonyl)amide $[(CF_3SO_2)_2N]^-$ anion with, for example, $[BMIM]^+$, the viscosity decreases with comparison to $[BMIM][CF_3SO_3]$. The viscosity of $[BMIM] [(CF_3SO_2)_2N]$ is 52 cP, which is 38 cP lower than $[BMIM][CF_3SO_3]$, which has a viscosity of 90 cP, despite it having greater van der Waals interactions.²¹ This result is due to the almost complete suppression of hydrogen bonding.

The structure of the cation also plays some role on the viscosity of the ionic liquid. Lower viscosities tend to be a result of low molar mass side chains that have sufficient mobility. Ionic liquids containing the $[EMIM]^+$ cation tend to have the lowest viscosities. Larger or fluorinated alkyl side chains have stronger van der Waals forces and so exhibit a greater viscosity.²¹

An increase in the temperature results in the viscosity of the ionic liquid decreasing. In some cases this can be quite a drastic effect.^{42,55} The addition of small amounts of organic cosolvents has also been shown to lower the viscosity significantly.⁵⁶⁻⁵⁸

1.4.5 Solubility Characteristics

By carefully selecting the cation and anion of an ionic liquid its solubility properties can be tuned. The effect of the cation is exemplified with the solubility of 1-octene in various tosylate melts.⁵⁹ It was showed that by increasing the non-polar character of the cation, the solubility of 1-octene increased.

The effect of the anion on solubility characteristics can be seen on the solubility of water in various $[BMIM]$ ionic liquids.²¹ Anions such as $[Br]^-$, $[CF_3COO]^-$ or $[CF_3SO_3]^-$ result in very high water solubility. When these anions are replaced by $[PF_6]^-$ or $[(CF_3SO_2)_2N]^-$, a biphasic mixture is formed with water. The water content is very low in either of these ionic liquids. In $[BMIM][(CF_3SO_2)_2N]$ the water content is only 1.4 weight percent at 20 °C.

1.4.6 Solvent Properties

The polarity of a solvent is the most common classification used to describe solvents. Polar solvents are solvents that will dissolve and stabilise dipolar or charged solutes.¹ It is generally thought that ionic liquids are polar solvents because for the most part they fulfil this criteria of polar solvents.¹ Work by Dimroth *et al.* has shown that

using a dye, such as Reichardt's dye, the measurement in the solvatochromic shifts of the absorption band give accurate information on the dipolarity, hydrogen bonding and Lewis acidity of the solvent.^{60,61} By definition, water has a value of 1.00 on the E_T^N scale that was introduced by Dimroth *et al*. The E_T^N values for a number of alkylammonium nitrate and thiocyanate salts show values in the range of 0.95-1.01.⁵⁹ Quaternary ammonium sulfonate salts have been shown to give lower values typically in the range of 0.45-0.65, which is more typical of organic solvents such as DMSO.⁶⁰ To separate the dipole-dipole polarizability effects from hydrogen-bonding effects the scales of π^* (dipolarity/polarizability), α (hydrogen-bond-donor acidity) and β (hydrogen-bond-donor basicity) were employed.⁶⁰ The greatest variation between ionic liquids was observed in the α and β scales.⁶³⁻⁶⁷ This work has led to the realisation that ionic liquids can be considered to be polar phases with the solvent properties being largely determined by the ability of the salt to act as a hydrogen-bond donor/acceptor.^{1, 63-67} The degree of the localisation of the charge on the anion also has a marked effect on its properties. This has a larger effect in the pyridinium and imidazolium based ionic liquids.

1.5 Applications of Ionic Liquids

There has been much work in recent years in the use of ionic liquids for many applications ranging from organic synthesis (Section 1.5.1) to catalysis (Section 1.5.2) to electrochemistry (Section 1.5.3) etc. There have been many discoveries that demonstrate the advantages of using ionic liquids over conventional organic solvents.

1.5.1 Organic Synthesis

1.5.1.1 Diels-Alder Reactions

Water has become a popular solvent for many Diels-Alder reactions, however some reagents are water sensitive and so the possibility of using ionic liquids as a potential polar substitute for water has been investigated. One of the first studies carried out was the reaction of methyl acrylate and cyclopentadiene in $[\text{EtNH}_3][\text{NO}_3]$.⁶⁸

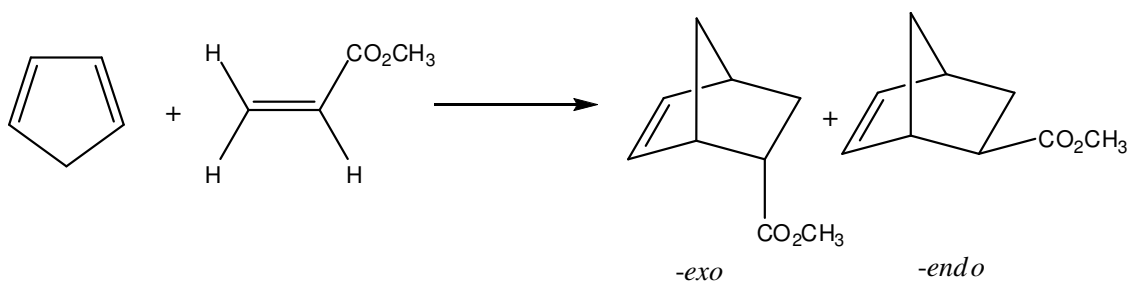


Figure 1.4: Diels-Alder formation of both *-endo* and *-exo* norborn-5-ene-2-carboxylic acid methyl ester from cyclopentadiene and methyl acrylate.¹

This reaction leads to the formation of both *endo* and *exo* products, however the ratio of these products is dependent on the solvent. This phenomenon has been attributed to the ‘internal pressure’ of the system generated by the solvophobic interactions.¹ This in turn promotes the association of the reagents in a ‘solvent cavity’ during the activation process. When this reaction is carried out in [EtNH₃][NO₃] there is a very strong preference for the *endo* product and shows enhanced reaction rates over non-polar organic solvents.⁶⁸ Other ionic liquids such as [EMIM][BF₄] and [EMIM][PF₆] etc. also show a greater preference for *endo* product and faster reaction rates than non-polar solvents, albeit somewhat weaker. Despite the reaction rates and product selectivity in ionic liquids is better than conventional non-polar organic solvents, water still shows the best rates and product selectivity. Consequently water is still a preferential solvent for many Diels-Alder reactions, however, the use of ionic liquids means that water sensitive reagents can be used for Diels-Alder reactions and the reactions will still occur with relatively fast reaction rates.

1.5.1.2 Friedel-Crafts Reactions

Chloroaluminate ionic liquids have been shown to be very useful for carrying out Friedel-Crafts reactions (Figure 1.5).^{19,69} Work by Fremantle has suggested that when carried out in certain ionic liquids, the reaction can reach 100 % conversion in as little as 30 seconds whereas in regular organic solvents it can take around 6-7 hours to achieve only 80 % conversion.⁴⁷

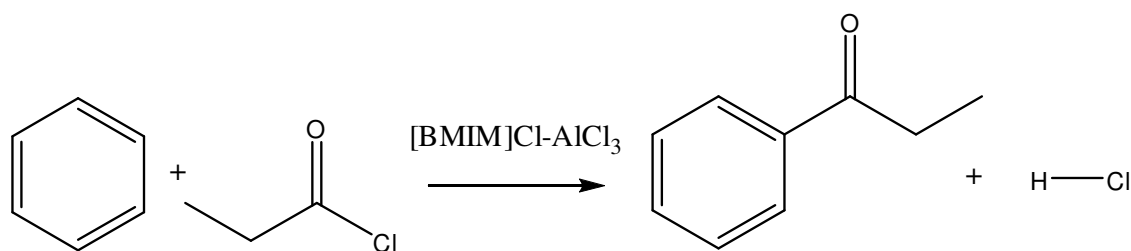


Figure 1.5: Friedel-Crafts reaction of benzene and chloroacetone to form propiophenone

The Lewis acidic AlCl₃ catalyses the reaction.¹⁹ However, AlCl₃ is very difficult to handle and its recovery from this reaction is difficult so by turning the catalyst into the solvent catalyst so recovery is easier as well as handling.^{47,69} This led to the use of chloroaluminate ionic liquids such as [BMIM]Cl-AlCl₃. Work in this area has discovered that use of chloroaluminate ionic liquids instead of a conventional organic solvent system used, increases both the yield and reaction kinetics of the reaction. Recovery of the Lewis Acid catalyst simply involves removing the products and excess reagents from the ionic liquid.

1.5.2 Transition Metal Mediated Catalysis

1.5.2.1 Hydrogenation Reactions

Ionic liquids were first used successfully in hydrogenation reaction in 1995 by de Souza⁷⁰ and Chauvin²⁰. De Souza successfully used a rhodium catalyst to hydrogenate cyclohexene in [BMIM][BF₄]. Whereas Chauvin et.al used [BMIM] ionic liquids using various anions i.e. [BF₄]⁻, [PF₆]⁻, [SbF₆]⁻ to dissolve the ‘Osborn complex’ [Rh(nbd)(PPh₃)₂][PF₆]. This ionic catalyst solution was used for the biphasic hydrogenation of 1-pentene as can be shown in Figure 1.6.

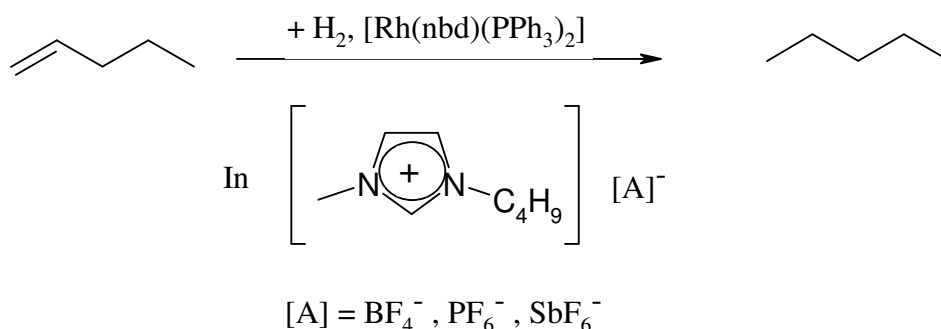


Figure 1.6: Hydrogenation reaction carried out in an ionic liquid

Results for the [BMIM][SbF₆] ionic liquid showed a reaction rate five times greater than the reaction in acetone.²⁰ The ionic catalysts were ready for reuse after the reaction and could be reused multiple times. In addition, the rate of leaching of the rhodium catalyst into the organic phase was found to be lower than the detectable limit of 0.02%. These reactions showed for the first time that it is possible to ‘immobilise’ a rhodium catalyst in a polar solution without having to use specially designed ligands.^{5,20}

1.5.2.2 Hydroformylation Reactions

Hydroformylation using ionic liquids was reported as early as 1972 by Parshall in which platinum catalysed hydroformylation of ethene in tetraethylammonium trichlorostannate melts.⁷¹ Further work carried out by Wasserscheid *et al.*, used the [BMIM]Cl/SnCl₂ ionic liquid for the hydroformylation of 1-octene as shown in Figure 1.7.⁷²

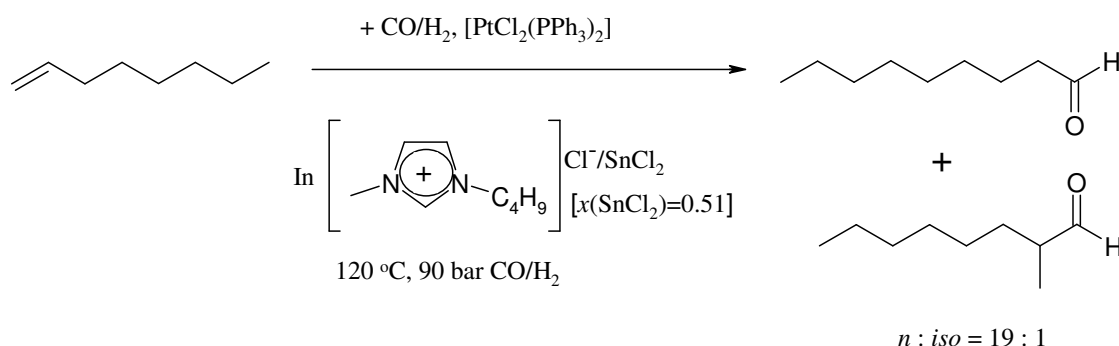


Figure 1.7: Hydroformylation reaction carried out in an ionic liquid^{5,72}

Despite the solubility of 1-octene is limited at best in the ionic catalyst phase, the activity of the platinum catalyst is very high (Turnover Frequency (TOF) = 126 h⁻¹).

Product separation is simplified due to the biphasic nature of the system. Parshall and co-worker found no leaching of the catalyst into the organic phase.⁷²

1.5.3 Electrochemical Applications

Perhaps the most widely investigated area of ionic liquids is the electrochemical applications. Ionic liquids are good electrical conductors. They can conduct between 10^{-3} and $10^{-2} \Omega^{-1} \text{cm}^{-1}$.⁷³ The conductivity of conventional organic solvents is negligible since they tend not to contain any species that are capable of carrying charge. Most ionic liquids have been shown to have a electrochemical window of 2-4 V, which is much higher than organic solvents.^{73,74} This wider electrochemical window reduces the possibility of any unwanted side reactions occurring. It is these properties that make them interesting for potential use in many electrochemical techniques.

1.5.3.1 Electrodeposition of Metals

Ionic liquids have a much larger electrochemical window than organic solvents. Certain metals can be electrochemically deposited that are otherwise inaccessible to organic solvents.^{73,74} The wider electrochemical window reduces the possibility of any side reactions, such as hydrogen evolution occurring that can affect the deposition of the metal onto the substrate,. For example it has been possible to use chloroaluminate ionic liquids to deposit aluminium onto a range of substrates by various electrochemical methods.⁷⁵⁻⁷⁷ The cluster size of the aluminium deposits on the substrate is affected by the current density, with higher current densities forming smaller crystals.⁷³ Addition of organic solvents such as dry toluene⁷⁸ or benzene⁷⁹ have shown that mirror-bright finishes can be obtained after deposition. The miscibility of the chloroaluminate based ionic liquids with organic solvents such as toluene or xylene means that the ionic liquid can be washed away from the sample after electrodeposition has taken place. The scope for electrochemically depositing metals successfully is large with the use of ionic liquids. Metals such as In,⁸⁰ Sb,⁸¹ Te,⁸² Cd,⁸³ Cu,⁸⁴ Ag,⁸⁵ Ni,⁸⁶ Co,⁸⁷ Pd,⁸⁷ Au,⁸⁹ Zn,⁹⁰ Sn,⁹¹ have all successfully been plated onto various substrates.

1.5.3.2 Electrodeposition of Semiconductors

The electrodeposition of semiconductors using ionic liquids is an area still in its infancy but early work has shown promising results.⁷³ Semiconductors such as GaAs,⁹² InSb,⁹³ ZnTe,⁹⁴ Ge,⁹⁵ have been effectively electrodeposited using ionic liquids. Because most basic studies of semiconductors have to be carried out under ultrahigh vacuum conditions, ionic liquids are a relatively ideal solution to carry these types of reaction out in. To form certain semiconductors, the kinetic barrier of formation must be overcome. In a vast majority of organic solvents this temperature is too high and the solvent will evaporate. Since ionic liquids can have very high thermal stability, the system can be heated to the temperature required for the semiconductor to form. Temperature has also been shown to affect the quality of the semiconductor deposit.⁹⁶

1.5.3.3 Applications in Electrochemical Devices

Currently, most electrochemical devices contain an aqueous, gel or polymer electrolyte.⁷⁴ The conductivity and stability determine the performance and lifetime of the device. Since most room temperature ionic liquids have high conductivities, wide potential windows and stability to moisture and air, they are potential alternatives as unreactive, stable electrolytes for the development of such devices. Electrochemical devices containing a mixture of a BF_4^- / PF_6^- based ionic liquid and a π -conjugated polymer have been reported and show high stability and lifetime.⁹⁷ No appreciable degradation was seen after 1×10^6 cycles, which is an improvement by a factor of ten over previous systems. New types of ionic liquid that use DNA as the anion have been developed and are currently being employed in electronic microelectrode arrays for biological purposes.⁹⁸ These can be controlled by choice of nucleic acid. The use of room temperature ionic liquids have been explored for the use as electrolytes to improve the conversion efficiency of dye-sensitized solar cells.⁹⁹ Double layer capacitors composed of activated carbon electrodes and either $[\text{EMIMF}][\text{HF}]_{2,3}$, or $[\text{EMIM}][\text{BF}_4]$ have been reported.¹⁰⁰ The results found that these ionic liquid based systems performance was somewhere between the currently employed aqueous and non-aqueous systems.

1.6 Deep Eutectic Solvents

In Section 1.5 the advantages of using ionic liquids for a wide range of applications has been described, however, there are two key disadvantages of using them. They can be very expensive and difficult to handle. The alternative to using these ionic liquids are Deep Eutectic Solvents (DES) which essentially are an extension of the ionic liquid model.¹⁰¹⁻¹¹³ They are basically molten salts that interact by formation of hydrogen bonds or metal halide bonds through the anion of a salt, as opposed to relying purely on electrostatic forces between anion and cation as in the case of ionic liquids. There are various types of DES's which will be explained further on.

The reason they have been termed DES's is because when the two components are added together in the correct ratio a eutectic point can be seen. The eutectic point of a mixture, point *e* in Figure 1.8, is the molar ratio of two compounds which affords the lowest melting point possible. A diagrammatic representation of this can be seen in Figure 1.8.

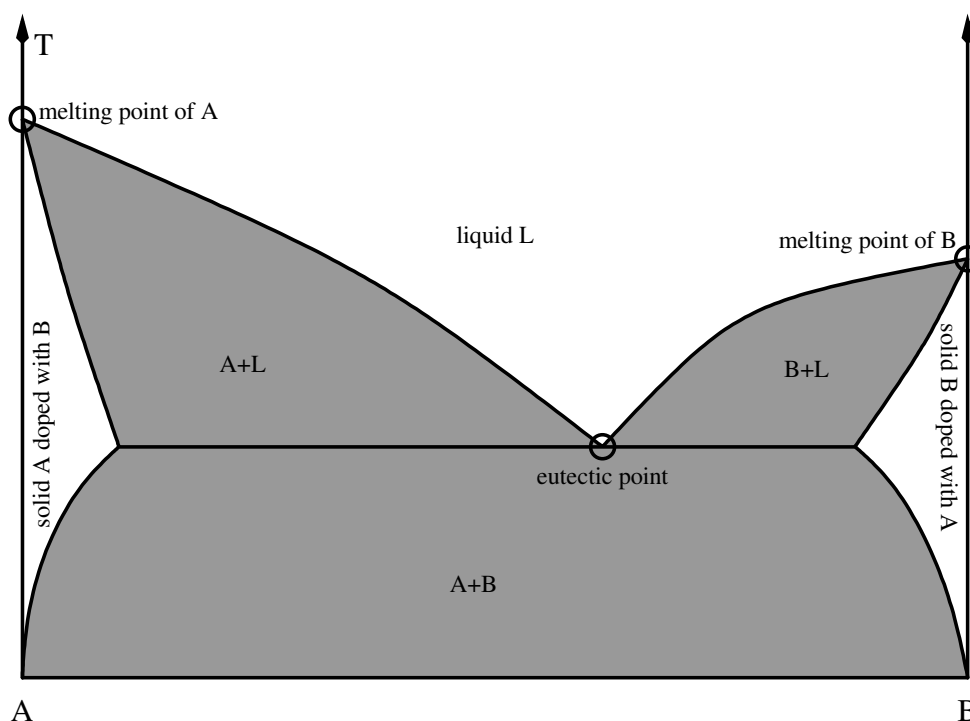


Figure 1.8: Diagrammatic representation of the theory behind eutectic mixtures

The Abbott group has been the first to pioneer this new technology and there has been a large amount of work in the area of eutectic mixtures.¹⁰¹⁻¹¹³ The work has been varied, and has focused on using metal halide salts, both hydrated and non hydrated, quaternary ammonium salts and hydrogen bond donors. The term DESs, has been coined as a means to differentiate them from true ionic liquids, and also to reflect the large depression in the freezing point of the eutectic mixture. It has been observed that the depression of the freezing point at the eutectic mixture can be as much as several hundred °C.

1.6.1 Anhydrous Metal Halide Substituted Quaternary Ammonium Salt Mixtures

This type of DES, the form of the complex anion governs the chemistry of these ionic liquids.¹⁰¹⁻¹¹⁴ The scope of this type of DES is quite large. Some of the most investigated systems are contain ZnCl_2 , SnCl_2 and FeCl_3 all with a variety of quaternary ammonium salts. The metal halides, SnCl_2 , ZnCl_2 , and FeCl_3 , when mixed with choline chloride (ChCl) in a 1:2 ratio, all form materials that have freezing points below 100 °C. This is very in keeping with the idea of DES in that they exhibit very large depressions in freezing point. One of the interesting properties with these liquids is that despite many of them containing metal halides of the same general formula MX_n , there can be quite a difference in the eutectic composition of the system between. For example the eutectic composition of ZnCl_2 and ChCl is 2:1, whereas SnCl_2 and ChCl is at 2.5:1. This is thought to be due to form of the metal species in the system. Initially at low concentrations of ZnCl_2 , the amount of ZnCl_3^- relative to the initial ZnCl_2 concentration is high. As the molar ratio of ZnCl_2 increases past 50 %, the amount of ZnCl_3^- begins to drop in favour of formation of the larger Zn_2Cl_5^- anion. The reason this results in a eutectic composition at 2:1, is because of the nature of these anions. The ZnCl_3^- is a smaller more densely charged anion that has a stronger electrostatic interaction with the chloride ion, thus increasing the lattice energy of the system, resulting in an increase in the freezing point. Hence as the mole fraction reaches 67 %, a reduction in the freezing point is seen since there will be more larger Zn_2Cl_5^- anions than ZnCl_3^- . As the mole fraction increases above 67 % an increase in the freezing point is seen again. This is believed to be due to the increase in concentration in the much larger Zn_3Cl_7^- anion,

with the size of the anion being the contributing factor of the increase in freezing point. The reason the SnCl_2 : ChCl eutectic composition is at 2.5:1 is believed to be due to SnCl_2 being a weaker Lewis Acid than ZnCl_2 and so it requires a greater amount of SnCl_2 to push the equilibrium for the reaction $\text{SnCl}_2 + \text{SnCl}_3^- \rightleftharpoons \text{Sn}_2\text{Cl}_5^-$ to the optimum Sn_2Cl_5^- composition. This is good indication that formation of these metal halide based Deep Eutectic Solvents is down to the strength of the interaction between the constituent parts and not simply how many bonds form. From this it can be seen that despite having similar structure metal salts, each system behaves very differently and can obviously tailored for different situations, this what distinguishes them most from the hydrogen bond donor/quaternary ammonium salt systems.

1.6.2 Hydrated Metal Halide/ Substituted Quaternary Ammonium Salt Mixtures

A slight variation on the DESs described in Section 1.6.1 replaces the metal salt with a hydrated metal halide as the anionic complexing species. This general idea has lead to the formation of several useful DES that are liquid at relatively low temperatures.¹⁰¹⁻¹¹³ For example chromium (in the form of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$), has been used to form a DES with ChCl . It is not possible to form this liquid with the non hydrated version of CrCl_3 , even if anhydrous CrCl_3 is added with 6 molar equivalents of H_2O . This indicates that the coordination sphere of water molecules has a large effect on coordination chemistry around the chromium centre. This would also suggest that this liquid is not just a concentrated aqueous solution and is in fact ionic liquid like. These liquids much simpler to make than conventional metal containing ionic liquid methods. Because they are hydrated metals they are water and air sensitive as well as being much cheaper. The low cost enables their use in large-scale industrial applications. Again these are not truly ionic liquids and hence come under the DES bracket. This is because the system is not made up of one anion and one cationic species that do not fully interact due to the steric bulks of one another. These ionic liquids are slightly different from conventional ionic liquids in that they do not purely interact via ionic interactions but in these cases they interact through the formation of a bond between the anion attached to the quaternary ammonium salt and the metal salt.

1.6.3 Deep Eutectic Solvents Made From Hydrogen Bond Donor and Quaternary Ammonium Salt Mixtures

One of the biggest areas in the DES field is the use of a quaternary ammonium salt and complexing it with a hydrogen bond donor.^{105,109} The various hydrogen bond donors that have been looked at involve polycarboxylic acids, polyamides, polyalcohols. These liquids are easy to prepare in a pure state, they are non-reactive with water and many of them are bio-degradable. Despite the basic principle of the way these liquids work being very similar to that of ionic liquids, they are not considered true ionic liquids because they do not contain purely anions and cations. These systems contain a cation and an anion and more importantly there is a hydrogen bond donating species there as well. The end result is similar however, a liquid that is made up a cation and an anion is formed, but its route to the reduction of lattice energy of the system is different. This occurs through of the hydrogen bond donor complexing to the anion and withdrawing the electron density of the anion from the cation. This separation results in a weaker anion/cation interaction, which is the way ionic liquids achieve their low melting temperatures.

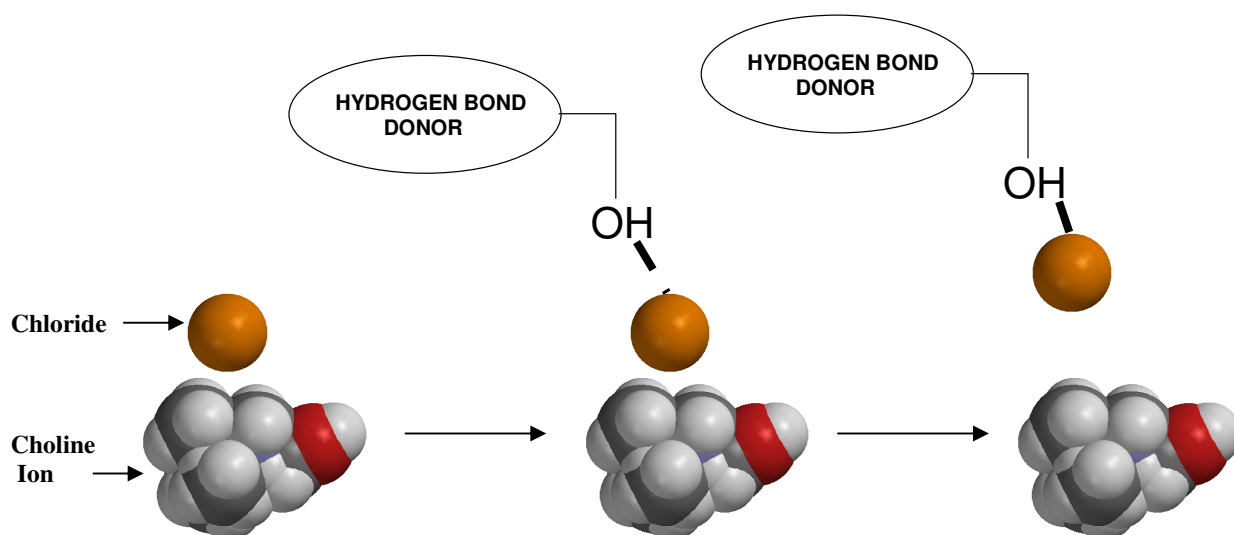


Figure 1.9: Diagrammatic representation of how hydrogen bond donors interact with a quaternary ammonium salt

One of the first DES systems that was investigated, contained ChCl and urea, in a ratio of 1:2 respectively.¹⁰⁵ There has also been a lot of work using carboxylic acids. Abbott *et al.* used phenylic carboxylic acids (phenylpropionic acid and phenylacetic acid) and showed that the eutectic composition with a quaternary ammonium salt was analogous to the urea ChCl case. This 2:1 ratio indicates that it requires two carboxylic acid molecules to complex with the chloride ion to form a eutectic mixture. However it was not possible to form DESs using monocarboxylic acids. By replacing the monocarboxylic acids with dicarboxylic acids with ChCl, there was a eutectic point reached and this eutectic was formed at a ratio of 1:1. This reinforces the theory that each anion is complexed by two hydrogen bonds.¹⁰⁹ It has also been shown that tricarboxylic acids can be used as the hydrogen bond donor. The eutectic point is reached when the composition is between 30-35 molar percentage composition of the acid. Because there are so many hydrogen bond donating groups in these systems, they exhibit the rheology of gels. This is thought that there is extensive bridging of the acids between neighbouring chloride ions. There is also considerable evidence for the depression in the freezing points of the system being in part governed by the molecular weight of the acid, with smaller molecular weight acids exhibiting greater depression in the freezing points. In general, the freezing point of any mixture containing a quaternary ammonium salt and a hydrogen bond donor is dependent on many things but the two most important factors are firstly, how large the individual lattice energies of both the hydrogen bond donor and the quaternary ammonium salt is and secondly the degree to which the anion-hydrogen bond donor interact. If the anion-hydrogen bond donor interaction is strong, the entropy of the system increases, resulting in a more disordered system, therefore offering a lower freezing point. To a certain degree, the depression in the freezing point can be a measure of the entropy change.

These types of DES have been used very successfully for many purposes such as electrochemical applications. Liquids such as Maline 100 (ChCl : malonic acid) and Ethaline 200 (ChCl : 2 x 1,2-ethanediol) have generated a lot of industrial interest in their use for both polishing and plating of metals.

1.6.4 Anhydrous Metal Halide Substituted Hydrogen Bond Donor Mixtures

This is a relatively new area of research in the DESs area.¹¹³ The idea of these systems is to use the metal halide, which in Section 1.6.3 was shown to be the complexing species that disrupts the interaction of the anion/cation interaction of the quaternary ammonium salt, the hydrogen bond donor reverses the role of it. Essentially the metal halide is the replacement for the quaternary ammonium salt. The hydrogen bond donor complexes to one or more of the halides of the metal and withdraws it from the metal centre. The majority of work in this area has been using ZnCl_2 as the metal halide and hydrogen bond donors that have been used are acetamide, 1,6-hexanediol, urea and 1,2-ethanediol.¹¹³ Again, as described in Section 1.6.3., the eutectic point is not always as obvious as counting two hydrogen bond donations per halide ion. This is seen with the case for ZnCl_2 with both acetamide and 1,2-ethanediol (1:4), but with 1,6-hexanediol, the eutectic forms at 1:3. This is most probably down to the strength and size of the hydrogen bond donating species, and also the form of the metal halide species.

1.7 The Use of Choline Chloride (hydroxyethyltrimethylammonium chloride) As The Common Quaternary Ammonium Salt

In the area of DESs, the most common quaternary ammonium salt to be used is choline chloride. Initially, this was because of the physical properties it offered when used as part of a DESs. When mixed with most hydrogen bond donors or metal halides, the physical properties were almost always greatly improved over the use of most other quaternary ammonium salts. The depression in freezing point tended to be one of the largest, if not the largest. An example of this is the ChCl : urea mixture. By themselves they have freezing points of 303 °C and 135 °C respectively. It also showed lower viscosities than many other systems containing different quaternary ammonium salts and conductivities were often higher when ChCl was used. The main reason behind ChCl being such a useful quaternary ammonium salt is to do with the fact it is an asymmetric quaternary ammonium salt with a polar functional group, but is also small. The asymmetric nature of this molecule reduces the freezing point of the ionic-

molecular liquid, as does the polar functional group. By combining these two compounds in a ratio of 1:2 (ChCl: urea), the product formed has a freezing point of 12 °C.

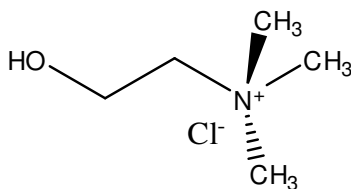


Figure 1.9: Structure of Choline Chloride (hydroxyethyltrimethylammonium chloride)

Perhaps in terms of public perception of this being used as a part of a potential replacement for conventional solvents, the fact that choline chloride is essentially non-toxic is a large plus point for its use. Choline chloride is also known as pro-vitamin B4 and has a recommended daily allowance of ~500 mg. It has been used for many years primarily as a chicken feed additive so is very cheap to buy. With the current economic and industrial explosion occurring in China, it has become possible to buy it from Chinese chemical companies for almost £1 per Kg.

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CHAPTER 2

Experimental

2.1 Materials

2.2 Purification of Choline Chloride

2.3 Physical Properties Experiments

2.3.1 Synthesis of ChCl: alcohol systems

2.3.1.1 Synthesis of 33%:67% ChCl: 1,2-Ethanediol system

2.3.1.2 Synthesis of 25%:75% ChCl: 1,4-Butanediol system

2.3.1.3 Synthesis of 25%:75% ChCl: 1,6-Hexanediol system

2.3.1.4 Synthesis of 20%:80% ChCl: 1,3-Butanediol system

2.3.1.5 Synthesis of 20%:80% ChCl: 1,2-Butanediol system

2.3.1.6 Synthesis of 20%:80% ChCl: 2,3-Butanediol system

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2.3.2 Viscosity Measurements

2.3.3 Conductivity Measurements

2.3.4 Surface Tension Measurements

2.3.5 Density Measurements

2.4 Solvatochromism Experiments

2.5 Esterification Experiments

2.5.1 Synthesis of 1:3 ChCl: Glycerol System for Esterification Reaction

2.5.2 Gel Permeation Chromotography Analysis of Esterification Reactions

2. Experimental

2.1 Materials

Table 2.1: List of compounds used during the project

Compound	Purity	Molecular Weight	Melting Point
1,2-ethanediol	99%	62.07	-13 °C
1,2-butanediol	99%	90.12	-50 °C
1,3-butanediol	99%	90.12	0 °C
1,4-butanediol	99%	90.12	16 °C
2,3-butanediol	98%	90.12	25 °C
choline chloride	99%	139.63	303-305 °C
meso-erythritol	99%	122.12	118-120 °C
D-(-)fructose	99%	180.16	119-122 °C
D-glucose	99%	180.16	150-152 °C
glycerol	99%	92.09	18 °C
1,6-hexanediol	98%	118.18	43-45 °C
lauric acid	99%	200.31	44-46 °C
N,N,-dimethyl-4-nitroaniline	99%	166.18	163-165 °C
4-nitroaniline	99%	138.13	146 °C
phenol	99%	94.11	40-42 °C
Reichardt's Dye	90% +	551.68	271-275 °C
trifluoroacetic Acid	98%	114.02	-15 °C
xylitol	99%	152.15	94-97 °C

2.2 Purification of Choline Chloride

Choline chloride (ChCl) is recrystallised to obtain the highest purity possible to be used in all experiments. Approximately for every 100 grams of ChCl, 100 mL of ethanol is used to recrystallise the ChCl. The solution is heated under reflux for approximately 2 hours, by which time all the choline chloride has dissolved, hot filtered,

and the filtrate allowed to cool. Upon cooling crystalline choline chloride reforms and the impurities stay dissolved in the ethanol. The crystalline product is vacuum filtered using a large sintered funnel and dried and kept under vacuum. Pure white crystals are obtained. Purity was determined by melting/decomposition point which was in the range of 302-305 °C, which corresponds to the known decomposition point of ChCl.

2.3 Physical Properties Experiments

2.3.1 Synthesis of ChCl: alcohol systems

The procedure for the formation of selected systems used in Chapter 3, are as follows:

2.3.1.1 Synthesis of 33%:67% ChCl: 1,2-Ethanediol system

To 20 cm³, (22.26 g, 0.359 mol) of 1,2-ethanediol, 24.664 g (0.177 mol) of ChCl was added and heated at ~ 60 °C, until fully dissolved. When the ChCl was fully dissolved the mixture was then cooled to the appropriate temperature before any measurements were taken.

2.3.1.2 Synthesis of 25%:75% ChCl: 1,4-Butanediol system

To 20 cm³, (20.34 g, 0.226 mol) of 1,4-butanediol, 10.505 g (0.075 mol) of ChCl was added, it was stirred and heated at ~ 60 °C, until fully dissolved. When the ChCl was fully dissolved the mixture was then cooled to the appropriate temperature before any measurements were taken.

2.3.1.3 Synthesis of 25%:75% ChCl: 1,6-Hexanediol system

To 20 g, (0.254 mol) of 1,6-hexanediol, 7.877 g (0.056 mol) of ChCl was added, it was stirred and heated at ~ 80 °C, until fully dissolved. When the ChCl was fully dissolved the mixture was then cooled to the appropriate temperature before any measurements were taken.

2.3.1.4 Synthesis of 20%:80% ChCl: 1,3-Butanediol system

To 20 cm³, (20.1 g, 0.223 mol) of 1,3-butanediol, 7.786 g (0.056 mol) of ChCl was added, it was stirred and heated at ~ 60 °C, until fully dissolved. When the mixture was fully homogenous, the mixture was then cooled to the appropriate temperature before any measurements were taken.

2.3.1.5 Synthesis of 20%:80% ChCl: 1,2-Butanediol system

To 20 cm³, (20.12 g, 0.223 mol) of 1,2-butanediol, 7.793 g (0.056 mol) of ChCl was added, it was stirred and heated at ~ 60 °C, until fully dissolved. When the mixture was fully homogenous, the mixture was then cooled to the appropriate temperature before any measurements were taken.

2.3.1.6 Synthesis of 20%:80% ChCl: 2,3-Butanediol system

To 20 cm³, (19.9 g, 0.221 mol) of 2,3-butanediol, 7.708 g (0.052 mol) of ChCl was added, it was stirred and heated at ~ 60 °C, until fully dissolved. When the mixture was fully homogenous, the mixture was then cooled to the appropriate temperature before any measurements were taken.

2.3.1.7 Synthesis of 33%:67% ChCl: Glycerol system

To 20 cm³, (25.12 g, 0.273 mol) of glycerol, 19.041 g (0.136 mol) of ChCl was added, it was stirred and heated at ~ 80 °C, until fully dissolved. When the mixture was fully homogenous, the mixture was then cooled to the appropriate temperature before any measurements were taken.

2.3.2 Viscosity Measurements

The viscosity of various eutectic mixtures was measured using a Brookfield DV-E Viscometer fitted with a thermostated jacket. The viscometer jacket was connected to a

thermostated water bath. The water bath was always approximately 0.5°C warmer than the sample in the viscometer so the thermostat of the water bath was always set at 0.5°C higher than the desired temperature. The viscosity measurements were obtained using a spindle attachment, which measures the ease at which the spindle can move at a set amount of revolutions per minute. Readings were taken after 25-30 minutes for each temperature to ensure good equilibration of temperature between the water bath and the sample.

2.3.3 Conductivity Measurements

The conductivity of various eutectic mixtures was measured using a Jenway 4071 Conductivity Meter conductivity probe. Measurements were carried out at exactly the same temperatures as the viscosity experiments were for the same eutectic mixture. To ensure good correlation between the results, the sample used for conductivity was made from the same batch as that used in the viscosity experiments. The readings were taken after 25-30 minutes for each temperature selected to ensure good equilibration of temperature between the water bath and the sample.

2.3.4 Surface Tension Measurements

The surface tension of various eutectic mixtures was measured using a Krüss Tensiometer K9 with a platinum plate. The plate is dipped into the liquid so it is just touching the surface and the resulting reading is recorded and then the plate is removed from the liquid.

2.3.5 Density Measurements

The densities of the systems are measured on the Krüss Tensiometer K9. The density probe is submerged into the liquid for 5 minutes so the apparatus can reach equilibrium, and then the reading on the tensiometer is taken.

2.4 Solvatochromism Experiments

All the systems investigated in Chapter 4 were made in an analogous way to those in Chapter 3. A Shimadzu Model UV-1601 Spectrophotometer was used to measure the solvatochromic shift of the different indicator dyes in the visible absorbance spectrum. The path length was 1 cm. The program UV PROBE was used to obtain the maximum absorbance of the UV-Vis spectra of the solvatochromic dyes in each eutectic mixture. The spectrum of the solvatochromic probe in the systems were measured at a resolution of 0.05 nm per data point. The estimated uncertainty in the wavelength maximum is less than 0.5 nm. The concentration of samples were kept in the range of 10^{-5} – 10^{-6} mol dm⁻³ in order to reduce any possible solute-solute interactions being observed.

2.5 Esterification Experiments

In Chapter 5, it is mentioned that various molar amounts of lauric acid are used. The following data are the exact amounts of lauric acid added to the systems for each data set.

Table 2.1: Weights of lauric acid used

Molar amount of lauric acid	0.1 M	0.2 M	0.3 M	0.4 M	0.6 M
Weight of lauric acid	20.032 g	40.064 g	60.096 g	80.128 g	120.192 g

2.5.1 Synthesis of 1:3 ChCl: Glycerol System for Esterification Reaction

To 60 cm³, (75.36 g, 0.82 mol) of glycerol, 38.084 g (0.27 mol) of ChCl was added and heated at ~ 80 °C, until fully dissolved. When dissolved the mixture was heated to 150 °C. At this point the lauric acid and 6 cm³ (9.21g, 0.08 mol) trifluoroacetic acid catalyst was added and then sealed in the reaction vessel. The mixture was homogenised using a mechanical stirrer at 800 rpm. All other systems were made up in analogous method to this.

2.5.2 Gel Permeation Chromotography Analysis of Esterication Reactions

The progression of the esterification reactions was measured by gel permeation chromatography (GPC). The GPC used was a Polymer Laboratories PL-GPC 220 with two PLgel 5 μ m 50Å columns. The analysis was carried out at 40 °C at a flow rate of 1 cm/min. The solvent used was still dried THF. Each sample vial contained 0.02 g of product and was dissolved in 1.25 mL of dry THF. Under this setup the elution times of the reagents and products are shown in Figure 2.2.

Figure 2.2: Peak elution time of reagents and products of esterification reactions using GPC

Reagent/Product	Lauric Acid	Mono Ester	Di Ester	Tri Ester
Elution Time /min	14.7	14.2	13.3	12.9

CHAPTER 3

Physical Properties of Alcohol Based Deep Eutectic Solvents

3.1 Variation of the Chain Length of the Hydrogen Bond Donor

3.1.1 1,2-Ethanediol

3.1.2 1,4-Butanediol and 1,6-Hexanediol

3.2 Effects Hydrogen Bond Donor Group Positioning

3.3 Variation of the Number of Hydrogen Bond Donating Groups

3.3.1. Physical Properties of Glycerol with ChCl

3.4 At Which Composition do DESs Become Ionic Liquids?

3.5 Poly-Alcohol/Sugar Based Deep Eutectic Solvents

3.6 Mono Functional Alcohol Deep Eutectic Solvents

3.7 Conclusions

3.8 References

3. Introduction

“Deep Eutectic Solvents” can be described by the following general formula:



This general formula encompasses in excess of 10^6 possibilities and clearly not all variants can be studied. The aim of this part of the project is to characterise the effect of elements C and D in equation (3.1). For this study, only choline chloride (ChCl) has been used as the quaternary ammonium salt. Other cations and anions have previously been studied and some basic models of phase behaviour have been developed. ChCl has been chosen as it is the most commonly used precursor for eutectic based ionic liquids and already has a number of industrial applications. It offers optimal environmental and cost benefits and can therefore be applied to large-scale processes.

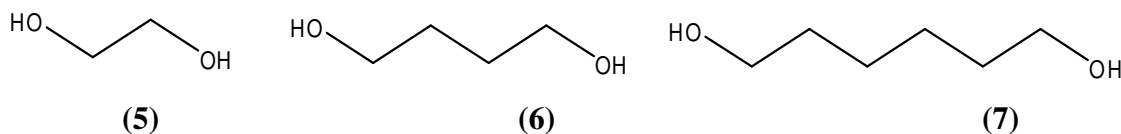
Eutectic mixtures of ChCl with ethylene glycol have already been applied to the electropolishing of stainless steel,^{1,2} the plating of metals and alloys,³ the electroless deposition of silver on copper^{4,5} and the recovery of metals from complex metal oxide matrices.⁶ and understanding of the phase behaviour, viscosity, conductivity and density would therefore be useful for the development of new and improved DESs.

3.1 Variation of the Chain Length of the Hydrogen Bond Donor

In this section R_5 from the general formula (3.1) is varied. So far there has been a lot of work in the variation of the hydrogen bond donor (C) and (D). Previously various dicarboxylic acids and diamides have been studied but very little work has been carried out using diols. This section will investigate various glycols, which will alter the variable (C) but keep variable (D) constant. The length of the chain of the glycol was altered to determine the effect this has on the physical properties of the system.

The viscosity, conductivity, surface tension and density were measured as both a function of temperature and a function of molar composition. The glycols used were 1,2-ethanediol (5), 1,4-butanediol (6) and 1,6-hexanediol (7). The estimated error in these measurements is believed be approximately +/- 1% due intrinsic errors from the

instrumentation, which is approximately the same size as the data markers, so have not been included.



3.1.1 1,2-Ethanediol

Mixtures of ChCl with 1,2-ethanediol (5) were made ranging from 5% to 33% ChCl. The viscosity of these systems show a decrease exponentially as the temperature is increased due to increased kinetic energy. By adding more ChCl the viscosity of the systems increase as would be expected. This can be seen in Appendix Figure 7.1. The viscosity of these liquids is significantly less than other eutectic based ionic liquids as can be seen from Figure 3.1.

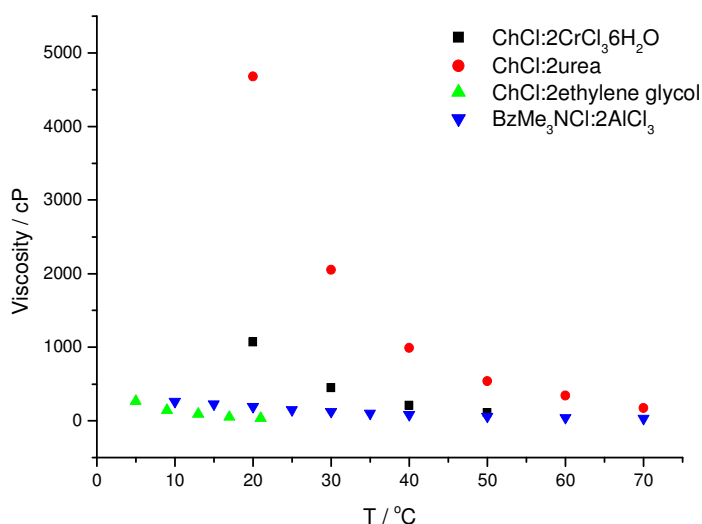


Figure 3.1: Viscosity of various eutectic based ionic liquids as a function of temperature redrawn from the literature⁷⁻⁹

The viscosity of an ionic liquid has been fitted to two types of model; one based on an Arrhenius model and one based on the Vogel–Tamman–Fulcher (VTF) model. In this work the former model will be applied as suitable correlation is observed and it allows correlation to previously reported data. The energy of activation of viscous flow (E_η) of each of the systems was obtained by plotting a graph of \ln viscosity versus inverse temperature according to equation 3.2:

$$\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \quad (3.2)$$

where η_0 is a constant.

The data are shown in Figure 3.2 and the values of both E_η and $\ln \eta_0$ are reported in **Table 3.1** along with the values obtained for the other glycols studied.

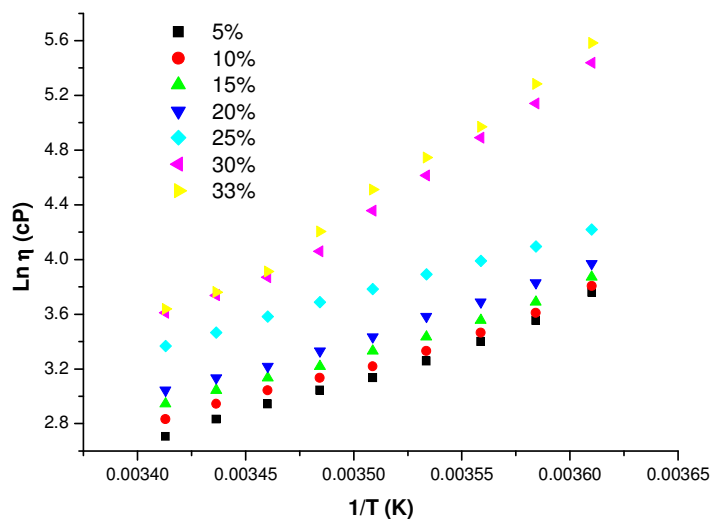


Figure 3.2: Plot of inverse temperature versus log viscosity as a function of ChCl composition in 1,2-ethanediol

The conductivity, κ , for the systems shown in Figure 3.2 were also obtained and these are shown in Appendix Figure 7.2. In an analogous manner to the viscosity data the conductivity data can be fitted to an Arrhenius based equation of the form

$$\ln \kappa = \ln \kappa_0 - \frac{E_\kappa}{RT} \quad (3.3)$$

where E_κ is the energy of activation of conductivity and κ_0 is a constant, by plotting \ln conductivity versus inverse temperature, as can be seen in Figure 3.3.

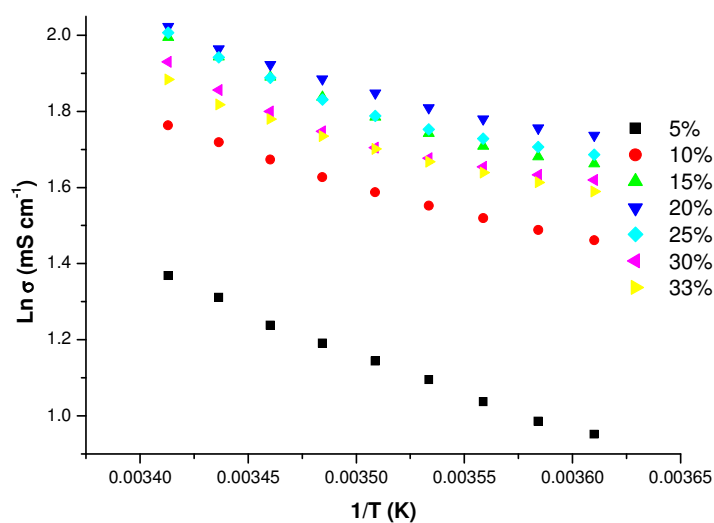


Figure 3.3: Plot of inverse temperature versus log conductivity as a function of ChCl composition in 1,2-ethanediol

The data obtained for conductivity offers some interesting information on these systems. In the case of viscosity as a function of composition, there was an increase in the viscosity as more ChCl was added. The observed trend in conductivity shows an increase from 5% to 20% as would be expected since more charge carrying species is being added to the system, however from 20% to 33% there is a decrease in the conductivity. This can be seen more clearly in Figure 3.4 by just plotting the data at 293 K.

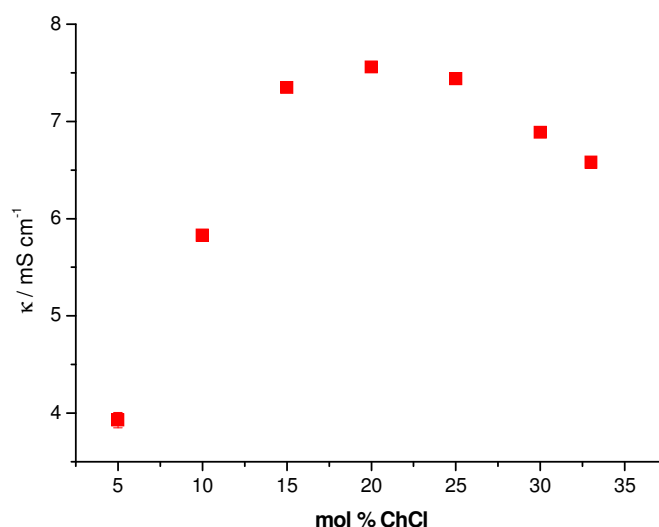


Figure 3.4: Plot of molar percentage composition of ChCl in 1,2-ethanediol versus conductivity at 293K

This is believed to be due to the effect of viscosity being greater than the effect of conductivity on the system after more than 20 % ChCl is added. Despite the fact there are more charge carrying species (ChCl) in the system, the viscosity of the system impedes the flow of ions through the system. Probably the most important observation about the data in Figure 3.3 however is the magnitude of the conductivity which is significantly greater than the other ChCl based eutectics reported previously.^{7,8} The data are also comparable with some of the highest conductivities reported for room temperature ionic liquids with discrete anions.¹⁰⁻¹³ This suggests that the motion of ions in these liquids may be different to other choline based eutectics.

The conductivity of concentrated quaternary ammonium electrolytes in non-aqueous solutions has previously been modelled using the Fuoss Kraus theory.¹⁴ The molar conductivity, Λ is given by

$$\Lambda = \frac{\Lambda^0 \sqrt{K_p}}{\sqrt{c}} + \frac{\Lambda_t^0 \sqrt{K_p c}}{K_t} \quad (3.4)$$

Where Λ^0 and Λ_t^0 are the limiting molar conductivity of the single and triple ions respectively, c is the concentration of the electrolyte and K_p and K_t are the ion pair and triple ion dissociation constants respectively. This has subsequently been modified to account for the activity coefficient of the electrolyte, but this theory is only valid at relatively low concentrations ($< 0.1 \text{ mol dm}^{-3}$). It was proposed that in these systems

ion-ion interactions were strong and ion pairs and triple ions dominated charge transport.

The mobility of ions in ionic liquids is significantly different from that in non-aqueous solvents and there have been very few attempts to model the conductivity of ionic liquids. The Walden rule ($\Lambda\eta = \text{constant}$) has been applied to ionic liquids, where Λ is the molar conductivity and η is the viscosity.¹⁴ Deviations from the Walden rule seen in proton transfer ionic liquids have previously been used to explain ionic association.^{15,16} This rule is not fully applicable to ionic liquids as it is only valid for ions at infinite dilution where ion-ion interactions can be ignored, which is clearly not the case in ionic liquids.

Hole theory has been used to analyse the viscosity of ionic liquids.¹⁷ It was initially developed by Fürth¹⁸ in an attempt to explain the properties of the liquid state and was later expanded by Bockris *et al.* for use with molten salts.^{19,20} This model was also found to have serious limitations in molten salts because the ionic association significantly affects the ionic activity. Stillinger has provided a discussion of the various models for pure fused salts.²¹

Abbott *et al.* recently showed that E_η is related to the size of the ions and the size of the voids present in the liquid for ionic liquids with discrete anions and DESs.^{7,17,22} It was shown that the viscosity of ambient temperature molten salts is several orders of magnitude higher than high temperature molten salts. This was due partially to the difference in size of the ions, but also due to the increased void volume in the liquid.

Abbott later showed that hole theory can be applied to both ionic and molecular fluids to account for viscosity.^{17,22} It has been shown that the viscosity of a fluid, η , can be modelled by assuming it behaves like an ideal gas. Its motion however is restricted by the availability of sites of the ions/molecules to move into. Hence it was shown that

$$\eta = \frac{\bar{mc} / 2.12\sigma}{P(r > R)} \quad (3.5)$$

Where m is the molecular mass (for ionic fluids this was taken as the geometric mean), \bar{c} is the average speed of the molecule ($= (8kT/\pi m)^{1/2}$) and σ is the collision diameter of the molecule ($4\pi R^2$). The probability of finding a hole of radius, r , greater than the radius of the solvent molecule, R , in a given liquid, ($P(r > R)$), is given by integration of the following expression²⁴;

$$Pdr = \frac{16}{15\sqrt{\pi}} a^{7/2} r^6 e^{-ar^2} dr \quad (3.6)$$

where $a = 4\pi\gamma / kT$ and γ is the surface tension. There is good correlation obtained between the calculated and measured viscosities, which show that the viscosity of fluids as being limited by the availability of holes large enough for the mobile species to be able to move into. It should be noted that inspection of equations (3.5) and (3.6) shows that a decrease in the viscosity can be obtained by decreasing the surface tension of the liquid i.e. increasing the free volume, or by decreasing the ionic radius.

There is comparatively little surface tension data reported on ionic liquids but work by Branco *et al.*²⁴ and Huddleston *et al.*²⁵ showed that ionic liquids with fluorinated anions have low surface tensions and low viscosities. This explains why the ionic liquids with highly fluorinated anions exhibit the lowest viscosities. The effect of the cation on viscosity however is less clear. In the case of the imidazolium cation, an increase in the length of the R group should result in a decrease in the viscosity as the degree to which the ion-ion interactions occur will be reduced and hence the surface tension will decrease. On the other hand however, the increase in size of the alkyl group will reduce its mobility due to a lack of suitably sized voids for the larger cations to move into. This explains the data presented by Tokuda *et al.* who showed a minimum in viscosity for ethyl methyl imidazolium salts.²⁶

Since it has been shown that viscosity is limited by the availability of holes large enough for the mobile species to move into, then charge mobility can be considered as being equal to the migration of holes in the opposite direction to that of the ions. The fraction of suitably sized holes in ambient temperature ionic liquids is very low (*c.a.* 10^{-6}), therefore the holes can be assumed to be at infinite dilution. The migration of the mobile species should therefore be described by a combination of the Stokes-Einstein and Nernst Einstein equations

$$\lambda_+ = z^2 F e / 6 \pi \eta R_+ \quad (3.7)$$

where z is the charge on the ion, F is the Faraday constant and e is the electronic charge. With the Stokes-Einstein equation being valid for both the cation and anion, the conductivity of the salt can be determined since

$$\Lambda = \lambda_+ + \lambda_- \quad (3.8)$$

an expression can be written for the conductivity, κ

$$\kappa = \frac{z^2 Fe}{6\pi\eta} \left(\frac{1}{R_+} + \frac{1}{R_-} \right) \frac{\rho}{M_w} \quad (3.9)$$

where ρ is the density and M_w is the molar mass of the ionic fluid. Therefore, all of the theories developed for limiting molar conductivities in molecular solvents are also applicable to ionic liquids where there is an infinite dilution of suitably sized holes.²⁷

It should be noted that equation (3.9) is not applicable to high temperature molten salts because the fraction of suitably sized holes is much larger (c.a. 0.5). The ionic activity therefore becomes an important factor and because there are smaller ions than in the high temperature analogues, the ionic association constant will be significant.

By using equations (3.5) and (3.9), it is possible to predict the minimum viscosity and conductivity that an ionic liquid is able to achieve. In order to obtain an optimum conductivity and viscosity, the surface tension and the size of the ions both need to be as small as possible. This explains why the highest reported conductivity for an ionic liquid to date is that of $[\text{EtNH}_3]^+[\text{NO}_3]^-$ (c.a. 150 mS cm⁻¹ at 298K).¹⁵

Angell¹⁵ has shown that the molar conductivity is inversely proportional to the viscosity of the liquid for ionic liquids with discrete anions. This correlation is virtually independent of the cation and anion. The properties of ionic liquids have been defined using this method. Since the size of most ionic species that form ionic liquids are approximately the same size ($R \approx 3\text{-}4 \text{ \AA}$), it is clear that equations (3.7) and (3.9) explain Angell's observation, and that a correlation exists between the molar conductivity and the fluidity. Hole theory therefore potentially provides a method by which the dilution of ionic liquids can be quantified because equation (3.9) will no longer be valid when hole mobility does not limit conductivity.

To apply hole theory it is necessary to determine the surface tension of the liquids as this feeds into equation (3.9). The average hole size of the system can be calculated from equation (3.9);

$$4\pi \langle r^2 \rangle = 3.5 \frac{kT}{\gamma} \quad (3.10)$$

where k is the Boltzmann constant and γ is the surface tension at temperature T . Surface tension could be expected to follow similar trends to viscosity since it is a measure of how strong the intermolecular forces are in the liquid, similar to the measure of viscosity. It is reasonable to expect that as viscosity increases as the molar composition of ChCl increases, the surface tension should increase as the molar

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composition of ChCl increases. A plot of surface tension as a function of temperature can be seen in Figure 3.5.

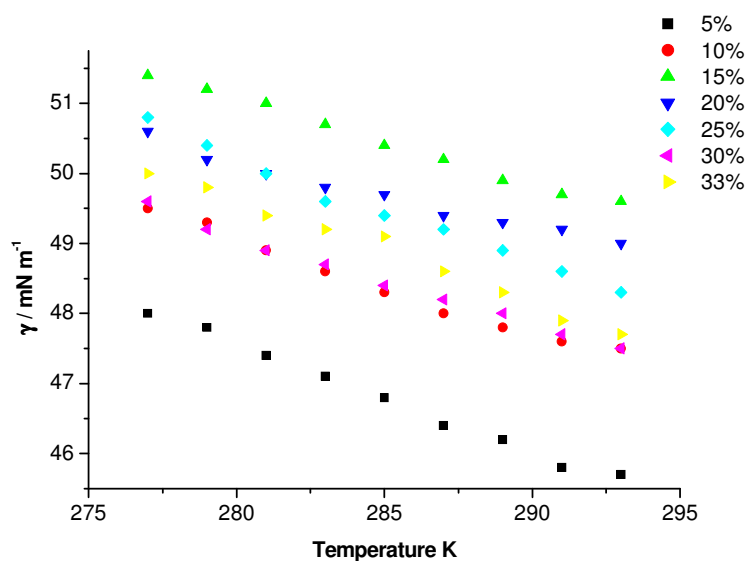


Figure 3.5: Plot of temperature versus surface tension as a function of ChCl composition for 1,2-ethanediol systems

The trend is more obvious in Figure 3.6 where again the data at 293 K alone are plotted.

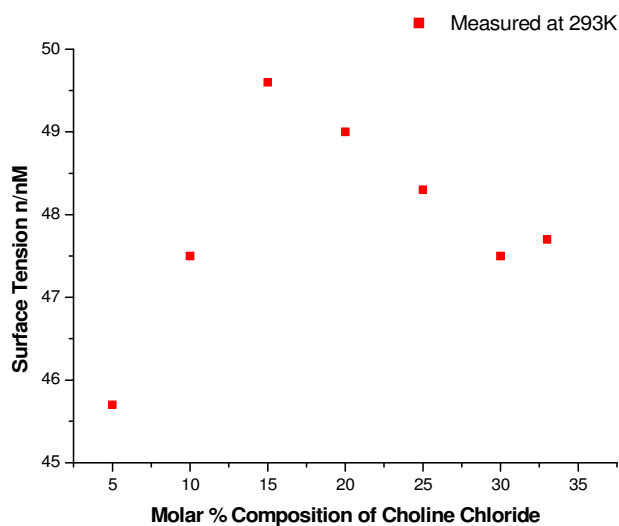


Figure 3.6: Plot of surface tension as a function of ChCl composition at 293K for the 1,2-ethanediol systems

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The average hole radius at 293 K is approximately 1.52 Å. The volume of the theoretical mobile complexed species was calculated to be 345.3 Å³.²⁸ The assumed complexed species consists of two 1,2-ethanediol molecules (2 x 80.54 Å³), one choline cation (149.20 Å³) and one chloride anion (35.02 Å³). The radius of the mobile species r_s was calculated from the average of the cationic species (i.e. choline) and the anionic species (i.e. chloride and two 1,2-ethanediols). The average radius of mobile species is 3.45 Å. It has previously been shown that there is an empirical correlation between the activation energy for viscous flow and the ratio of the ion an hole size r_i/r_h . Figure 3.7 shows the correlation between E_η and r_i/r_h . From the data above the r_i/r_h for the ChCl: 2 1,2-ethanediol system is 2.27 which would suggest a E_η value of *c.a.* 100 kJ mol⁻¹.

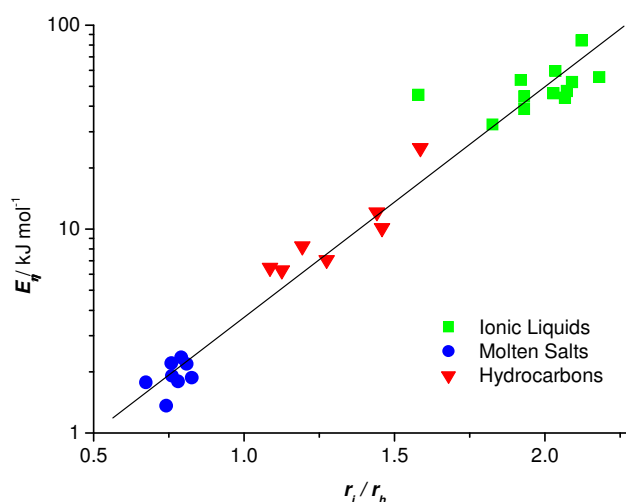


Figure 3.7: Energy for activation of viscous flow as a function solvent to hole radius ratio

Table 3.1 lists the energies of activation of viscosity and conductivity calculated from Figure 3.2 and Figure 3.3. The values for E_η are considerably below 100 kJmol⁻¹ and suggest a mobile species which is much smaller than the anion with two bound glycols. Below 25 mol % ChCl the roughly constant E_η value suggests a mobile species of approximately 2.3 Å radius whereas above 30 mol % ChCl the radius is approximately 2.9 Å. Clearly this equates to an average ionic radius but it suggests that there may be a contribution from a free chloride anion ($r = 1.81$ Å) passing between 1,2-ethanediol molecules, a free 1,2-ethanediol molecule ($r = 2.68$ Å) or a chloride anion bound to a 1,2-ethanediol molecule (3.03 Å). It seems to suggest that there is a change in mobile species occurring which corresponds to the concentration at which the

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conductivity passes through a maximum. FAB-MS shows the presence of the chloride coordinated to both one and two glycol molecules and presumably the composition of the two species will depend upon the composition of the two components in the mixture.

It has previously been shown that for other DESs such as those based on urea or acetamide, the mobile species correspond to the chloride anion bound to two hydrogen bond donors.⁷ The results shown above suggest the high conductivities and low viscosities presented in Figures 3.2 and 3.3 arise from smaller mobile species which results from weaker anion-HBD interactions.

Table 3.1: Energies of activation of both viscosity and conductivity for 1,2-ethanediol based systems

Mol. % ChCl	E_{η} (kJmol ⁻¹)	$\ln \eta_0$	E_{κ} (kJmol ⁻¹)	$\ln \kappa_0$
5	42.28	-14.67	-17.65	8.60
10	39.05	-13.22	-12.82	7.01
15	37.71	-12.56	-14.45	7.91
20	39.26	-13.10	-11.95	6.90
25	35.48	-11.19	-13.37	7.46
30	79.50	-29.15	-12.73	7.11
33	84.48	-31.15	-12.02	6.79

As more of the salt is added to the system it would be expected that the density of the system should increase at a linear rate. This can be seen in Figure 3.8. There is however only a slight change in the density. The addition of 33% molar ratio of ChCl to 1,2-ethanediol results in a small increase of 0.007 gcm⁻³. This results in an increase of only 0.6% of the density of the pure liquid. This would suggest that there is very little change in the structure of the system.

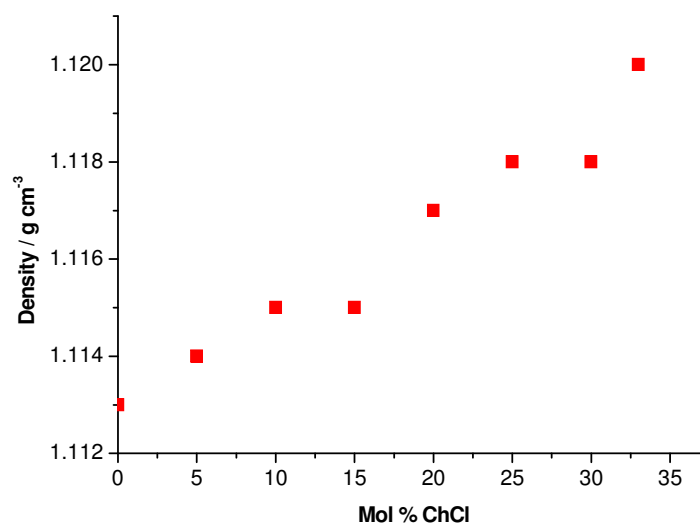


Figure 3.8: Plot of molar percentage composition of ChCl versus density at 293K for the 1,2-ethanediol systems

Using the density data the molar volume V_m can be calculated using

$$V_m = M_r / \rho \quad (3.11)$$

Where M_r is the relative molar mass of the liquid calculated from

$$M_r = x_{ChCl} M_{ChCl} + x_{HBD} M_{HBD} \quad (3.12)$$

where x is the mole fraction and M the relative molar mass of the two components. The actual volume occupied by the components can be calculated in a similar manner i.e.

$$V_{comp} = (x_{ChCl} V_{ChCl} + x_{HBD} V_{HBD}) N_A \quad (3.13)$$

Where V is the molecular volume of the component and N_A the Avogadro constant. Using this approach the fractional molar free volume can be obtained using

$$V_{free} = (V_m - V_{comp}) / V_m \quad (3.14)$$

A liner decrease in V_{free} with mole fraction ChCl can be observed in Figure 3.9 representing an almost 3 % contraction of the liquid compared to pure 1,2-ethanediol.

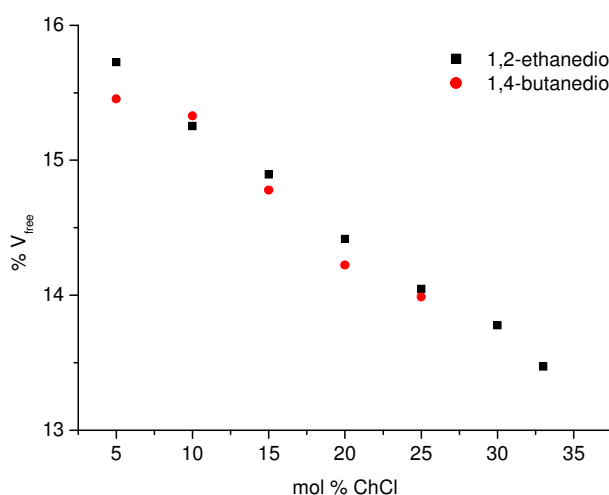


Figure 3.9: Plot of V_{free} as a function of mol % ChCl

3.1.2 1,4-Butanediol and 1,6-Hexanediol

Mixtures of ChCl with 1,4-butanediol (6) were made up ranging from 5% ChCl up to 25% ChCl. It was not possible to go to a higher concentration of ChCl than this as the mixture began to phase separate. The viscosity, conductivity, surface tension and density were all measured and the results are presented below. The results are exactly analogous to those observed for 1,2-ethanediol shown above.

It should be noted that 1,6-hexanediol is a solid at room temperature (melting point 40-43 °C) and so no density data could be obtained due to the high temperature required to form a liquid. The phase diagram of 1,6-hexanediol with ChCl is shown in Figure 3.10.

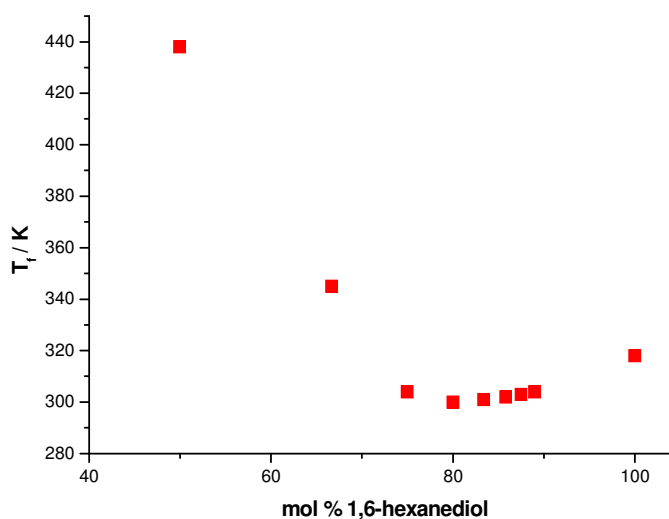


Figure 3.10: Phase diagram of 1,6-hexanediol with ChCl

The lowest freezing point appears to be at a ratio of 4:1 1,6-hexanediol: ChCl. The depression is very small compared to the other DESs studied previously such as malonic acid where the depression of freezing point is 212 °C. The depression of freezing point compared to an ideal mixture of the two components at the eutectic composition is 69 °C this corresponds to a mass fraction of HBD of 67% and fits relatively well to the empirical model presented previously for DESs.^{1-4,6-9,17}

Figures 3.11 and 3.12 show that the viscosities of the C₄ and C₆ diols are significantly larger than those of the C₂ diol. A concomitant decrease in the conductivities of the larger diols is also observed. The viscosity of these systems shows some strange behaviour. The viscosity of 5%, 10% and 15% is almost the same and there is a significant change in viscosity for 20% and 25% mixtures which are similar to each other.

As with the 1,2-ethanediol the conductivity of the 1,4-butanediol and 1,6-hexanediol systems increased as more ChCl was added, which is what would be expected since there are more charge carrying species in the system. Figures 3.13 and 3.14 however show no decrease in the conductivity at high ChCl concentrations as shown in Figure 3.4, but this is probably because such large concentrations could not be obtained with the higher diols. The energies of activation of conductivity and viscosity were calculated for each of the systems and the results are shown in Table 3.2.

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1,4-Butanediol

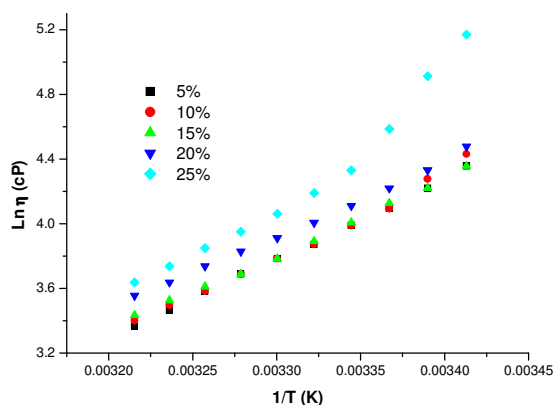


Figure 3.11: Plot of T^{-1} vs. $\log \eta$ as a function of ChCl

1,6-Hexanediol

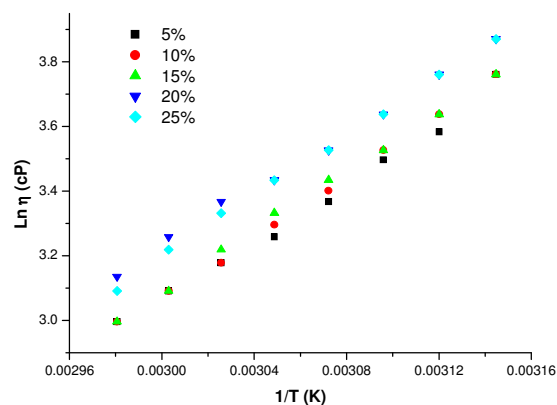


Figure 3.12: Plot of T^{-1} vs. $\log \eta$ as a function of ChCl

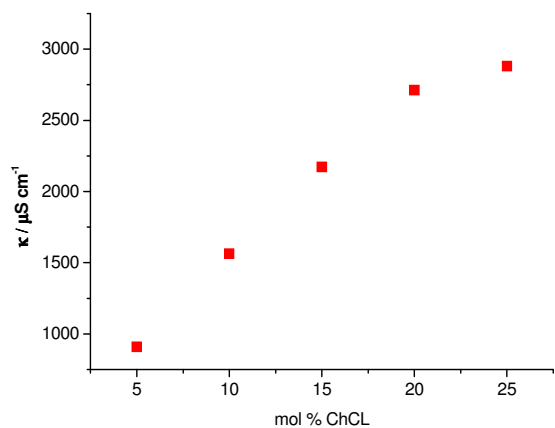


Figure 3.13: Plot of mol % ChCl vs. conductivity at 311K

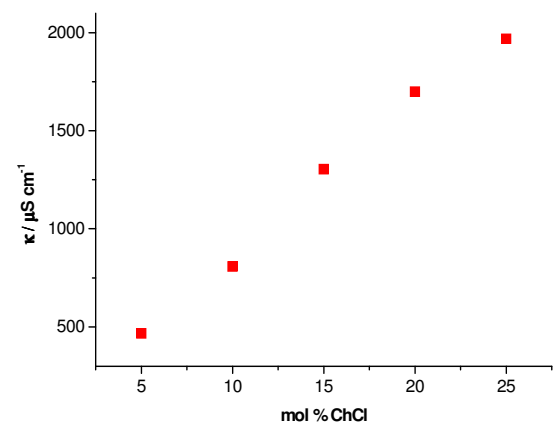


Figure 3.14: Plot of mol % ChCl vs. conductivity at 335K

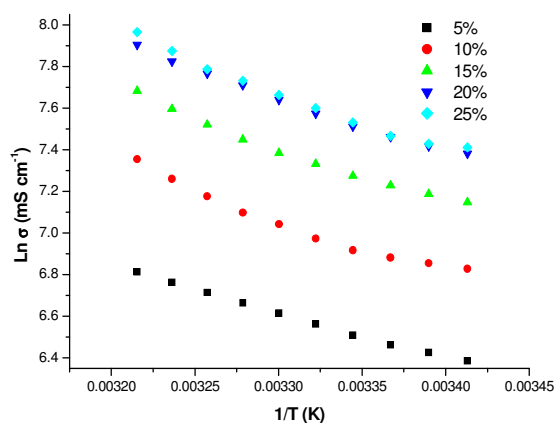


Figure 3.15: Plot of T^{-1} vs. $\log K$ as a function of ChCl composition

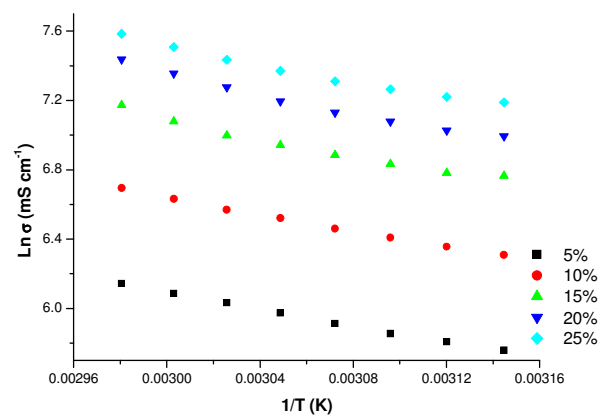


Figure 3.16: Plot of T^{-1} vs. $\log K$ as a function of ChCl composition

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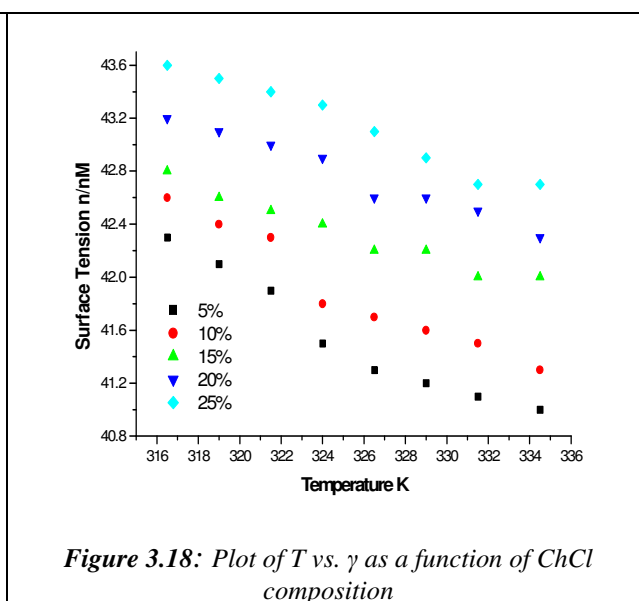
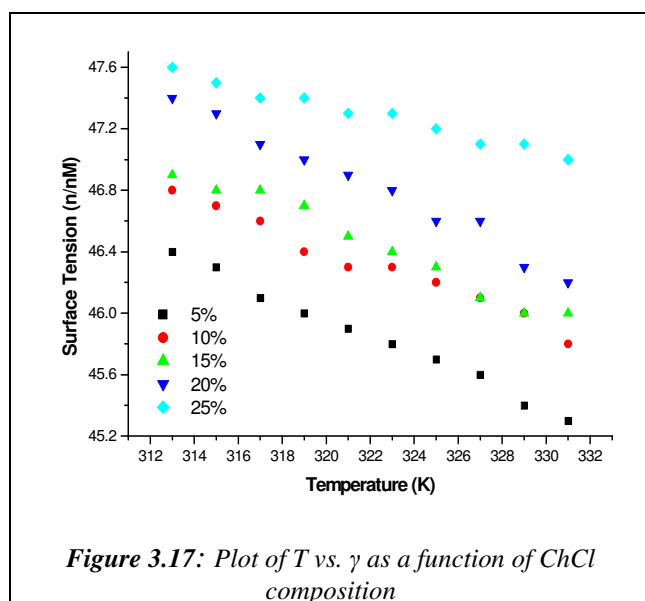


Table 3.2: Energies of activation of both viscosity and conductivity for 1,4-butanediol and 1,6-hexanediol systems

1,4-butanediol				
Mol. % ChCl	E_{η} (kJmol ⁻¹)	log η_0	E_{Λ} (kJmol ⁻¹)	log κ_0
5	40.71	-12.37	-18.36	13.91
10	42.01	-12.88	-22.11	15.85
15	38.61	-11.52	-22.24	16.24
20	37.92	-11.13	-22.35	16.52
25	62.13	-20.51	-23.80	17.13
1,6-hexanediol				
5	37.58	-10.50	-19.78	13.23
10	39.06	-11.02	-19.54	13.69
15	38.50	-10.80	-20.61	14.52
20	36.21	-9.83	-22.81	15.59
25	38.78	-10.80	-20.14	14.78

Table 3.2 shows that the E_{η} values are comparable with those observed for 1,2-ethanediol at the same mole fraction of ChCl (35-40 kJmol⁻¹). In the 1,4-butanediol and 1,6-hexanediol systems the average hole sizes calculated from the surface tension data were 1.55 and 1.68 Å respectively. Analogous to the results above for 1,2-ethanediol it is most likely that the mobile species are either ‘free’ chloride ions or those bound to one glycol molecule.

The density of the systems is expected to increase as more quaternary ammonium salt is added to the system and this is what was observed in Figure 3.19. Although the

density changes observed are significantly larger than those shown in Figure 3.8 they equate to exactly the same change in molar free volume (Figure 3.9) suggesting that the same structuring occurs in both liquids.

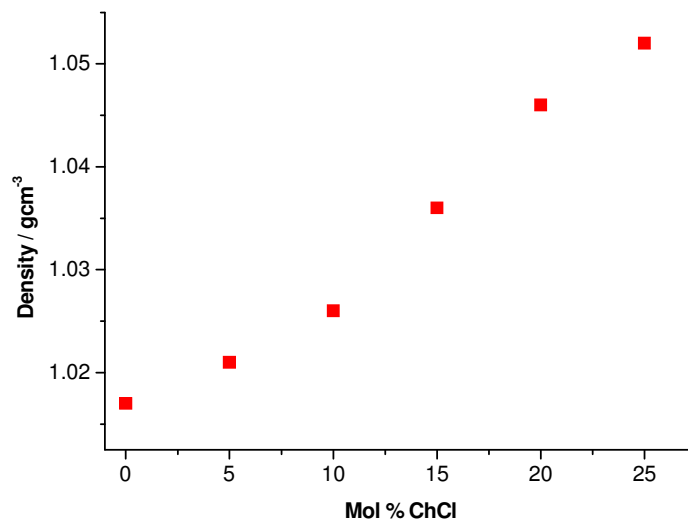


Figure 3.19: Plot of molar percentage composition of ChCl versus density at 293K for the various 1,4-butanediol systems

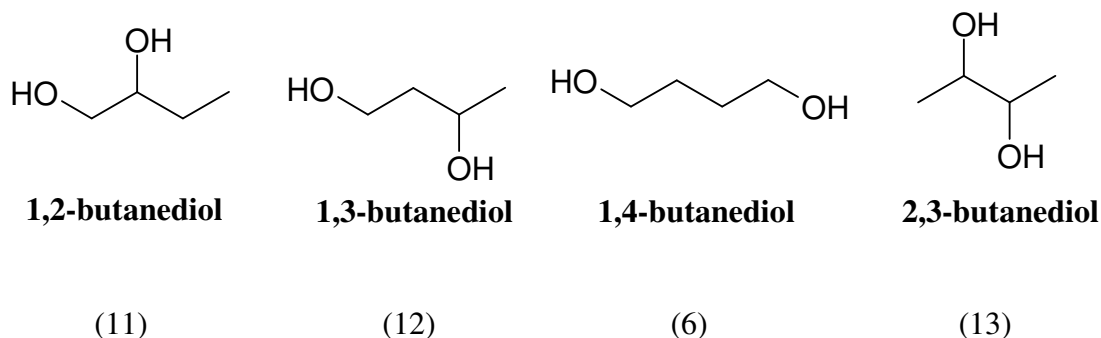
This section has shown that the chain length of the diol significantly affects the conductivity and viscosity of the mixtures. It has been shown that the cause of the instability in the glycol based eutectics arises from the low freezing point to the hydrogen bond donor. Since the depression of freezing point is related to the strength of interaction between the chloride anion and the hydrogen bond donor; a non-acidic proton combined with a low freezing point of the glycol means that a very shallow eutectic is formed. This may also explain why aliphatic alcohols do not form eutectics with ChCl.

3.2 Effects Hydrogen Bond Donor Group Positioning

The effects of altering the length of the glycol chain has been investigated in Section 3.1, but the effect of the positioning of the alcohol groups along the alkane chain has not been looked at. The physical properties of the various isomers of butanediol were investigated.

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This section looks at the physical properties (viscosity, conductivity, surface tension and density) of the various isomers of butanediol (1,2-, 1,3-, 1,4- and 2,3-butanediol) when mixed with ChCl, similar to the experiments carried out in **Section 3.1**.



This section is looking at what affect the organic groups on the hydrogen bond donor molecules have. The interaction between the OH moiety and the chloride anion are unknown (current EXAFS studies are attempting to quantify these) however one way in which the different isomers could affect the packing density in the liquid is shown schematically in Figure 3.20.

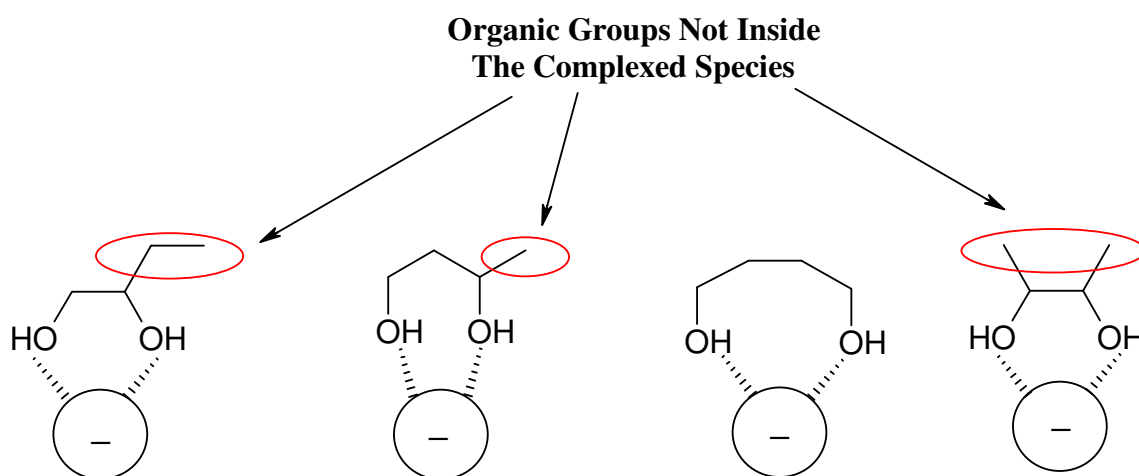


Figure 3.20: Schematic representation of possible complex species that could be formed between the various isomers of butanediol with the chloride anion

One way of gaining an insight into the structural differences occurring in the liquids is to analyse the physical properties.

The viscosity of the systems all showed an exponential decrease as temperature is increased. The various plots can be seen in Appendix Figures 7.3, 7.7, 7.11 and 7.15.

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It is also seen that by adding ChCl to the system there is an increase in the viscosity of the liquid, as was seen in the case of the glycol based systems. Figure 3.21. shows that the viscosity decreases in the order the order of 2,3 > 1,3 > 1,4 > 1,2.

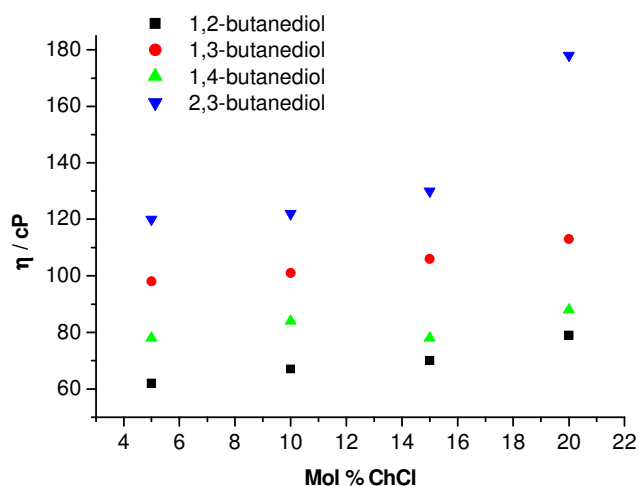


Figure 3.21: Viscosity of the various isomers of butanediol as a function of molar composition of the system in terms of ChCl at 298K.

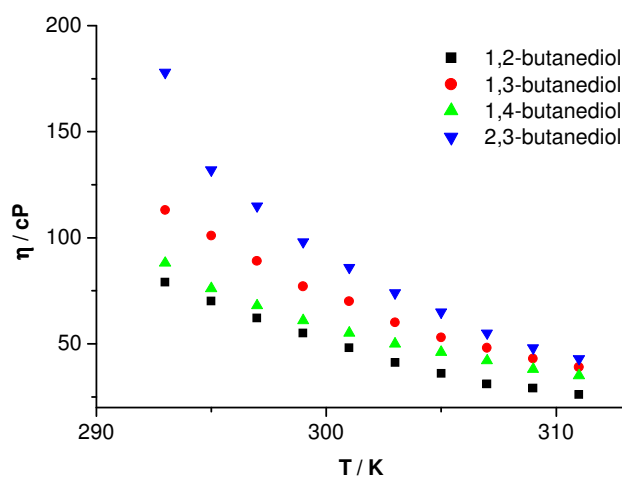


Figure 3.22: Plot of viscosity as a function of temperature for all the butanediol systems at 20% ChCl

Figure 3.22 shows the change in viscosity with temperature and it can be seen that the position of the hydrogen bond donors can have a large effect on the physical properties of the system. Simply by shifting the hydrogen bond donors one carbon over from a 1,2 to a 2,3 position, the viscosity more than doubles. A plot of inverse

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temperature versus log viscosity for all systems at 20% ChCl can be seen in Figure 3.23. This plot has been used to calculate the energy of activation of viscosity (E_η) which can be seen in Table 3.3. Figure 3.20 shows a very linear correlation in each case.

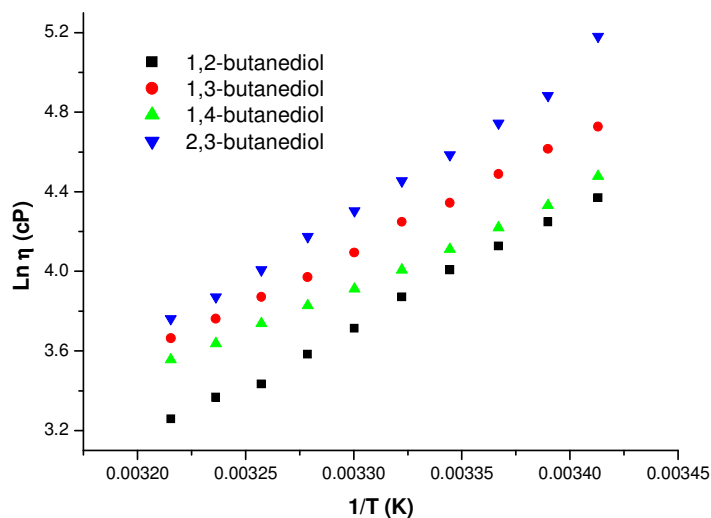


Figure 3.23: Plot of inverse temperature versus log viscosity for all the butanediol systems at 20% ChCl

Figure 3.24 shows the conductivity of the various butanediol isomers as a function of ChCl composition

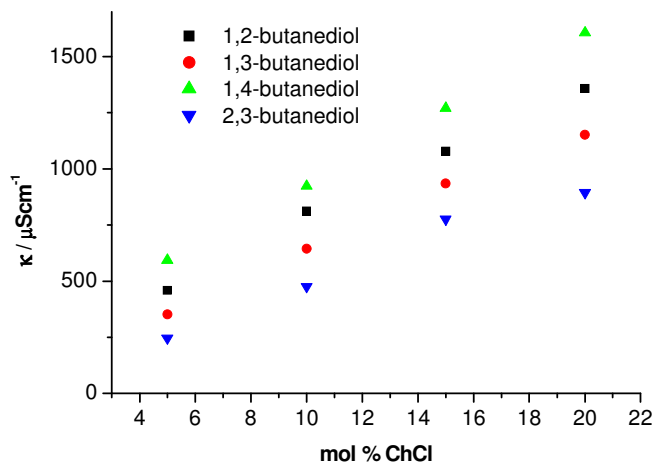


Figure 3.24: Conductivity of the various isomers of butanediol as a function of molar composition of ChCl

From what has been seen in the viscosity experiments, it would be expected that the more viscous systems, in this case the 2,3 system, should be the least conductive, especially since each isomeric system contains exactly the same amount of charge

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carrying species. Hence the least viscous systems should conduct more. As can be seen in Figure 3.25, this is not the case.

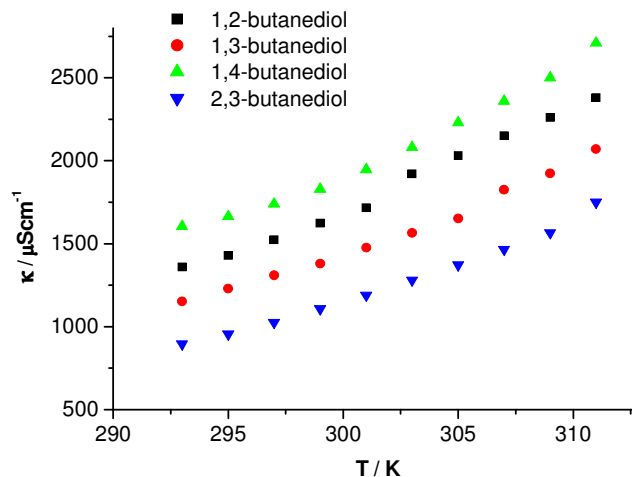


Figure 3.25: Plot of conductivity as a function of temperature for all the butanediol systems at 20% ChCl

From the viscosity results the proposed trend for conductivity would be $2,3 < 1,3 < 1,4 < 1,2$. However the order of the 1,4 and 1,2 isomers is in fact inverted suggesting that there is a difference in the way 1,4-butanediol complexes to the chloride ion of ChCl compared to the other butanediols. A possible explanation could be that when 1,4-butanediol complexes to the chloride ion, it is able to “wrap” around the anion more tightly than the other diols due to the hydrogen bond donors being on the end of the alkane chain, which would possibly result in a smaller volume. The smaller the complex, the more easily it should be to move around in the system and pass the electrical charge between the other charge carriers. An alternative explanation may come from the fact that 1,4-butanediol may only complex one molecule to the anion, rather than two as is believed to be the case with the other butanediols.

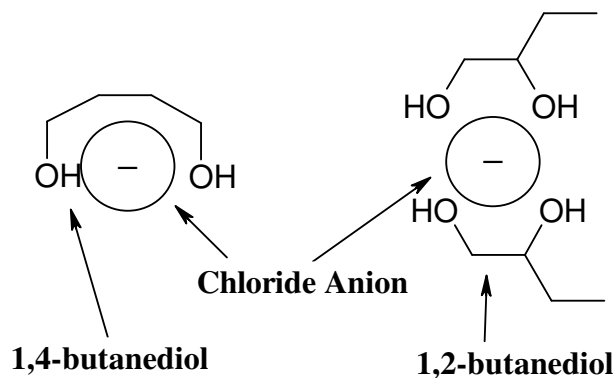


Figure 3.26: Diagrammatic representation of the possible complexes of the various isomers of butanediol

From the diagram shown in Figure 3.26, it is possible that one molecule of 1,4-butanediol has a large enough space between the hydrogen bond donor groups, that it envelopes the chloride anion so much that only one molecule can complex around it. It is thought that the space between the hydrogen bond donor groups on the other butanediols, for example 1,2-butanediol, is not large enough to completely “wrap” around the chloride anion and so more than one molecule can complex.

A plot of inverse temperature versus log viscosity for all systems at 20% ChCl can be seen in Figure 3.27. This plot has been used to calculate the energy of activation of conductivity (E_A) which can be seen in Table 3.3.

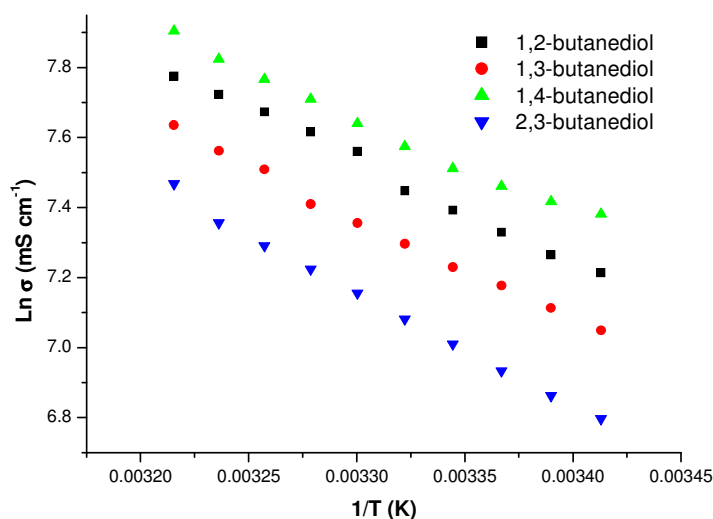


Figure 3.27: Plot of inverse temperature versus log viscosity for all the butanediol systems at 20% ChCl

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As has been suggested throughout Section 3.1., as the viscosity of the system decreases, the surface tension of the system should be seen to increase as well. The surface tension data for the four isomers can be seen in Figure 3.28.

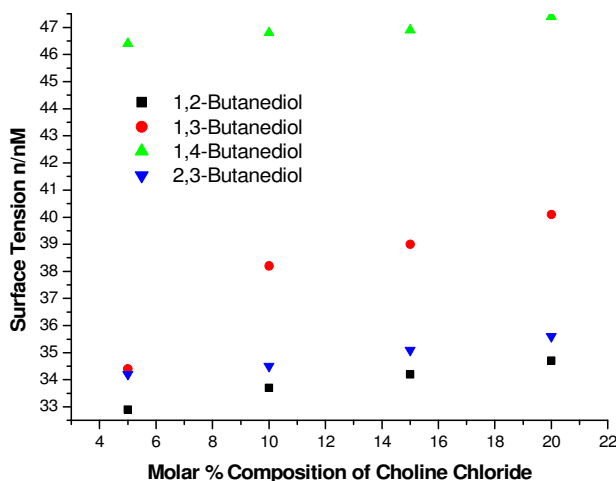


Figure 3.28: Surface tension of the various isomers of butanediol as a function of molar composition of the system in terms of ChCl

The data shown in Figure 3.28 shows a different trend to that observed for the viscosity results. The results for viscosity followed the trend $2,3 > 1,3 > 1,4 > 1,2$, whereas the surface tension trend follows $1,4 > 1,3 > 2,3 > 1,2$. 1,4-butanediol has the highest surface tension, due to the nature of its intermolecular hydrogen bonding, since 1,4-butanediol has hydroxyl groups on the two ends of the molecule, the hydrogen bonding causes a linear “chain” which essentially holds the dialcohol in a fixed conformation which therefore requires greater force to penetrate through than the other butanediol isomers. The other diols, when complexed, have the hydrogen bond donors locked into a fixed position but the substituents on the outside of the hydrogen bond donors are not locked into any conformation and so have free rotation. This results in less dense packing of the system, which gives the systems a lower surface tension.

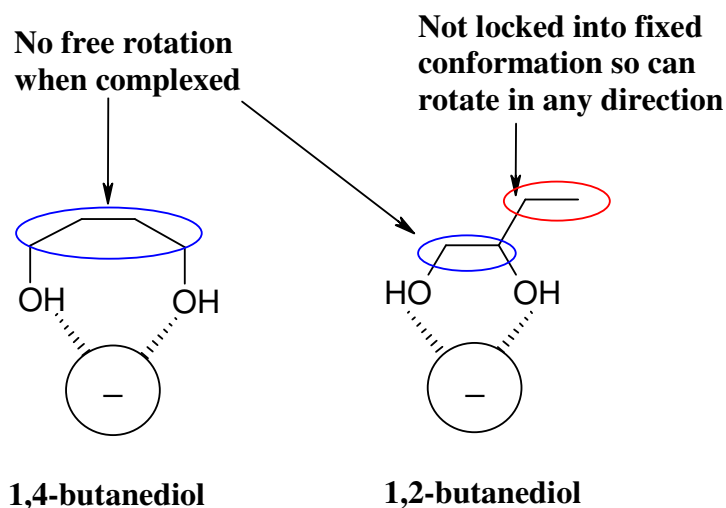


Figure 3.29: Diagrammatic representation of the possible free rotations of the various butanediol isomers

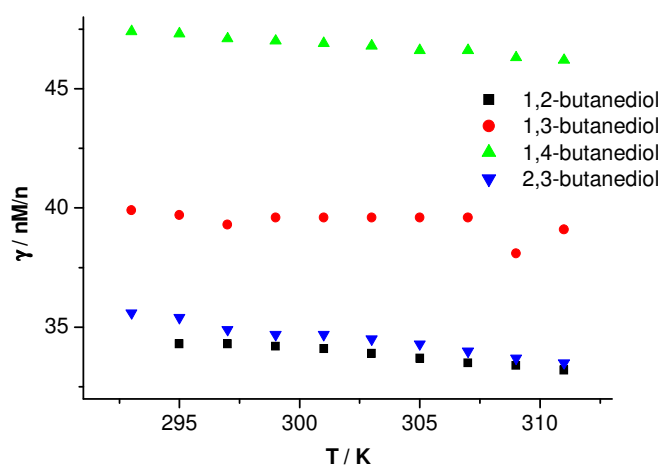


Figure 3.30: Plot of surface tension as a function of temperature for all the butanediol systems at 20% ChCl

The plot in Figure 3.30 shows that there is quite a variation in the surface tension of the various isomeric systems. Again by using the surface tension data, the average hole sizes have been calculated and compared to the energies of activation of viscosity and conductivity that have also been calculated. These data can be seen in Table 3.3. Using Figure 3.7 which shows the correlation between E_η and r_i/r_h it can be seen that for the 1,4- isomer the average ion size is 2.31 Å whereas for the 2,3- isomer the average ion size is 3.03 Å.

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Table 3.3: Select energies of activation of both viscosity and conductivity for all butanediol isomer based systems

HBD	Mol % ChCl	E_{η} (kJmol ⁻¹)	$\ln \eta_0$	E_{κ} (kJmol ⁻¹)	$\ln \kappa_0$	rh (Å)
1,2-butanediol	20	48.38	-15.48	-24.72	17.35	1.802
1,3-butanediol	20	45.74	-14.05	-24.48	17.09	1.676
1,4-butanediol	20	37.92	-11.13	-22.35	16.52	1.542
2,3-butanediol	20	57.31	-18.44	-27.53	18.09	1.779

More insight can be gained from the density of each of the systems. Figure 3.31 shows that as expected the density increases with increasing ChCl concentration.

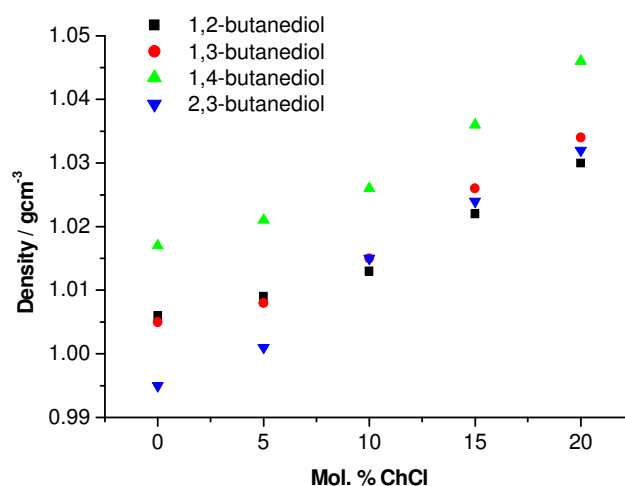
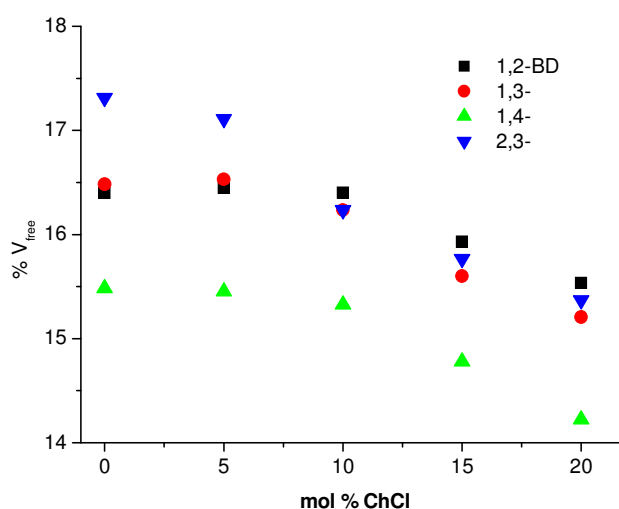


Figure 3.31: Density of the various isomers of butanediol as a function of molar composition of the system in terms of ChCl



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Figure 3.32: Percentage molar free volume of the various isomers of butanediol as a function of molar ChCl composition

At low ChCl content the salt has little effect upon the free volume of the liquid. Above 10 mol % a linear decrease in V_{free} is observed. It is noteworthy that the 1,2-, 1,3- and 2,3- isomers have similar V_{free} values whereas the 1,4- isomer has significantly less free volume suggesting a more ordered structure. This explains the higher viscosity and surface tension of the 1,4- isomer compared to the other isomers, but not why the 1,4, isomer has a significantly larger conductivity than the other liquids. This difference must come from a change in the mobile species as discussed above. The data presented here do not, however, allow a definitive mobile species to be identified.

3.3 Variation of the Number of Hydrogen Bond Donating Groups

So far this report has only investigated the effects of using two alcohol groups on each hydrogen bond donor when forming a DES with ChCl. This section will look at the effect of taking the basic 1,2-ethanediol structure and adding $(CHOH)_x$. The compound investigated is glycerol.

3.3.1 Physical Properties of Glycerol with ChCl

With glycerol, viscosity, conductivity and surface tension have all been measured as functions of temperature and molar percentage composition with ChCl.

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As with all viscosity measurements carried out during this study, the results for glycerol show exponential decay as the temperature is increased. Pure glycerol is a viscous liquid. In fact it is much more viscous 1,2-ethanediol (approximately 20 times greater) and so initially results are expected to show very high viscosities when ChCl is added. Figure 3.31 however shows that as the ChCl content increases the viscosity actually decreases.

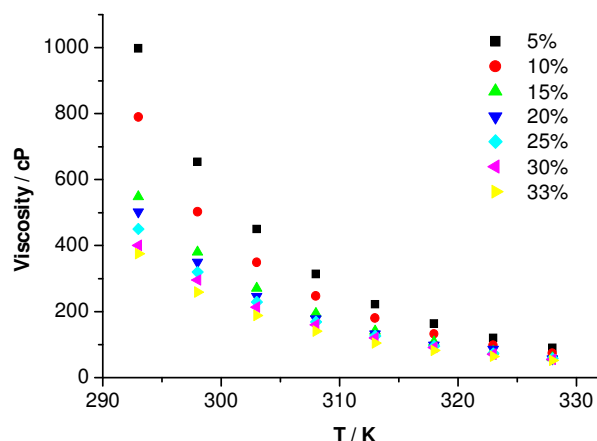


Figure 3.33: Plot of temperature versus viscosity as a function of ChCl composition for glycerol the systems

This trend is more obvious when the viscosity is taken at one temperature and compared as a function of molar percentage composition of ChCl. This can be seen in Figure 3.34.

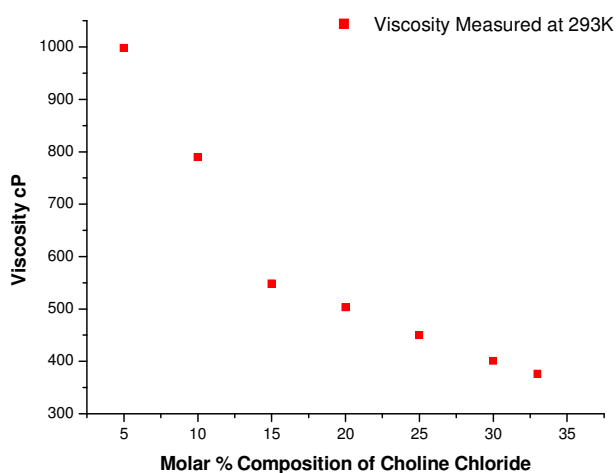


Figure 3.34: Plot of molar percentage composition of ChCl versus viscosity at 293K for the glycerol systems

The reason for this is thought to be due to the additional alcohol group increasing the amount of intermolecular forces in the pure system which results in a 3-D as shown in Figure 3.35.

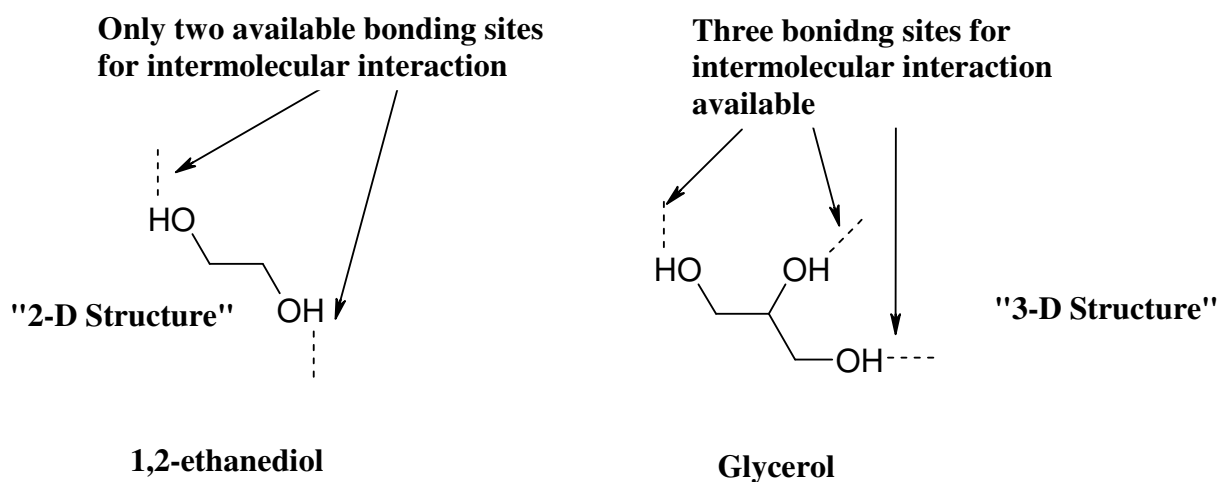


Figure 3.35: Schematic diagram of the interactions occurring in 1,2-ethanediol and glycerol

The fact there are three hydrogen bond donor sites in glycerol as opposed to two in 1,2-ethanediol, means that there is a greater degree of hydrogen bonding to other molecules and so the addition of ChCl interrupts this structure since some of the alcohol groups no longer interact between each other they interact with the ChCl. The end result of this is a system with a greater degree of freedom, hence the reduction in viscosity.

With viscosity decreasing as more charge carrying species are added to the system, it is largely expected that conductivity should increase as more ChCl is added. Despite the viscosity decreasing as more ChCl is added, the viscosity is still relatively high and so the conductivity would be expected to significantly smaller than for 1,2-ethanediol. This is exactly what is seen and can be seen in Figure 3.36.

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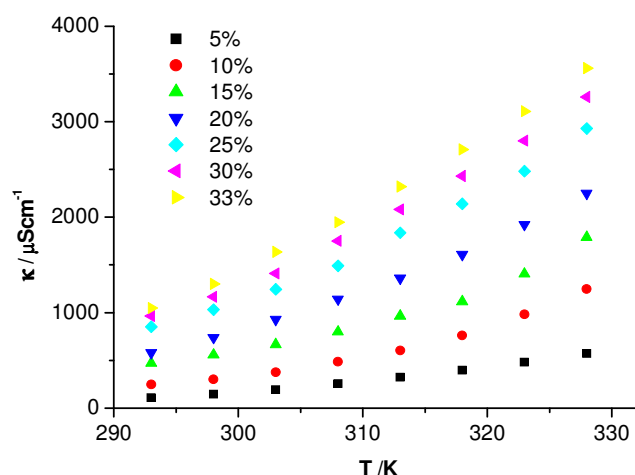


Figure 3.36: Plot of temperature versus conductivity as a function of ChCl composition for glycerol systems

However, what is interesting in these results is the rate of increase of conductivity as more ChCl is added. Since viscosity is decreasing as more charge carrier is added, it would be expected that the rate of increase of conductivity would be more of an exponential growth as molar percentage composition of ChCl increases than a linear relationship. This however is not the case. As can be seen in Figure 3.37, the rate of increase in conductivity is linear.

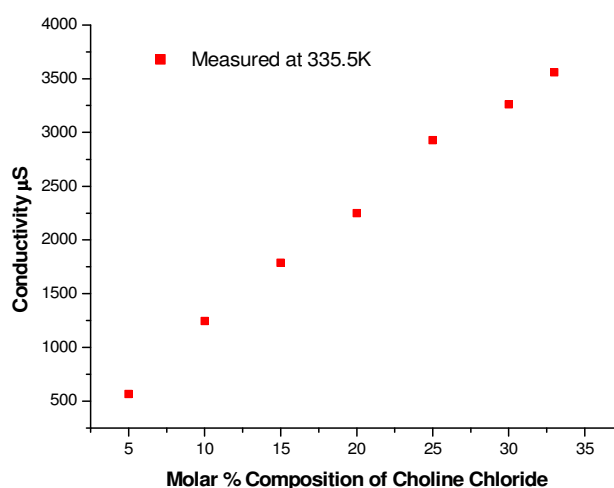


Figure 3.37: Plot of molar percentage composition of ChCl versus conductivity at 335.5 K for glycerol systems

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The surface tensions of the various compositions show very linear relationships as function of temperature. As would be expected from the viscosity results, the surface tensions decrease as more ChCl is added to the system. A plot of temperature versus viscosity can be seen in Figure 3.38. This is further evidence that the ChCl is breaking up the intermolecular forces of the glycerol as described in Section 3.3.1. What is interesting to note is that although 1,2-ethanediol and glycerol have significantly different viscosities in the pure state (20 and 1412 cP respectively at 303K) the addition of 33 mol% ChCl results in eutectic liquids with broadly similar viscosities (36 and 376 cP respectively).

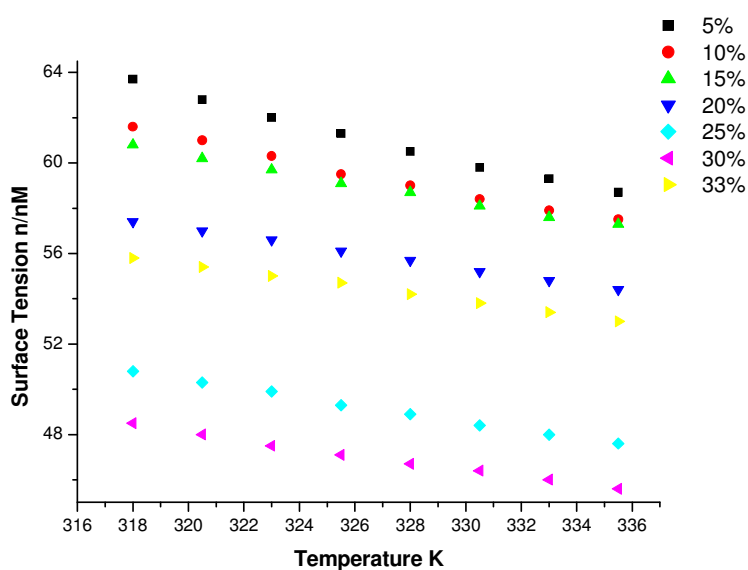


Figure 3.38: Plot of temperature versus surface tension for the glycerol systems

There is however a slight deviation from the predicted results. Although surface tension decreases as more ChCl is added to the system, there is an increase from 30% to 33%, despite the viscosity being at its lowest at 33%. This can be seen in Figure 3.39.

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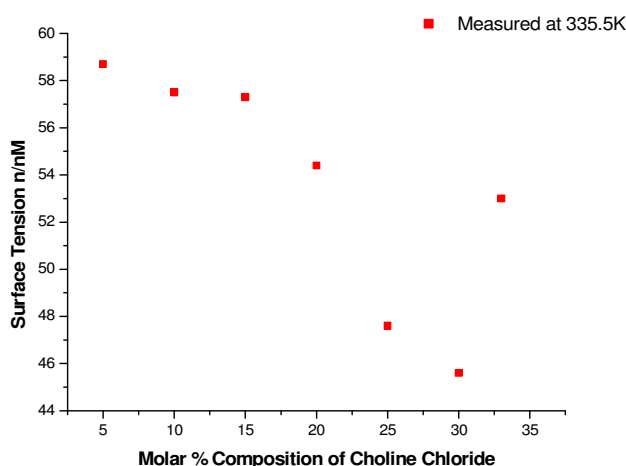


Figure 3.39: Plot of molar percentage composition of ChCl versus surface tension for the glycerol systems

From Figure 3.39, it can be seen that the surface tension of the systems decrease up to 30% ChCl with quite a step drop in surface tension going from 15% to 30%. It can be seen from this plot that from 30% to 33% there is a large rise in the surface tension. This would suggest that there is quite a change in the structure at this composition which equates to a 1:2 ratio of ChCl to glycerol. It is however more likely an indication of some errors in the measurements at 25% and 30%.

From the surface tension data it is possible to calculate the average hole size in the system. This data can be seen in Table 3.4.

Table 3.4: Energies of activation of both viscosity and conductivity for the glycerol systems

Mol % ChCl	E_{η} / kJmol^{-1}	$\ln \eta_0$	E_{Λ} / kJmol^{-1}	$\ln \kappa_0$	r_h / \AA
5	54.72	-15.60	-38.51	20.52	1.386
10	53.35	-15.29	-37.54	20.85	1.409
15	50.24	-14.34	-29.85	18.37	1.418
20	48.26	-13.63	-30.68	18.99	1.458
25	46.99	-13.21	-28.36	18.39	1.551
30	45.46	-12.67	-28.05	18.40	1.588
33	45.06	-12.62	-27.90	18.44	1.481

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As a result of the decrease in viscosity it would be expected that the density should decrease as well. This is exactly what is observed and a plot of this data can be seen in Figure 3.40.

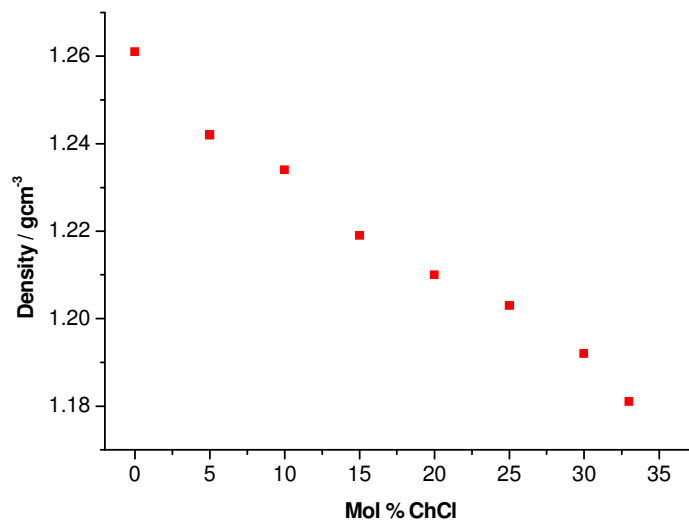


Figure 3.40: Density of the glycerol systems as a function of molar composition of the system in terms of ChCl

Figure 3.9 shows the change in V_{free} for the ChCl/diol systems. The free volume decreases for the ChCl/diol systems but for glycerol it increases as can be seen in Figure 3.41.

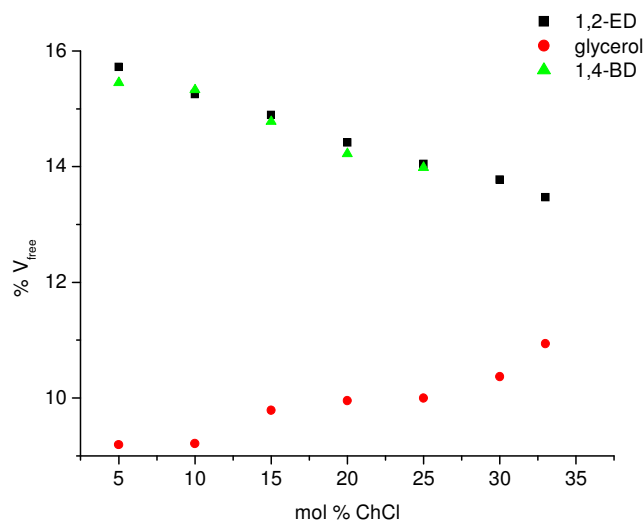


Figure 3.41: Plot of V_{free} as a function of mol % ChCl

This is consistent with the idea that pure glycerol is highly structured and the chloride anion breaks up this structure and increases the free volume of the liquid and decreases the fluid viscosity. It is clear that the structure of the glycerol eutectic is significantly different in structure from that of the diols described above.

3.4 At Which Composition do DESs Become Ionic Liquids?

As described above Walden plots have previously been used to describe the conductivities of ionic liquids. While there is clearly no validity behind the application of the Walden rule to ionic liquids it is interesting to carry out this analysis for DESs to see how they compare with ionic liquids with discrete anions. Figure 3.42 shows a plot of molar conductivity vs. fluidity ($1/\eta$) for the data presented in a recent review by Galiński *et al.* for ionic liquids with discrete anions.²⁹ The scatter in Figure 3.42 is thought to be primarily due to the difference in size between the ions. It has previously been shown that eutectic mixtures of quaternary ammonium salts with hydrogen bond donors form liquids at ambient temperatures and the conductivity of these liquids obey equation (3.9).¹⁴ It has therefore been assumed that DESs can therefore be classified as ionic liquids and Figure 3.42 shows some that these data presented above fit the classification of Angell.¹⁵

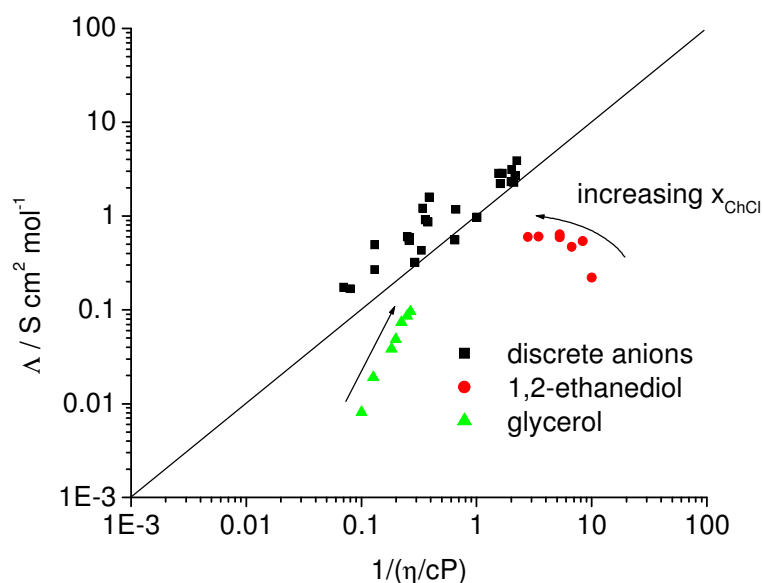


Figure 3.42: Plot of molar conductivity vs. fluidity for a range of ionic liquids with discrete anions and mixtures of ChCl with glycerol and ethylene glycol at 293 K

The ability to vary the composition of Lewis or Brønsted acid adds an additional dimension to the tuneability of the eutectic-based ionic liquids. To test the hypothesis that an ionic liquid can become a solution is relatively difficult as most complexing agents are solid at ambient temperature and hence a true test should be conducted at the melting point of the complexing agent. This adds the additional complexity that the interaction between the anion and the complexing agent will be significantly affected by the temperature. Lecocq *et al.* used ^{13}C and ^{35}Cl NMR spectroscopy to show that at 110°C $1\text{BMMICl}:1\text{ZnCl}_2$ varies its structure with time from $[\text{BMMI}]^+[\text{ZnCl}_3]^-$ to $[\text{BMMI}\dots\text{Cl}\dots\text{ZnCl}_2]$.³⁰ What is important however is the behaviour of ionic liquids at ambient temperature. The only exceptions that we have found are with diols and triols which are liquid at ambient temperature and form relatively shallow eutectics when mixed with quaternary ammonium salts.

Figure 3.43 shows the molar conductivity of ChCl in a number of glycolic liquids. The molar conductivity was calculated by

$$\Lambda = \kappa M / \rho \quad (3.15)$$

where κ is the conductivity, ρ is the density and M is the molar mass which is take as being the molar mass of the two components multiplied by their mole fraction in the mixture. The ionic radii were calculated using commercially available software assuming that each chloride ion is coordinated by one glycol molecule.²⁸

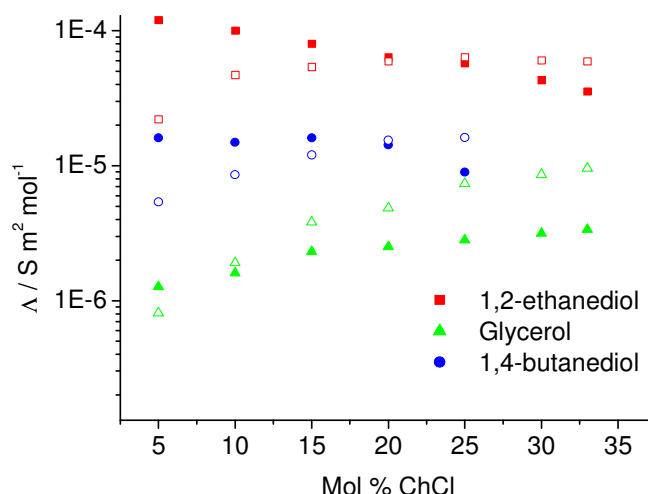


Figure 3.43: Plot of molar conductivity vs. ChCl content for a variety of mixtures with different glycols at 293 K. Open symbols are the measured values and filled symbols are the values calculated using equation 3.8.

At low concentrations most of the ions exist as ion pairs and the molar conductivity is relatively low. As the concentration of salt increases, concentration of triple ions increases which results in a rise in the molar conductivity.



This is well known to occur in non-aqueous solutions.^{20,21} As the salt concentration increases the amount of free solvent decreases and at some point there must be no free solvent molecules as they are all coordinated to the ions. At this point the movement of free “solvent” is prohibited and it is only ionic species that can move. Under these conditions the mobility of the complex species is severely hindered due to their size and the decreased free volume of the liquid. For 1,2-ethanediol a maximum is observed in molar conductivity at approximately 20 mol % ChCl. According to equation (3.9) the limiting molar conductivity will be inversely proportional to the viscosity and it would be expected that the molar conductivity would decrease as hole mobility replaced ion mobility as the dominant factor in charge transport. It is at this composition where hole mobility overtakes ion mobility as the dominant mechanism for charge transfer that we propose an ionic liquid is formed.

Figure 3.41 shows the molar conductivity of the glycolic mixtures as a function of fluidity. It is clear that the molar conductivity values of the dilute solutions differ significantly from the Walden rule which is to be expected as the conductivity is dependent upon the number of charge carriers and the main mobile species which govern the fluidity of the liquid are the glycol molecules. Hence the conductivity is greater than that predicted by equation (3.8). As the concentration of salt increases the number of free solvent molecules decrease and the conductivity approaches that of the other liquids where mobility is limited by hole mobility. Hence the definition by Angell that all ionic liquids obey the same conductivity vs. fluidity correlation is a good approximation to determining whether a material is an ionic liquid. A more rigid definition is possibly that an ionic liquid is a fluid where equation (3.8) is valid the justification being that in an ionic liquid the transport of charge is limited by hole mobility.

To determine the composition at which the eutectics in Figure 3.43 change from being ionic liquids to solutions of salt in glycols, the molar conductivity was calculated

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using equation (3.8) and plotted against the measured conductivity and it can be seen that significant deviations are seen up to a composition of 20% 1,2-ethanediol and 1,4-butanediol. Thereupon relatively good correlation was observed. 1,4-butanediol could not be studied above 25 mol % because the temperature at which a homogeneous solution formed was above 20°C. The other isomers of butanediol (1,2-, 1,3- and 2,3-) were also tested and showed similar trends to those observed for 1,4-butanediol but these all reached supersaturation above 20 mol% at 20°C and hence approached the properties of ionic liquids but could not exhibit the decrease in molar conductivity with concentration.

For glycerol the correlation between the values calculated from equation (3.8) and the measured values is closer at lower concentrations. This could be seen as an exception that shows the validity of the assumption, in so far as the very high viscosity of the pure fluid and the low free volume, as indicated by the high surface tension, mean that charge transport is still limited by hole transport, only in this exceptional case the mobility of the “solvent” molecules (i.e. glycerol) is not due to them all being complexed to the Cl⁻ but rather in this case they are hindered from moving by other solvent molecules.

If the mobility of charge is limited by the availability of suitably sized holes then one diagnostic test for determining where most ionic liquids take on the properties of solutions would be that the molar conductivity passes through a maximum where ion mobility and hole mobility are at equilibrium.

3.5 Poly-Alcohol/Sugar Based Deep Eutectic Solvents

In addition to the di and tri alcohols investigated in sections 3.1., 3.2. and 3.3. other OH containing species were investigated. The polyols investigated are erythritol (14), xylitol (15), D-(-) fructose (16) and D-glucose (17). Each compound was added to ChCl and phase diagrams were constructed for each system.

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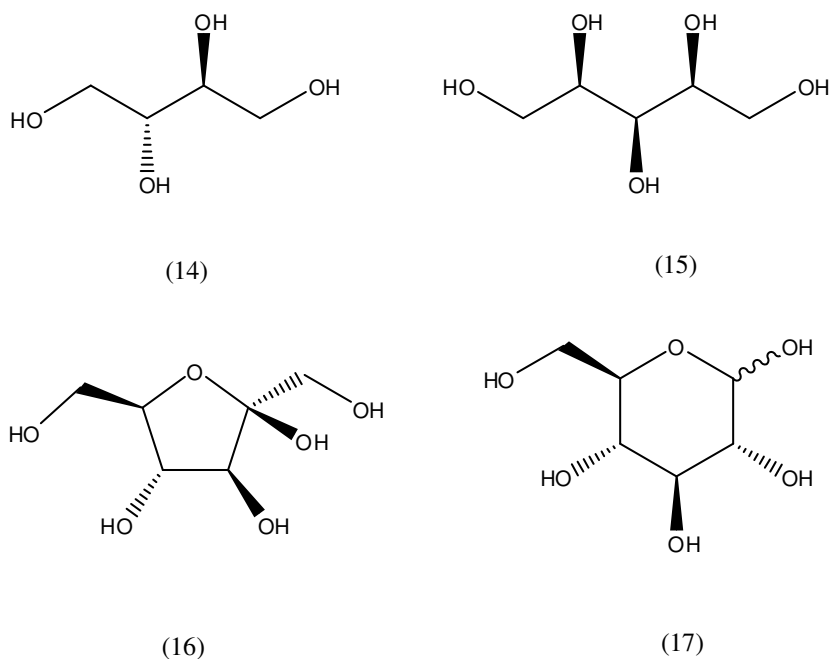


Figure 3.44: Diagrammatic representations of polyols investigated in section 3.5.

Table 3.5: Freezing point data for ChCl:Polyol systems investigated

Ratio of ChCl:Polyol	T _f ChCl:Erythritol	T _f ChCl:Xylitol	T _f ChCl:D-(-) Fructose	T _f ChCl:D- Glucose
2.5:1	N/A	16 °C	37 °C	44 °C
2:1	0 °C	-4 °C	10 °C	15 °C
1.5:1	-10 °C	2 °C	13 °C	24 °C
1:1	-16 °C	-3 °C	20 °C	31 °C
1:1.5	-8 °C	4 °C	28 °C	39 °C
1:2	30 °C	7 °C	33 °C	N/A
1:2.5	N/A	N/A	36 °C	N/A
1:3	N/A	N/A	40 °C	N/A

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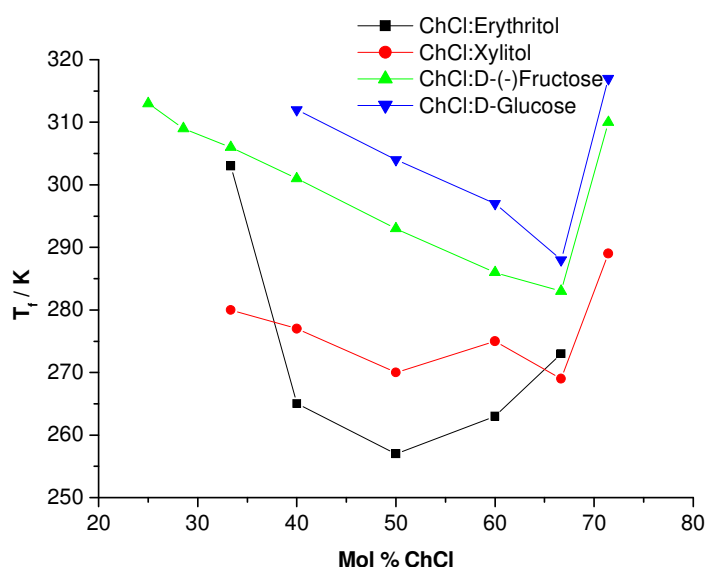


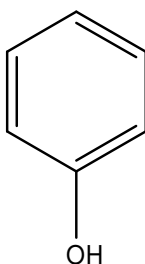
Figure 3.45: Phase diagram of ChCl:Polyol mixtures

From the data shown in Figure 3.45, there are some interesting trends with regards to the number of OH groups there are in the polyol. It can be seen that DES's can be formed in molar ratios where ChCl is in molar excess. The results for the 4 OH containing species erythritol (14), show that the eutectic point occurs at a ratio of 1:1 ChCl:polyol. As the number of OH groups increases to 5, the eutectic point shifts from a ratio of 1:1 to a ratio of 2:1 ChCl:polyol as seen in the D-(-) fructose (16) and D-glucose (17) cases. What is perhaps most interesting about the data shown in Figure 3.44 is that the data for xylitol (15) shows two inflection points suggesting two eutectic points. These point occur at 1:1 which is the same as the erythritol system and at 2:1, the same seen in the D-(-) fructose (16) and D-glucose (17) systems. The erythritol system is thought to form the eutectic at a ratio of 1:1 due to the ChCl being able to hold 4 OH interactions, analogous to the eutectic of diols being at a ratio of 1:2 ($2 \times 2 \text{ OH} = 4 \text{ OH}$). Since xylitol, D-(-) fructose and D-glucose all contain 5 OH groups more than one ChCl molecule is thought to interact. Because both D-(-) fructose and D-glucose are in cyclic form the angle of interaction between the Cl anion and OH groups is more favourable to allow 2 ChCl molecules to form hydrogen bonds. This would explain the larger depression in freezing point than in the case of xylitol. Because of the straight chain nature of xylitol it is possible to allow 2 Cl anions to form hydrogen bonds with

OH groups however the repulsion between ChCl molecules is likely to reduce this interaction.

3.6 Mono Functional Alcohol Deep Eutectic Solvents

This chapter has gone into a lot of detail about the use of alcohols with two or more –OH groups to form DES's but it is possible to form a DES from choline chloride and phenol which contains only one –OH group.



(18)

From the viscosity and conductivity data shown in Figures 3.45 and 3.46 respectively, the eutectic point appears to be at a ratio of 4:1 (Phenol:ChCl). The surprising result is perhaps the viscosity of these systems, where the eutectic point exhibits a viscosity of 30 cP at 2 °C. Due to the extremely low freezing point of some of these mixtures near the eutectic point (< -40 °C), a phase diagram was not constructed due to the large degree of inaccuracy of measuring the freezing points at such low temperatures.

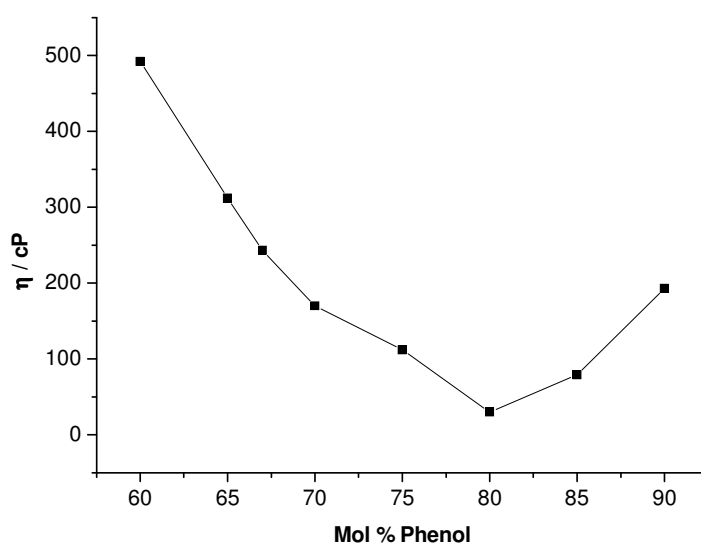


Figure 3.45: Viscosity of ChCl:Phenol mixtures as a function of composition at 275K

The viscosity of this system is amongst one of the least viscous DES's formed from two solid components. Currently it is thought that it offers the lowest viscosity of any ChCl/hydrogen bonding compound mixture. This is attributed to the electron-withdrawing effects of the delocalised π -electron system in the aromatic ring. Through the hydrogen bond between the OH and Cl formed, the aromatic group increases the amount of delocalisation of Cl anion from the choline cation, hence an increase in entropy of the system, which results in the lower viscosity.

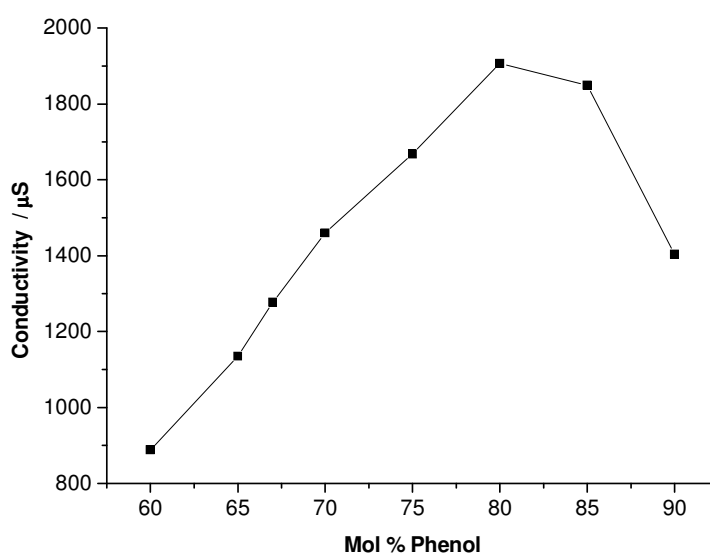


Figure 3.46: Conductivity of ChCl:Phenol mixtures as a function of composition at 275K

The conductivity, as shown in Figure 3.45, of this system reaches a maximum at a ratio of 1:4 (ChCl:Phenol), the same ratio at which the viscosity is at its lowest. From this it can be inferred that this is the eutectic point of this mixture.

3.7 Conclusions

This chapter has characterised the conductivity and fluidity of numerous ChCl/ alcohol based systems. A variety of alcohols form DESs but it was found that only those where the freezing point of the pure alcohol is close to or above ambient temperature do stable liquids form. A wide variety of polyols form stable liquids, including sugars. This offers the potential to create benign, even edible liquids from naturally occurring salts and sugars.

It has been shown that mixtures of quaternary ammonium salts with glycols form homogeneous fluids with the properties of ionic liquids when the mole fraction of the salt exceeds 0.2. At higher salt concentrations the dominant mode of charge transport is via the mobility of holes and the mixture has the viscosity and conductivity characteristic of an ionic liquid and below this concentration the properties can be described by the theories related to concentrated ionic solutions.

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CHAPTER 4

Investigation of Intramolecular Interactions in Deep Eutectic Solvents Using Solvatochromic Probes

4.1 Introduction

4.1.1 Solvatochromism

*4.1.2 Kamlet-Taft Parameter, Polarisability/Dipolarity π^**

4.1.3 Hydrogen Bonding - Hydrogen Bond Donor and Hydrogen Bond Acceptor Parameters α and β

4.1.4 $E_T(30)$ Betaine Dye Scale

4.1.5 Polarity of Ionic Liquids

4.2 Results and Discussion

4.2.1 $E_T(30)$ Betaine Dye Scale Results

4.2.2 Polarisability and Hydrogen Bond Acceptor/Donor Parameters π^ , α and β*

4.2.3 Effect of Choline Chloride Concentration

4.3 Conclusions

4.4 References

CHAPTER 4 - Investigation of Intramolecular Interactions in Deep Eutectic Solvents Using Solvatochromic Probes

4.1 Introduction

Solvent polarity has in the past been measured by simple electrostatic models for intermolecular solute–solvent interactions.¹ By assuming the solvents to be a non-structured homogeneous continuum, dielectric constants, ϵ_r , dipole moments μ , and refractive indices n_D , have been used as macroscopic summations of solvent polarity.¹ However, there is a fundamental flaw in these measurements. As solute–solvent interactions take place on a molecular–microscopic level, there are individual, mutually interacting solvent molecules surrounding the ions or molecules of the solute. This leads to solvation shells of a varying degrees of proximity to the solute molecule, commonly referred to as the cybotactic region.²⁻⁹ Other specific interactions such as hydrogen-bond donating/accepting, electron pair donating/accepting or solvophobic effects add to the poor correlation of solvent effects using the macroscopic solvent parameters.¹

Since the 1970's there has been a considerable amount of research carried out to investigate the cybotactic region of the solute molecule.²⁻⁹ Measurements of solvatochromatic shifts have been used to determine solute-solvent interactions such as the polarisability/dipolarity parameter, π^* , of the solvent as well as giving information about hydrogen bond donor (HBD), α and/or acceptor (HBA), β abilities of the solvent.⁹

To understand the behaviour of a solvent involved in a reaction, it is important to understand the solute-solvent interactions of the system. Since this project is in the area of Deep Eutectic Solvents, this chapter investigates the polarisability and hydrogen bond donor/acceptor properties of several Deep Eutectic Solvents.

4.1.1 Solvatochromism

The ability of a chemical substance to change colour in a variety of solvent polarities is termed solvatochromism.¹⁰ The change in colour is due to changes in the electronic absorption and emission spectra of the chemical substance. The displacement of the electronic spectrum for a specific solute in different solvents is known as a solvatochromic shift. There are two types of shift that can be observed in solvatochromism. A positive shift with increasing solvent polarity is termed bathochromic shift, or red shift, and a negative shift with increasing solvent polarity is

CHAPTER 4 - Investigation of Intramolecular Interactions in Deep Eutectic Solvents Using Solvatochromic Probes

termed hypsochromic shift, or blue shift. The solvatochromic shift depicts the relationship of the absorption/emission spectra and the polarity of the solvent and gives information on the electronic excited states of the molecule. These electronic states each have a specific energy, denoted E . In quantum mechanics the Schrödinger equation relates this energy to the wavefunction, Ψ , and the Hamiltonian operator, H , by ¹¹

$$H\Psi = E\Psi \quad (4.1)$$

The initial relaxed electronic states correspond to the most stable nuclear configurations of a molecule in an isolated environment. It is proposed by the Franck-Condon principle that the solvation pattern of both the initial relaxed and the first excited state, also known as the Franck-Condon state, are the same. This is because the time required to electronically excite the molecule ($\sim 10^{-15}$ s), is much less than the time required for the molecule to carry out vibrational or rotational transitions ($\sim 10^{-12}$ - 10^{-10} s).¹² This means that the nuclei of the absorbing molecule and the solvation sphere do not exhibit much change during the electronic transition. Reorientation of the solvation sphere will only occur if the lifetime of the excited state is large enough.

Figure 4.1 shows the processes involved in absorption/emission, $S_0 + h\nu \rightleftharpoons S_1$. In the process of absorption/emission the initial (S_0) and final (S_1) states are linked by a radiative transition. In Figure 4.1 it can be seen that the environment in which the molecule being excited is in, the energy levels in which (S_0) and (S_1) are affected. The first environment shown in Figure 4.1 is the absorption ($S_0 \rightarrow S_1$) of energy under gas phase conditions ($h\nu_{\text{vac}}$) and the second is that of the absorbing molecule surrounded by a solvent ($h\nu_{\text{sol}}$). The energy that stabilises these electronic states is known as the solvation energy, E_s . The polarity of the solvent is the determining factor in the solvation energy and it is this difference between the solvation energies of the initial and final state (E_s^0 and E_s^1 respectively) that causes the solvatochromic shift.

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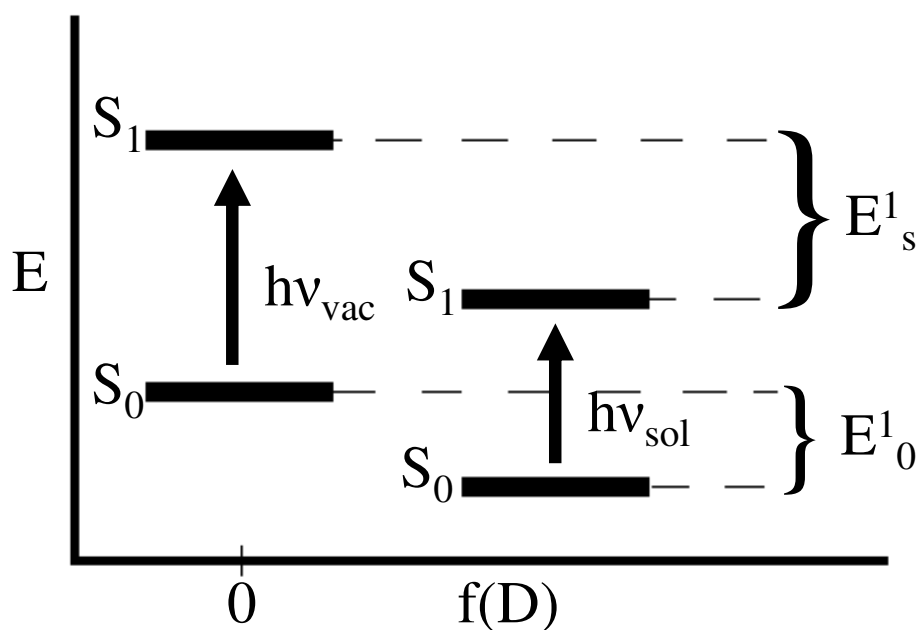


Figure 4.1 Solvatochromic shift energy diagram for the case of a vacuum and a solvent $f(D)$ is the Onsager solvent polarity function $2(\epsilon - 1)/(2\epsilon + 1)$

A bathochromic shift results from the greater stability of the S_1 state by solvation, over the S_0 state. For a hypsochromic shift the S_0 state is stabilised more strongly than the S_1 state by solvation. By observing the solvatochromic shifts in various solvents, it is possible to describe the relative energies of the electronic states of a molecule. The data obtained from the shifts, can be used to determine a number of the physical properties of the molecule such as the dipole moment and polarisability, π^* . In addition, information about specific interactions such as hydrogen bonding, α/β , can be obtained.

For a particular probe molecule to be considered useful for measuring these properties of the solvent, several requirements described by Reichardt must be met;¹

- 1) The compound should be available by either easy synthesis or commercially
- 2) It should be in a crystalline form that has definite chemical structure, is easy to handle and is stable in storage, and more importantly stable in solution.
- 3) It should possess sufficient solubility in both non-polar and polar solvents.
- 4) There should be no chemical reaction with the solvent.
- 5) The extent to which the longest wavelength UV/vis/near-IR absorption band is shifted, either bathochromically or hypsochromically, with increasing solvent polarity, should be as large as possible.

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4.1.2 Kamlet-Taft Parameter, Polarisability/Dipolarity π^*

The origins of the π^* scale stems from a combination of different methods previously used to describe the polarity of a solvent. In 1948, Winstein introduced the Y scale.¹³ This was the first empirical parameter used to describe the ‘solvent ionising power’. By 1958 the first spectroscopic solvent polarity scale was developed by Kosower, known as the Z scale.¹⁴ This scale was compiled by using the solvent-sensitive intermolecular charge-transfer (CT) absorption of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide. There have since been many solvent polarity scales based on ultraviolet (UV)-visible or near infra-red (IR) spectroscopy developed.

The π^* scale was developed by measuring the solvent induced shift of several nitroaromatic indicators and is one of the most popular scales employed to date.^{15,16} The solvents were placed in order of longest to shortest wavelength seen in the $\pi \rightarrow \pi^*$ absorption band. The electronic transition is a result of intramolecular charge transfer from the electron donating group to the electron accepting group through the aromatic ring of the dye molecule. The π^* scale currently has been normalised to give the range of 0.00 to 1.00 referring to cyclohexane and dimethyl sulfoxide respectively. These solvents were chosen because they are completely non-hydrogen bond donating. To prevent the inclusion of specific dye/solvent effects and spectral anomalies, more than one dye was used and the solvatochromic shifts averaged. The value obtained from the π^* data arises from a measurement of dispersive, inductive and electrostatic dye/solvent interactions. This data therefore corresponds to a mix of both the dipolarity and the polarizability of the solvent.

The π^* scale is dependant upon a linear solvation energy relationship (LSER) combining a number of possible solvent effects on a solute.^{17,18} This relationship has the general form

$$XYZ = XYZ_0 + a\alpha + b\beta + SPPE \quad (4.2)$$

where XYZ and XYZ_0 can represent a particular solvent-dependent property of the system for a given solvent and in a standard reference solvent respectively. These solvent-dependent properties may be reaction rates, equilibrium constants or a position/intensity of spectral absorption. The α term is a measure of the hydrogen bond donor (HBD)

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interaction strength towards a solute. The β term is a measure of the hydrogen bond acceptor (HBA) strength of the solvent.¹⁵⁻²⁰ The a and b parameters are the respective hydrogen bonding constants associated with the solute. The *SPPE* term refers to the solvent polarity/polarisability effect. This term can be broken down further and expressed by its constituent parts as

$$XYZ = XYZ_0 + yY + pP + eE + bB \quad (4.3)$$

where the Y term represents one or the other solvent “polarity functions” and the P term refers to the “polarizability function”. The terms $a\alpha$ and $b\beta$ have been replaced by eE and bB which refer to electrophilicity and nucleophilicity respectively.

By using the LSER in equation 4.2, Kamlet and Taft *et al.* were able to correlate the characteristic values of the HBD, HBA and SPPE parameters for various solvents from the shift in peak position of a UV-visible absorption maximum of an indicator solute. They showed that the SPPE term could be simplified and expressed as a single parameter, π^* , which is a measurement of the ability of the solvent to stabilize a neighbouring charge or a dipole by dielectric interactions. The term π^* refers to the solvatochromic effects on $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic spectral transitions.

With the SPPE term substituted by π^* the equation becomes

$$XYZ = XYZ_0 + s(\pi^* + \partial\delta) + a\alpha + b\beta + h\delta_H \quad (4.4)$$

The s term is the susceptibility of XYZ to changing *SPP* and is dependant upon the solute. The term δ is a polarisability correction term that is given different values depending upon the nature of the solvent. For non-halogenated aliphatics, the value is equal to 0.0, for halogenated aliphatics the value is 0.5 and for aromatic solvents it is 1.0. When the electronic spectrum is bathochromically shifted, the coefficient of the δ term, ∂ , is equal to zero and, therefore, δ can be neglected.

Equation 4.4 can be further simplified to equation 4.5 if the correct conditions are met. For equation 4.5 to work accurately $\alpha = \beta = 0$ must be true. If the solvent is neither hydrogen bond acceptors nor hydrogen donators then this is true. If the solvent is a hydrogen bond acceptor ($\beta \neq 0$) but is not a donator ($\alpha = 0$) then 4.5 is true if the indicator solute is non-hydrogen bond donating ($b = 0$).

$$\nu_{\max} = \nu_0 + s\pi^* \quad (4.5)$$

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A selection of organic solvents with the respective π^* values are shown in Table 4.1

Table 4.1: π^ values for some selected organic solvents at room temperature and 1 bar pressure in ascending order.¹⁶*

Solvent	Solvent Type	π^*
Cyclohexane	NHB	0.00
Triethylamine	HBA	0.14
Carbon Tetrachloride	NHB	0.28
Ethanol	HBA-D	0.54
Ethyl Acetate	HBA	0.55
Tetrahydrofuran	HBA	0.58
Benzene	Ar-NHB-HBA	0.59
Methanol	HBA-D	0.60
Acetic Acid	HBA-D	0.66
Acetone	HBA	0.71
Acetonitrile	HBA-HBD	0.75
Dichloromethane	NHB	0.80
Pyridine	Ar-HBA	0.87
Dimethylformamide	HBA	0.88
Dimethyl Sulfoxide	HBA	1.00
Water	HBA-D	1.09

NHB = non-hydrogen bonding solvent; **HBA** = hydrogen bond acceptor; **HBD** = hydrogen bond donor; **HBA-D** = amphiprotic hydrogen bond acceptor-donor; **Ar** = aromatic solvent

4.1.3 Hydrogen Bonding - Hydrogen Bond Donor and Hydrogen Bond Acceptor Parameters α and β

Other parameters that can be accounted for in the Kamlet-Taft method are the hydrogen bonding components of a given system α and β . These describe the hydrogen bond donating and accepting abilities respectively.

A donor-acceptor interaction that specifically involves a hydrogen atom is referred

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to as a hydrogen bond. A hydrogen bond between two species can be either intermolecular or intramolecular. The common representation of a hydrogen bond is a broken line and can be seen in Figure 4.2.²¹

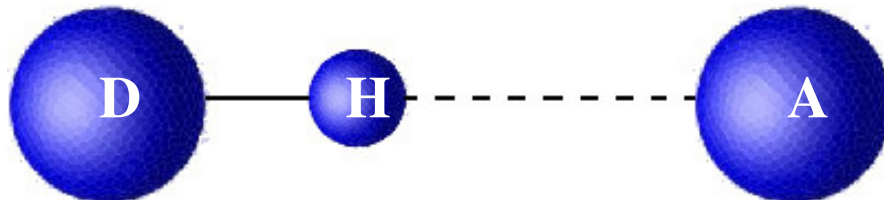


Figure 4.2 Representation of a hydrogen bond between a donor and an acceptor

A hydrogen bond can be formed between small and highly electronegative atoms, such as N, O or F. A species is capable of being a hydrogen bond donor when the electronegativity of the species, for example A in Figure 4.2, relative to H in a covalent bond is such that the withdrawal of electrons leaves the proton partially unshielded and the bond becomes capable of donating the proton. In order to interact with this donor bond, the acceptor species, for example B in Figure 4.2, must possess either a lone pair of electrons or polarisable π electrons. The strength of a hydrogen bond is found to be similar in strength to a van der Waals force, approximately 20 kJ mol^{-1} . The main difference between the two types of interaction is that a hydrogen bond is directional and this can give rise to discrete recognisable units which consist of two or more single molecules, whereas van der Waals forces are non directional. The hydrogen bonds found in compounds containing the groups -OH, -NH₂ or -NH- are an explanation for, among other effects, the higher boiling points than the isomeric molecules with no hydrogen directly attached to the oxygen or nitrogen atom. These stronger intermolecular forces result in larger lattice energies and hence require more energy to break the molecules apart.

Kamlet and Taft demonstrated that it is possible to measure the strength of a hydrogen bond by the UV-visible spectral data.^{17,18} Similar to the method for calculating π^* , a solvatochromic comparison method was used. From this method the α -scale of HBD acidities and β -scale of solvent HBA basicities were successfully constructed. By modifying equation 4.5 these hydrogen bonding interactions can be accounted for, as shown in equation 4.6

$$\nu_{\max} = \nu_0 + s\pi^* + a\alpha + b\beta \quad (4.6)$$

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The solvatochromic comparison method can be used to determine α values by comparison of solvent-induced shifts of the longest wavelength $\pi \rightarrow \pi^*$ absorption band of two similar probe molecules. Only one of these must be able to act as a HBA towards HBD solvents. The corresponding β values may be determined by an analogous method, where one of the probe molecules should act as a HBD towards solvents. Work by Kamlet and Taft^{17,18} and more recently by Marcus^{22,23} have produced values of α and β for a number of liquid solvents. As can be seen in Table 4.2, hydrogen bond donor/acceptor properties are both exhibited by some solvents, whilst some exhibit one, the other or neither.

Table 4.2: α and β values for some selected organic solvents at room temperature and 1 bar pressure.¹⁵⁻

20,22,23

Solvent	α	β
Cyclohexane	0.00	0.00
Triethylamine	0.00	0.71
Carbon Tetrachloride	0.00	0.00
Ethanol	0.83	0.77
Ethyl Acetate	0.00	0.45
Tetrahydrofuran	0.00	0.55
Benzene	0.00	0.10
Methanol	0.93	0.62
Acetic Acid	1.12	N/A
Acetone	0.08	0.48
Acetonitrile	0.19	0.31
Dichloromethane	0.30	-0.014
Pyridine	0.00	0.64
Dimethylformamide	0.00	0.69
Dimethyl Sulfoxide	0.00	0.76
Water	1.17	0.18

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4.1.4 $E_T(30)$ Betaine Dye Scale

The $E_T(30)$ scale is perhaps the most commonly used single parameter indicator series for solvatochromatic studies. The pyridinium *N*-phenolate betaine dye 2,6-diphenyl-4-(2,4,6-triphenylpyridio)-phenolate developed by Reichardt^{24,25} is the probe molecule used in this scale. This dye is often referred to as $E_T(30)$ because it was dye number 30 in a series of pyridinium *N*-phenolate betaine dyes tested by Reichardt.²⁴

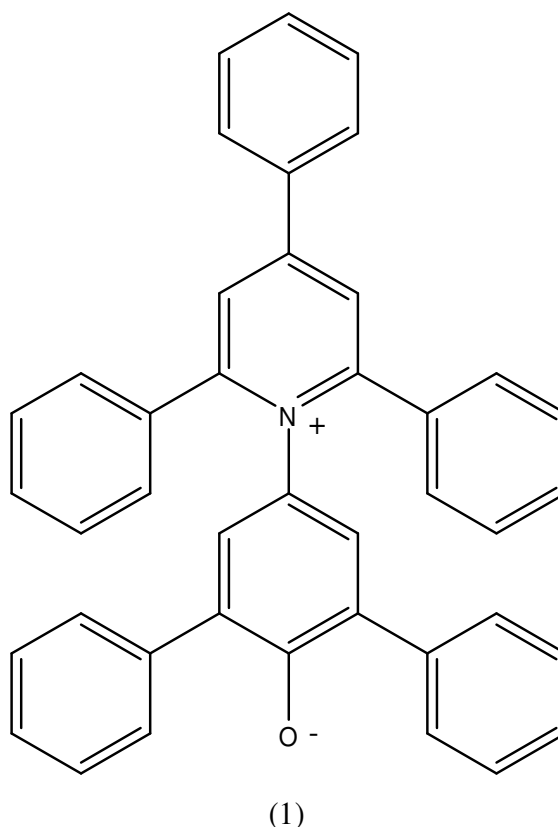


Figure 4.2 Electronic ground state structure of 2,6-diphenyl-4-(2,4,6-triphenylpyridio)-phenolate, $E_T(30)$

The 2,6-diphenyl-4-(2,4,6-triphenylpyridio)-phenolate molecule is largely polarisable due to its extensive aromatic 44 π -electron system. It consists of a strongly hydrogen-bonding/electron pair accepting group in the phenolate oxygen and a weak electron pair acceptor in the nitrogen of the pyridinium group.^{25,26} The electronic ground state of the molecule has been measured at $\mu \approx 15$ Debye.²⁷ This large dipole moment is suitable for the registration of dipole/dipole and dipole/induced dipole interactions

Reichardt's dye exhibit a very high degree of hypsochromacity. This negative

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solvatochromism is a result of the differences in the solvation on the ground state and first Franck-Condon excited state. As solvent polarity increases, the difference in the stability of the highly dipolar ground state, and the less dipolar Franck-Condon excited state increases. As can be seen in Figure 4.3, the Franck-Condon excited state is better stabilised in less/non-polar media than in polar media because the dipolarity of the excited state is much less than in the electronic ground state. As this excited state becomes less polar, (~ 15 Debye²⁷ to ~ 6 Debye²⁸) non-polar solvents exhibit a greater interaction with the solute hence offering a greater stability than the polar solvents.

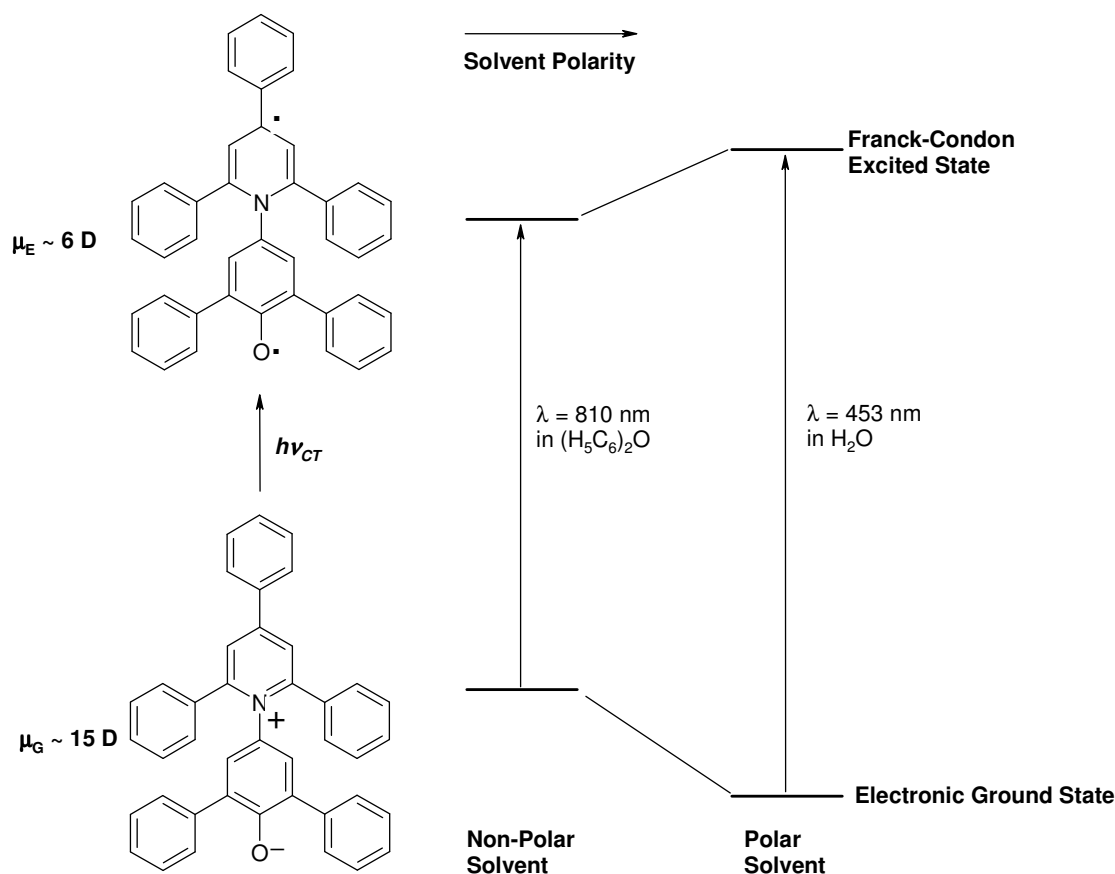


Figure 4.3 Diagrammatic representation of the solvent influence on the intramolecular charge-transfer visible absorption of 2,6-diphenyl-4-(2,4,6-triphenylpyridio)-phenolate ($\mu_G > \mu_E$)²⁶

The transition of $E_T(30)$ dye from the ground state to the Franck-Condon state has been shown to exhibit a change in the dipole moment of ~ 21 Debyes. This is because the Franck-Condon excited-state dipole moment of the $E_T(30)$ dye is antiparallel to that of the ground state, which means that when the ground state is excited by a photon, the

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dipole flip surmounts to $\Delta\mu \approx 15 \text{ D} - (-6) \text{ D} = 21 \text{ D}$.^{29,30}

The $E_T(30)$ scale is measured analogously to Kosower's Z values.^{1,14,24-26}

$$E_T(30) (\text{kcal mol}^{-1}) = hcv_{\max}N_A = (2.8591 \times 10^{-3}) v_{\max}(\text{cm}^{-1}) = 28591/\lambda_{\max} \quad (4.7)$$

Where E_T is the molar electronic transition energies of dissolved 2,6-diphenyl-4-(2,4,6-triphenylpyridio)-phenolate at 298 K and 1 bar pressure, v_{\max} is the frequency and λ_{\max} is the wavelength of the longest wavelength with the greatest maximum, h is Planck's constant, c is the speed of light and N_A is Avagadro's number.

In addition to the $E_T(30)$ scale, there is a normalised scale, the E_T^N scale. The E_T^N scale uses water and tetramethylsilane as extreme polar and non-polar reference solvents respectively. In this scale water is given the value 1.00 and tetramethylsilane is given the value 0.00.²⁴⁻²⁶ The normalised value for a solvent is calculated by the formula;

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{solvent}) - 30.7}{63.1 - 30.7} \quad (4.8)$$

A list of $E_T(30)$ and E_T^N for some selected molecular liquids are shown in Table 4.3.

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Table 4.3: $E_T(30)$ and E_T^N values for some selected organic solvents at room temperature and 1 bar pressure¹

Solvent	$E_T(30)$ (kcal mol ⁻¹)	E_T^N
Tetramethylsilane	30.7	0.000
Cyclohexane	30.9	0.006
Benzene	34.3	0.111
Tetrahydrofuran	37.4	0.207
Pyridine	40.5	0.302
Dichloromethane	40.7	0.309
Acetone	42.2	0.355
Dimethylformamide	43.2	0.386
Acetonitrile	45.6	0.460
Acetic Acid	51.7	0.648
Ethanol	51.9	0.654
Methanol	55.4	0.726
Water	63.1	1.000

As this chapter deals with the solvatochromism of Deep Eutectic Solvents, it would be wise to compare results of liquid organic salts and ionic liquids.

4.1.5 Polarity of Ionic Liquids

Solvent polarity is defined as being the sum of all possible intermolecular interactions that occur between the solute and the solvent molecules. It therefore should be expected that the polarities of molecular solvents and ionic liquids will differ due to the different degrees of intermolecular interactions experienced arising from the structural differences.

Work carried out using E_T^N scale shows that the addition of altering the size of the alkyl chain on the tetraalkylammonium cation in tetraalkylammonium sulfonate ionic liquids offers a slight increase in the E_T^N value.³⁰ In comparison, the alkyl chain length of the cation in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic

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liquids has virtually no influence on the E_T^N values. The biggest influence on the polarity of the cation in these ionic liquids is the addition of a functional group at the C2 position. Addition of a hydroxyl group significantly increases the E_T^N value, whereas the introduction of a methyl group at said position lowers the value.

Values for π^* in ionic liquids is generally high and usually greater than 0.9.³¹ The π^* values are affected by both the cation and anion. The π^* values tend to be higher in ionic liquids than most organic solvents due to the degree of delocalisation of the charge between the two anions. As more atoms are introduced into the anion the charge delocalised becomes more spread out and this results in the value of π^* decreasing, due to the decrease in the strength of the Coulombic interactions between the dye indicator molecule and the ion. In the cations, it appears that the decrease in Coulombic interactions between the dye indicator molecule and the ion, caused by delocalising the charge around the imidazolium ring is more than compensated for by the increased polarizability of the delocalised system.³¹ This observation is backed up by the relatively high π^* value seen in toluene (*c.f.* 0.532). Both the anion and the cation show that they both contribute to the polarisability parameter value. The α parameter is mainly governed by the cationic component of the ionic liquid. For example, values for [BMIM]⁺ based ionic liquids have moderately high α values, > 0.6, similar to *t*-BuOH, with very small changes being observed when the anion is changed.^{20,31} The β parameter is more dependant on the anion. Ionic liquids in general tend to show higher β values in comparison to other solvents than might be expected since the anions are effectively conjugate bases of strong acids, which would suggest lower β values should be observed, however this is not the case.

By using the solvatochromic probe Nile red the polarities of various [BMIM] ionic liquids have been shown to be related to the degree of charge. By changing the anion of [BMIM], Carmichael and Seddon have shown the polarity decreases in the order of [NO₃]⁻ > [BF₄]⁻ > [(CF₃SO₂)₂N]⁻ > [PF₆]⁻.³³ On first inspection this trend does not appear to agree with a decrease in polarity as the anion size increases since [(CF₃SO₂)₂N]⁻ is obviously the larger anion. However, there is crystallographic evidence from an analogous imidazolium [(CF₃SO₂)₂N]⁻ salt that reveals the negative charge is only partially delocalized within the anion. The results show that the negative charge is only delocalised over the S—N—S moiety, which is larger than the tetrafluoroborate anion but

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smaller than the hexafluorophosphate anion. Anionic effects on solvent polarity in ionic liquids become negligible when cation size increases. In the case of [HMIM] and [OMIM] ionic liquids, it was reported that there was no difference between the [BF₄] and [PF₆] series.³³ It has been shown that as the length of the 1-alkyl group on the imidazolium cation is increased the polarity increases. A maximum is reached at C₆, followed by a decrease in polarity as the length of the chain continues to increase. Table 4.4 shows selected ionic liquids and their respective E_T^N , α , β and π^* values.

Table 4.4: E_T^N , α , β and π^* values for some selected ionic liquids at room temperature and 1 bar pressure in ascending order

Ionic Liquid	E_T^N	α	β	π^*
[ethylammonium] ⁺ [NO ₃] [−]	0.95	0.85	0.46	1.24
[n-octyl-pyridinium] ⁺ [Tf ₂ N] [−]	0.588	0.51	0.28	0.99
[2-methyl octylpyridinium] ⁺ [Tf ₂ N] [−]	0.554	0.48	0.35	0.95
[3-methyl octylpyridinium] ⁺ [Tf ₂ N] [−]	0.576	0.50	0.33	0.97
[1-butyl-2,3-dimethylimidazolium] ⁺ [BF ₄] [−]	0.541	0.381	0.239	1.010
[1-butyl-3-methylimidazolium] ⁺ [BF ₄] [−]	0.630	0.627	0.376	1.047
[1-butyl-3-methylimidazolium] ⁺ [PF ₆] [−]	0.669	0.634	0.207	1.032
[1-butyl-3-methylimidazolium] ⁺ [TfO] [−]	0.656	0.625	0.464	1.006
[1-butyl-3-methylimidazolium] ⁺ [N(Tf) ₂] [−]	0.644	0.617	0.243	0.984
[n-butylmethyl pyridinium] ⁺ [N(Tf) ₂] [−]	0.544	0.427	0.252	0.954

4.2 Results and Discussion

To calculate the π^* , α and β values three indicator probe molecules were used. The molecules used to investigate these parameters were Reichardt's Dye 30 (1), 4-nitroaniline (2) and N,N-dimethyl-4-nitroaniline (3). For this work, the solvents investigated will be standardized around these single probe sets. This is common practice with many workers in the field. Other workers in this field however favour the use of

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several probes and then average the values obtained. The disadvantage of using many probes is that considerable effort is required to derive parameters for any new solvent. The single probe set approach has the advantage of being experimentally less involved, but also the data obtained will be comparable with published literature.¹

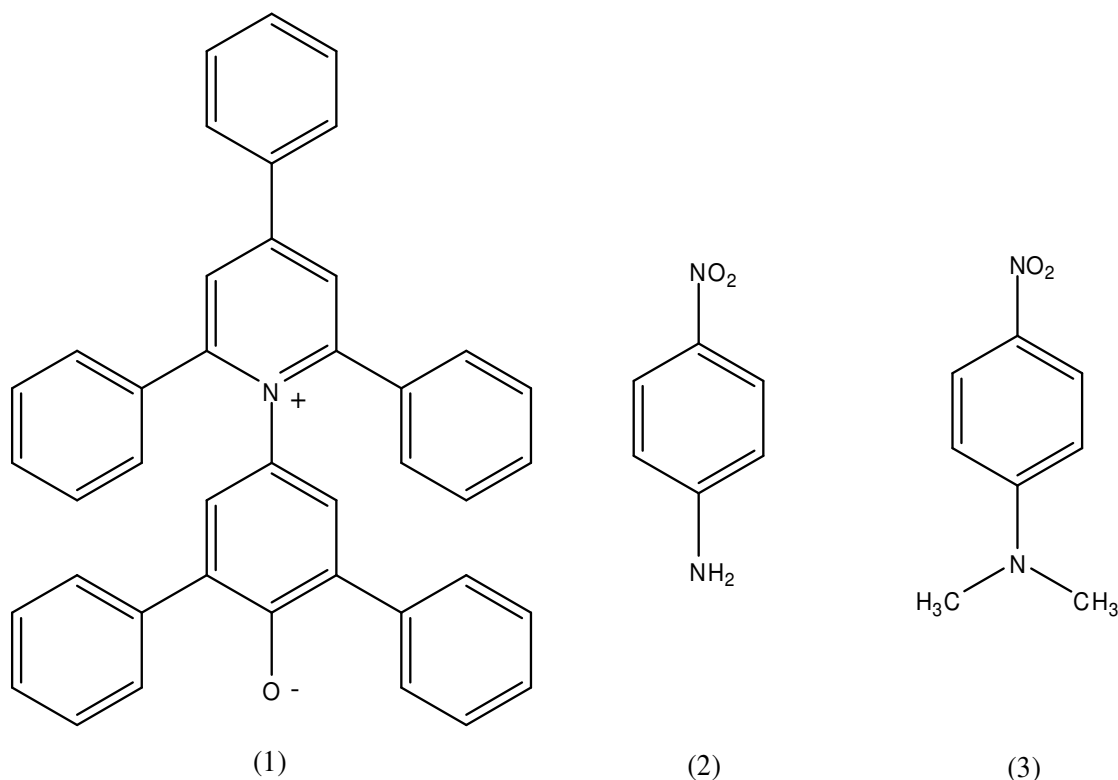


Figure 4.4 Diagrammatic representation of dyes used in calculating π^* , α and β

The main purpose of this chapter is to understand the solvent properties of several different alcohol based Deep Eutectic Solvents used throughout this study and to determine whether polarity parameters can explain the product distributions observed for a series of esterification reactions. Several different parameters will also be investigated such as choline chloride concentration and position of the alcohol groups along the carbon chain. The intrinsic error of the instrumentation was calculated to be approximately +/- 2%.

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4.2.1 $E_T(30)$ Betaine Dye Scale Results

The values for $E_T(30)$ for several Deep Eutectic Solvents used in this project can be seen in Table 4.6. As reported in section 4.1.4 the $E_T(30)$ value was calculated from the λ_{\max} value using the formula $E_T(30) \text{ (kcal mol}^{-1}\text{)} = 28591/\lambda_{\max}$, with

$$E_T^N = \frac{E_T(\text{solvent}) - 30.7}{32.4}$$

Table 4.5: $E_T(30)$ data obtained for several Deep Eutectic systems ($\Delta E_T(30)$ values compare the pure alcohol with that containing ChCl)

Solvent	$E_T(30) \text{ /kcal mol}^{-1}$	E_T^N	$\Delta E_T(30) \text{ /kcal mol}^{-1}$
Glycerol	57.17	0.817	N/A
ChCl:Glycerol 1:3	57.96	0.841	0.79
ChCl:Glycerol 1:2	58.58	0.860	1.41
ChCl:Glycerol 1:1.5	58.21	0.849	1.04
ChCl:Glycerol 1:1	58.49	0.858	1.32
Ethylene Glycol	56.38	0.793	N/A
ChCl:Ethylene Glycol 1:2	57.75	0.835	1.37
1,4-Butanediol	53.53	0.705	N/A
ChCl:1,4-Butanediol	54.76	0.743	1.23
1,3-Butanediol	52.62	0.677	N/A
ChCl:1,3-Butanediol	56.72	0.803	4.1
1,2-Butanediol	52.93	0.686	N/A
ChCl:1,2-Butanediol	55.41	0.763	2.48
ChCl: Urea 1:2	58.34	0.853	N/A

The data in Table 4.5 shows that the choline chloride based DES's exhibit a polarity that is similar to RNH_3^+X^- and $\text{R}_2\text{NH}_2^+\text{X}^-$ ionic liquids with discrete anions.²⁶ The diols and triol have $E_T(30)$ values that are similar to those for other alcohols although the values are in general slightly higher (*c.f.* Table 4.3) It can also be seen that the addition of choline chloride increases the $E_T(30)$ of the system. The magnitude of the change in

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$\Delta E_T(30)$ is unusual. The maximum change observed in $\Delta E_T(30)$ is that for the addition of ChCl to 1,3-butanediol which results in a change of approximately $4.1 \text{ kcal mol}^{-1}$. This is only comparable to the difference between pure glycerol and pure 1,3-butanediol. While this may seem anomalous it must be appreciated that in the eutectic mixture a proportion of the alcohol is replaced by the salt ions which in themselves are larger than the alcohol moieties.

This can be observed qualitatively by comparing the surface potentials of Ch^+ and glycerol as shown in Figure 4.5.

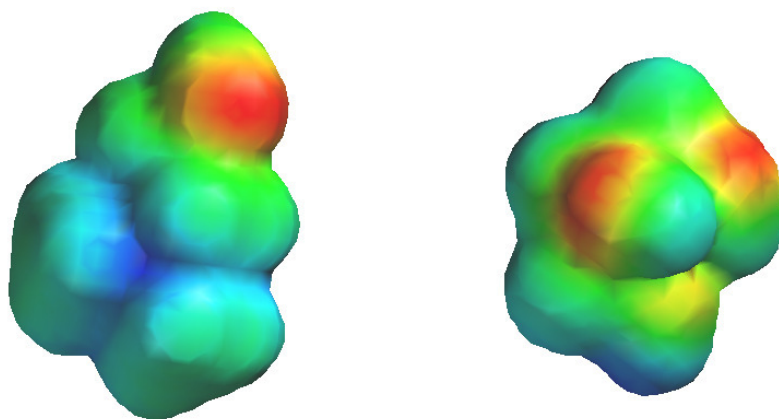


Figure 4.5: Surface potentials of Ch^+ and glycerol respectively, calculated using commercial software.³⁴

It could be argued that polarity in these systems is governed by the density of OH groups. Using the data calculated for the molar volume in the previous chapter it is possible to calculate a molar volume per OH group. This should correlate with the polarity parameters if dominated by hydrogen bond formation. Figure 4.6 shows that the $E_T(30)$ values for the pure liquids correlate well with this parameter. The eutectic mixtures also show a roughly linear trend, but it is not co-linear with the pure alcohols. This could suggest that the difference is due to the presence of the chloride ions which cause an approximate 3 kcal mol^{-1} increase in $E_T(30)$.

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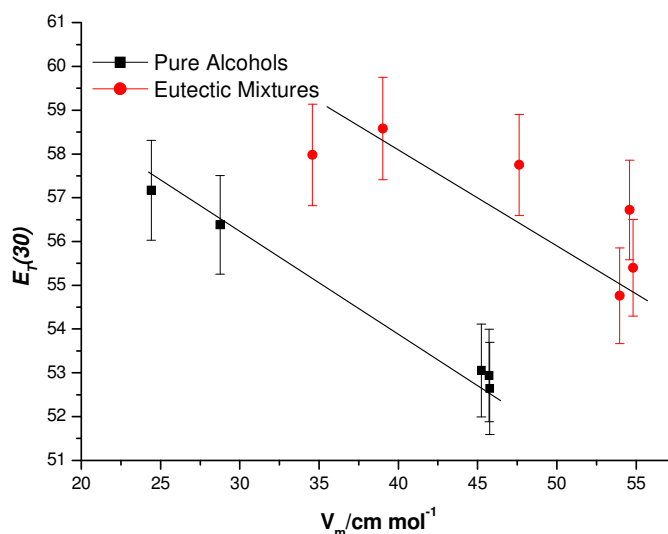


Figure 4.6: Correlation between $E_T(30)$ and the molar volume per OH group

4.2.2 Polarisability and Hydrogen Bond Acceptor/Donor Parameters π^* , α and β

Various methods have been used to calculate the polarity parameters from the Kamlet and Taft equation described earlier.¹⁵⁻²⁰ However, each method gives slightly different values. A multi-parameter fit depends significantly on the solvents used to calibrate the dyes and the literature values used in the fit. The main aim of this work is to be able to compare eutectic based ionic liquids with those containing discrete anions. Consequently, it was decided that it was most appropriate to follow the literature method used in ionic liquid systems such that the parameters would be comparable.³⁵⁻³⁹ To calculate π^* the following formula was used with the data obtained from the indicator molecule 4-nitroaniline

$$\pi^* = (V_{\text{solvent}} - V_{\text{cyclohexane}}) / (V_{\text{dmso}} - V_{\text{cyclohexane}}) \quad (4.9)$$

α values were calculated using $E_T(30)$ data and 4-nitroaniline π^* data using equation (4.5).

$$\alpha = (E_T(30) - 14.6(\pi^* - 0.23) - 30.31) / 16.5 \quad (4.10)$$

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

$$\beta = 0.9 (\Delta V_{\text{cyclohexane}} - \Delta V_{\text{solvent}}) / (\Delta V_{\text{cyclohexane}} - \Delta V_{\text{propan-1-ol}}) \quad (4.11)$$

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The resultant parameters are listed in Table 4.6 and the raw data is listed in Table 4.7.

Table 4.6: π^ , α and β data for several Deep Eutectic Solvents*

Solvent	π^*	α	β
Glycerol	0.956	0.882	0.658
ChCl:Glycerol 1:3	0.970	0.914	0.657
ChCl:Glycerol 1:2	0.984	0.937	0.657
ChCl:Glycerol 1:1.5	0.980	0.921	0.658
ChCl:Glycerol 1:1	1.003	0.923	0.658
Ethylene Glycol	0.890	0.877	0.696
ChCl:Ethylene Glycol 1:2	0.970	0.903	0.687
1,4-Butanediol	0.915	0.722	0.764
ChCl:1,4-Butanediol	1.174	0.646	0.791
1,3-Butanediol	0.856	0.707	0.796
ChCl:1,3-Butanediol	0.977	0.848	0.750
1,2-Butanediol	0.846	0.728	0.828
ChCl:1,2-Butanediol	0.941	0.802	0.748
Reline	0.990	0.922	0.642

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Table 4.7: λ_{\max} data for several Deep Eutectic Solvents

Solvent	4-nitroaniline λ_{\max} /nm	N,N-dimethyl- 4-nitroaniline λ_{\max} /nm	$E_T(30)$ λ_{\max} /nm
Glycerol	386.3	413.1	500.0
ChCl:glycerol 1:3	387.2	414.1	493.2
ChCl:glycerol 1:2	388.0	414.9	489.0
ChCl:glycerol 1:1.5	387.8	414.6	491.1
ChCl:glycerol 1:1	389.2	416.0	488.7
1,2-ethanediol	382.3	406.2	507.0
ChCl:1,2-ethanediol 1:2	387.2	411.8	494.9
1,4-butanediol	383.8	402.4	534.3
ChCl:1,4-butanediol 1:2	399.6	416.1	522.5
1,3-butanediol	380.2	396.3	540.1
ChCl:1,3-butanediol 1:2	387.6	407.3	515.9
1,2-Butanediol	379.6	393.2	543.2
ChCl:1,2-Butanediol 1:2	385.4	405.2	504.0
ChCl:urea 1:2	388.4	416.5	490.2

As with the $E_T(30)$ values described in section 4.2.1 the magnitude of the π^* , α and β values are very similar to those reported for the imidazolium based ionic liquids. Again it is surprising how little the values vary firstly from one another and secondly when compared to the pure alcohols.

In an analogous manner to that described for $E_T(30)$ above, a correlation should exist between the molar volume per OH group and some of the polarity parameters. Figure 4.7 shows the correlation for α with the molar volume per OH group and it is evident that the same correlation as seen in Figure 4.6 is present. This is slightly unexpected, however, since it could be argued that the addition of ChCl would cause a decrease in H-bond donor properties since the Cl^- would act as a strong H-bond acceptor. One possible explanation for this could be that the Cl^- acts as a structure breaking species as discussed in Chapter 3. This could disrupt the strong inter-glycerol interactions and permit more interaction with the indicator solute. There is also a similar correlation for the β parameter which can be seen in Figure 4.8.

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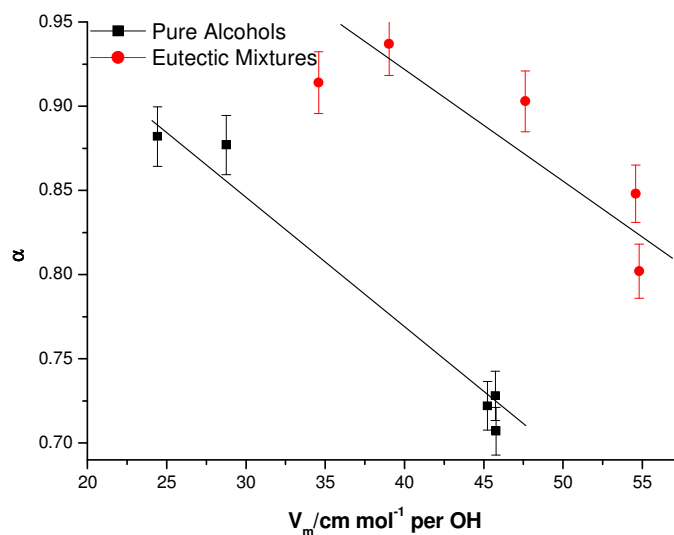


Figure 4.7: Correlation between α and the molar volume per OH group

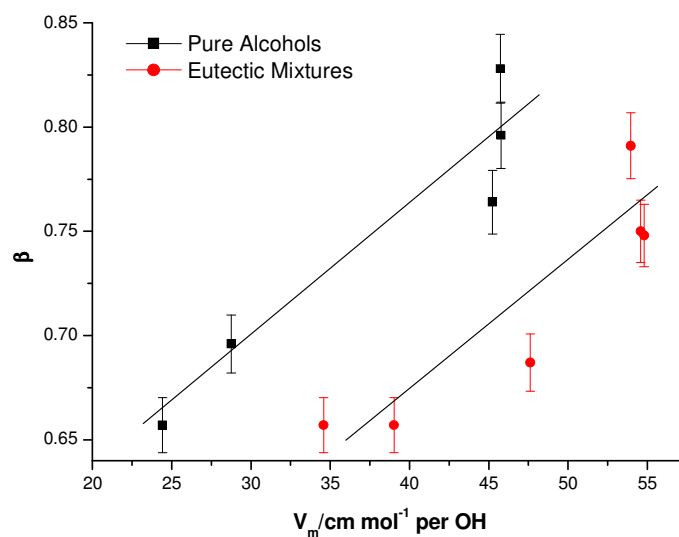


Figure 4.8: Correlation between β and the molar volume per OH group

However, there is negligible correlation between π^* and the molar volume per OH group showing that this simple model for the solvation in these eutectic systems is far from accurate.

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4.2.3 Effect of Choline Chloride Concentration

To measure the effect of choline chloride concentration on the polarity of a system, the system most stable to containing concentrations of choline chloride above the eutectic point needed to be used. In this case glycerol based systems were used. Although it has been shown in Chapter 3 the eutectic point of ChCl and glycerol is in a 1:2 ratio, higher levels of ChCl can be added without phase separation at room temperature. **Figure 4.8** shows a roughly linear increase in $E_T(30)$ with ChCl concentration. Extrapolating this trend to 100% ChCl gives a value of approximately 59 kcal mol⁻¹ which is comparable to that for ethylammonium nitrate (Table 4.4) which would seem reasonable.

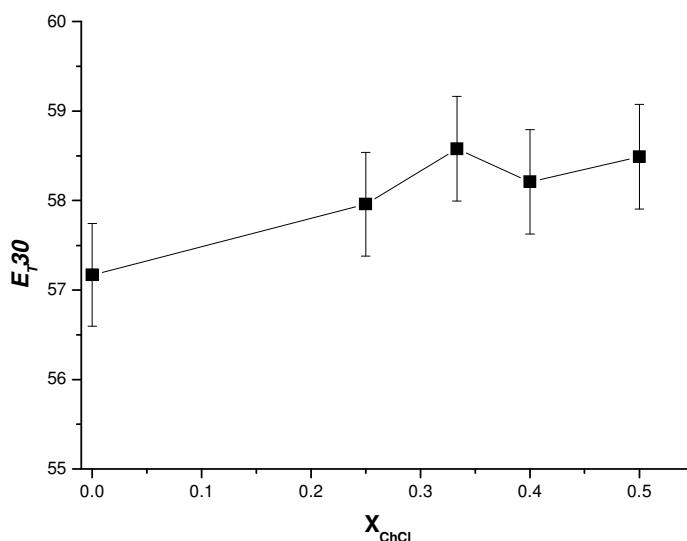


Figure 4.9: $E_T(30)$ as a function of choline chloride concentration for the glycerol base systems

Similar trends are observed for π^* , α and β although the parameters are relatively insensitive to changes in polarity. The β parameter in particular does not appear to show significant changes with increasing chloride concentration. To some extent this is not surprising since the number of glycerol OH groups is present in excess and will act as a better hydrogen bond donor than the indicator solute. It is proposed that in high polarity solvents solvatochromic indicators are insensitive to compositional changes because solvent-solvent interactions dominate over solvent-solute interactions.

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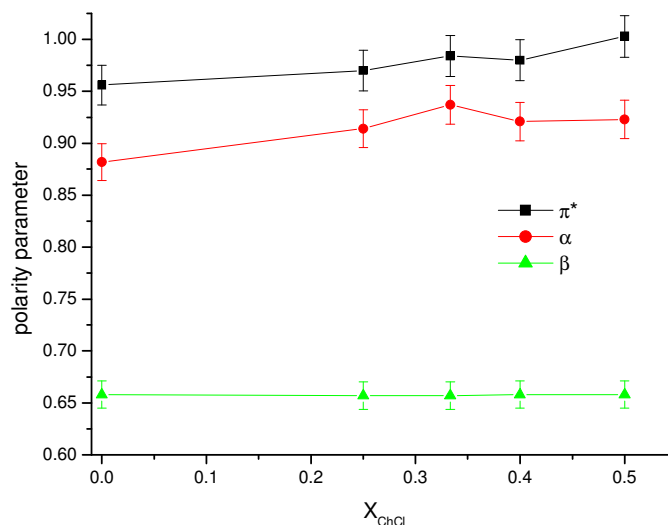


Figure 4.10: Variation of π^* , α and β with mole fraction of ChCl in glycerol

Table 4.7: Change in solvatochromic parameters as a function of ChCl concentration

System	$\Delta\pi^*$	$\Delta\alpha$	$\Delta\beta$	ΔE_T (30)
ChCl:Glycerol 1:3	0.015	0.032	-0.001	0.79
ChCl:Glycerol 1:2	0.028	0.056	-0.001	1.41
ChCl:Glycerol 1:1.5	0.025	0.039	0.000	1.04
ChCl:Glycerol 1:1	0.048	0.041	0.000	1.32
ChCl:Ethylene glycol 1:2	0.080	0.026	-0.009	1.37
ChCl:1,4-Butanediol	0.259	-0.076	0.027	1.23
ChCl:1,3-Butanediol	0.121	0.074	-0.046	4.10
ChCl:1,2-Butanediol	0.095	0.140	-0.080	2.48

4.3 Conclusions

This work has shown that the interactions between the glycols and ChCl are complex. The polarity parameters of the mixtures are dominated by the properties of the glycols and there is little effect of ChCl on the hydrogen bond donor or acceptor properties of the glycerol based liquids. There is however a more drastic effect of ChCl

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addition in the butanediol based systems, with the biggest change in polarity being observed in the 1,3-butanediol system. The addition of ChCl to glycerol is shown to increase the overall polarity of the system as more ChCl is added. The change in the polarisability parameter π^* is roughly a linear increase, as can be seen in Figure 4.10, which would be expected since the number of ionic species increases. In the glycerol based systems the addition of ChCl shows negligible change in the hydrogen bond accepting parameter β . In the diol systems, the addition of ChCl causes a decrease in this parameter, which would be expected since the Cl^- will be interacting with the OH moieties, reducing the ability to further accept hydrogen bonds. There also appears to be some correlation between the density of OH bonds in the liquid and the $E_T(30)$, α and β polarity parameters showing that hydrogen bonding is important in controlling solvation in these systems.

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4.4 References

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CHAPTER 5

Esterification of Glycerol in a Choline Chloride Based Deep Eutectic Solvent

5.1 Introduction

5.1.1 Glycerol Esters

5.1.2 Project Aim

5.2 Development of Analytical Technique

5.3 Results and Discussion

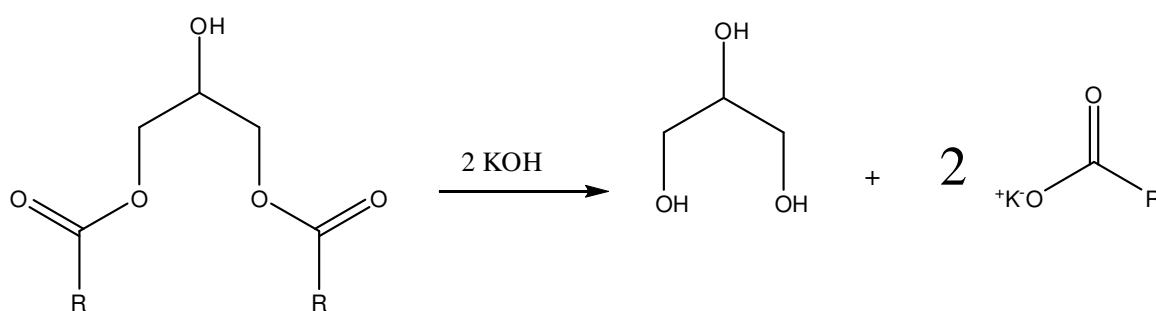
5.4 Conclusions

5.5 References

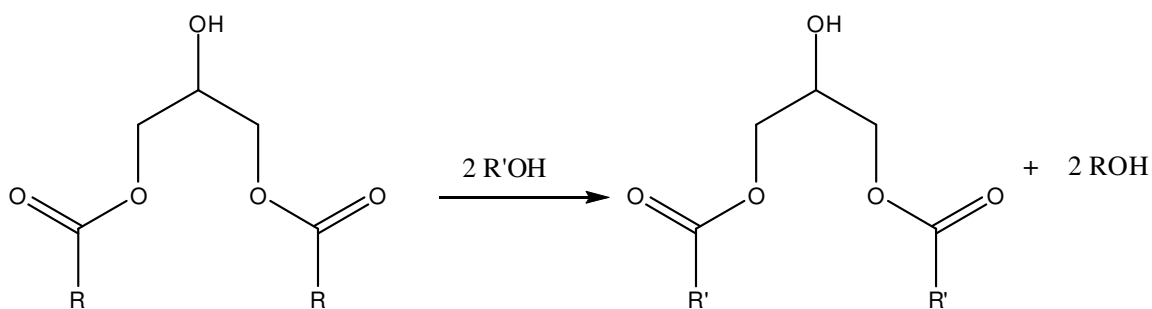
CHAPTER 5 – Esterification of Glycerol in a Choline Chloride Based Deep Eutectic Solvent

5.1 Introduction

Glycerol is a very important molecule as it is involved in a wide variety of biological processes in the production of fats, oils and phospholipids in both plant and animal cells. It is a compound that is produced on a large scale mostly as a waste material from the processing of oils. The saponification of oils to produce soap produces glycerol as does the transesterification of oil to produce biodiesel. Both of these processes are shown schematically in Figure 5.1



(1) Saponification of a diglyceride with KOH



(2) Transesterification of a diglyceride with R'OH

Figure 5.1: Saponification and transesterification schemes

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Current levels of glycerol production in Europe and the US are approximately 1 billion tonnes per year. The large worldwide scale of these processes has resulted in a huge surplus of glycerol which has very few uses. It is very difficult to burn and has little calorific value. It is used in some food and pharmaceutical applications, mostly as a thickening agent. There are many research groups and companies attempting to find applications for this material.

Glycerol can be used as a chemical feedstock from which to produce useful compounds including polyols, propylene glycol, acrolein, ethanol and epichlorhydrin.

5.1.1 Glycerol Esters

An alternative approach is to make mono- and di-esters of glycerol which can be used as emulsifiers, lubricants, surfactants, base materials for perfumes and antibacterial/antivirus drugs. Mono-esters are the most commonly used, although not exclusively, since they exhibit the highest surface activity of the acylglycerol types. More importantly, they offer very low toxicity to humans if ingested.

A considerable amount of work carried out on the esterification of glycerol.¹⁻¹⁰ Typically mono- and di-glycerides are formed by esterifying glycerol or by transesterifying the triglyceride, using acid or base catalysts respectively. Often these reactions are carried out in temperatures greater than 200 °C. However, the selectivity for the manufacture of mono-ester or di-ester has been shown to be difficult in typical esterification reactions using acid catalysts or by base catalysed transesterification of the triglyceride, where the product mixture contains the mono-, di- and tri-esters.¹⁻¹⁰

There has been a lot of work carried out using zeolites as catalysts for the esterification of glycerol. The zeolites have been shown to offer catalytic selectivity for many organic reactions.¹¹⁻¹⁴ In work by Machado *et al.* Si/Al containing zeolites have been used to carry out the esterification of glycerol with lauric acid.¹¹ Machado *et al.* compared the reaction rates and selectivity using commercially available Beta, Y and

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Mordenite zeolites. These zeolites contained different ratios of Si/Al and different pore sizes. Interestingly, it was observed that by choosing a zeolite with a high Si/Al, such as Beta, showed a higher selectivity could be obtained. This is attributed to two factors, firstly, the reduction in the Al sites results in stronger acid sites in the structure, and secondly, the hydrophobicity of the zeolite increase as the Si/Al ratio increases, which results in greater catalytic site activity. The smaller pore size in this system meant that di- and tri-ester formation is largely restricted. Al/Zr zeolites have also been employed for the formation of glycerol based esters under supercritical conditions.¹² Work from Van Rhijn *et al.* has shown that modifications of zeolites can increase the selectivity of the esterification products.¹³⁻¹⁴ By adding sulfonic groups to the zeolites structure, an increase in the catalytic rate zeolite is observed, as well as an improvement on the selectivity.

Supercritical fluids have been employed as a reaction media in the esterification of glycerol.^{12,15} Work by Moquin *et al.*¹⁵ has used both supercritical CO₂ and N₂ in the esterification of oleic acid with glycerol. The use of supercritical CO₂ and N₂ is to act as a solvent in the reaction and to aid the recovery of the oleic acid from the product when the reaction was completed. It was reported that there was no difference in the rates or product distribution of the reaction between CO₂ and N₂.¹⁵

The esterification of glycerol with fatty acids has been investigated using ionic resins as a method of catalysis of the reaction.¹⁶⁻¹⁷ These resins offer low operating temperatures and can act as shape selective material, due to their tunability to behave as gels or as macroporous resins, which improves the overall selectivity of the products. The catalytic properties of these sulfonic acid group containing cationic resins has been shown to be governed by the nature of the reagents. The adsorption of glycerol and fatty acid on the catalyst surface appears to show an effect on the catalytic activity. It is seen that several factors are involved in the activity of the reaction. The glycerol shows a show adsorption to the resin due to the strong interaction between OH moieties and the sulfonic groups on the resin, and this inhibits the rate of reaction of the esterification. As a result, excess glycerol further decreases the rate at which the reaction takes place hence increasing the selectivity towards the mono-ester. Work carried out by Rakotondrazafy *et al.*¹⁷ has shown

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that this method is not only suitable to cationic resins but anionic resins can be employed as well. The use of anionic resins gave rise to a high yield of monoglyceride.

Enzymes have been employed to form monoacylglycerols, and that the enzymes can be used to either esterify glycerol with the fatty acid or to selectively hydrolyse the triglyceride into the monoacylglycerol. Enzymes are known to exhibit regioselectivity and operate under very mild conditions for many organic synthetic reactions and so offer an alternative reaction pathway. Work by Monteiro *et al.*¹⁸ has shown that by using a lipase enzyme derived from *Rhizomucor meihei* it is possible to preferentially form the mono-ester product. The reaction was carried out in a solvent of *n*-hexane/*t*-butanol (1:1 v/v) so the system was homogenous. Work by Bornscheuer *et al.*¹⁹ has shown this using the lipase enzyme derived from *Pseudomonas cepacia*, both the esterification of glycerol with lauric acid and the transesterification of the trilaurin glyceride. The esterification reaction was carried out in a microemulsion system containing bis-(2-ethylhexyl)sulfosuccinate sodium salt (AOT)/isooctane, with an excess of glycerol: lauric acid (3:1). The mono-ester was formed preferentially in a ratio of ~2.3:1 mono- to di-ester. The isomeric form of these products was 1-monolaurin and 1,3-dilaurin. No evidence for esterification of the secondary OH moiety was observed. Lipase enzymes have also been shown to promote transesterification of triglycerides into biodiesel products such as propyl oleate.²⁰

Solventless methods to esterify glycerol show little control over the selectivity of products formed. The work in this chapter shows the esterification of glycerol, containing various molar equivalents of choline chloride (ChCl), with lauric acid. This chapter investigates the addition of ChCl to glycerol, forming a Type III Deep Eutectic Solvent (DES). The idea behind adding ChCl to glycerol is to use the complexing relationship of the salt to form hydrogen bonds with the –OH moieties on glycerol to act partly as a *pseudo*-esterification site inhibitor and to alter the position of equilibrium of the reaction. For esterification to occur the OH moiety must be available to nucleophilic attack from the carbonyl group of the carboxylic acid. Other effects such as viscosity and concentration are also investigated.

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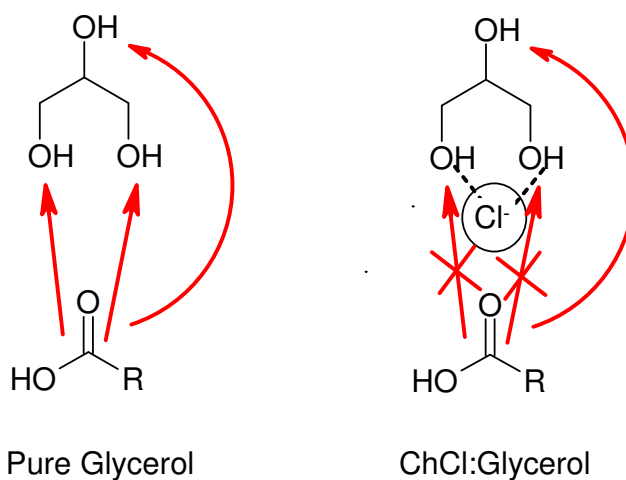


Figure 5.2: Diagrammatic representation of possible site inhibition from ChCl addition

The mechanism for the esterification of glycerol can be seen in Figure 5.3.

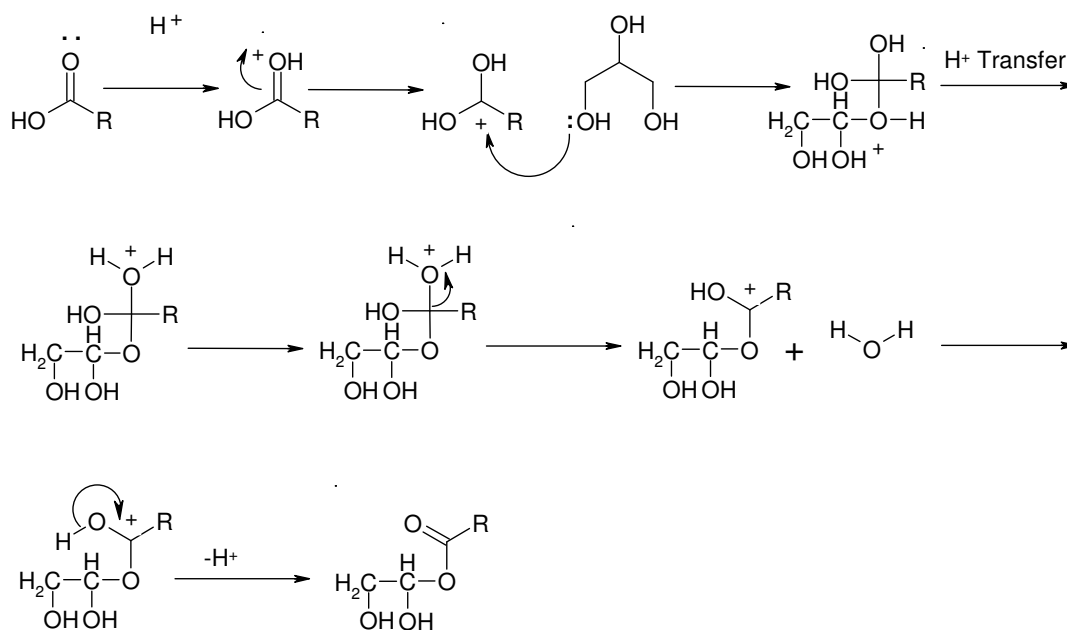


Figure 5.3: Mechanism of Glycerol Esterification

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5.1.2 Project Aim

The aim of this section of the project was to use eutectics of glycerol with choline chloride to determine whether esterification reactions could lead to different product distributions and ideally selective production of mono- or di- esters of glycerol.

5.2 Development of Analytical Technique

Previous studies reported in the literature have used HPLC and GC to determine the product distribution from esterification reactions.¹⁻¹⁹ However using these protocols, poor resolution of the products was obtained and so a new methodology had to be developed. Gel permeation chromatography (GPC) has been used as an analytical method for this type of experiment before, but it is a much less common technique to be employed.¹⁶ GPC is primarily used to separate large molecular weight products greater than 100,000 Daltons, such as polymers and proteins, however with specialist columns obtained from Polymer Laboratories, it has been possible to perform this method on molecules up to 2000 Daltons.

GPC is a chromatographic method that operates by performing size exclusion chromatography through a gel matrix. The main premise of this method is that larger molecules will not be trapped in the swollen matrix and therefore will elute faster from the stationary phase than the smaller molecules. In terms of the reaction being investigated, the tri-ester will elute first, followed by di-ester then mono-ester and finally the unreacted lauric acid. The technique however, is not designed to fractionate the various isomers of the mono- and di-esters as the column will only separate molecules of differing sizes. The eluent from the column is detected by refractive index. The solvent chosen to dissolve the products was THF. Sample spectra obtained can be seen in Figure 5.1.

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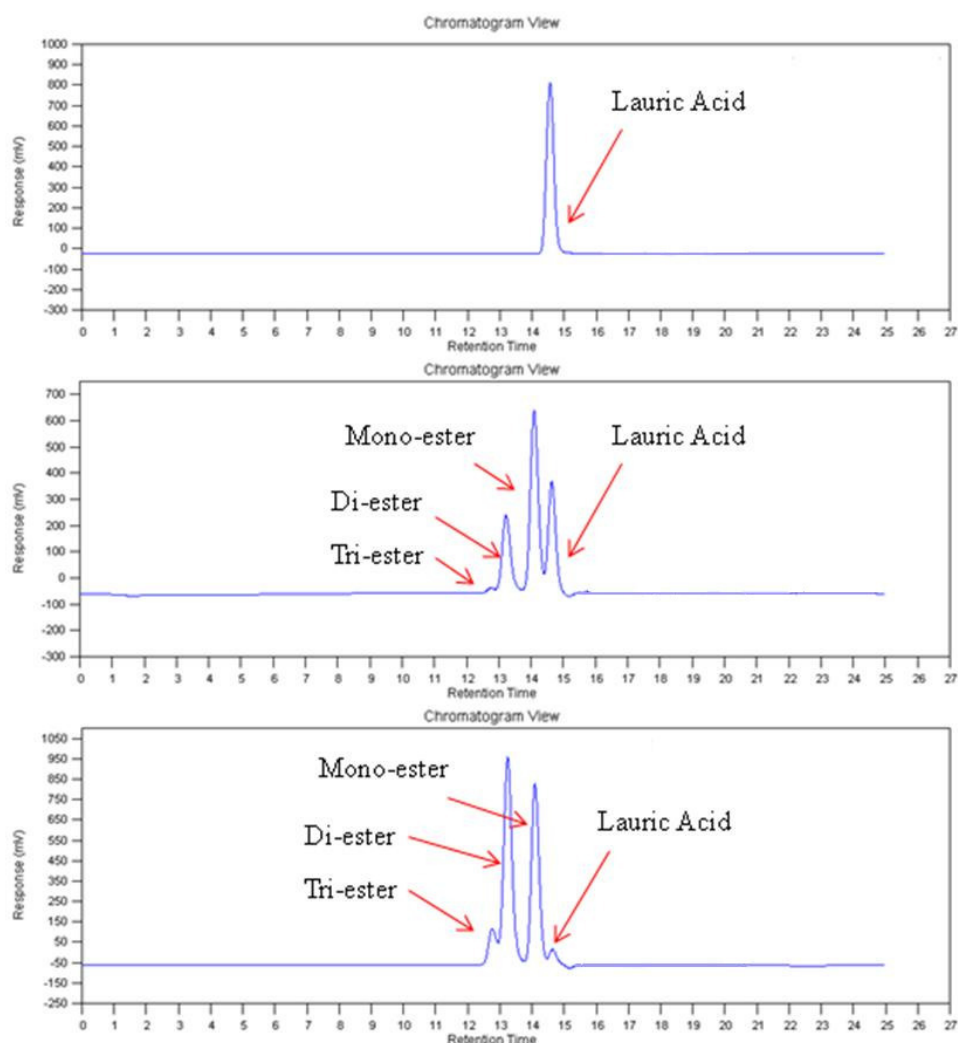


Figure 5.4: Three GPC spectra, the first showing lauric acid, the second showing how the product distribution has altered over time and the third showing how reaction had further progressed.

The data shown in Figure 5.4 is an example of the spectra obtained during analysis of the esterification reaction. In the first plot the data show the reaction at time zero, which only shows the presence of lauric acid. The second and third plots show how the spectra changes as the reaction progresses over time. It can be seen that the lauric acid peak decreases, while the mono-, di- and tri-ester peaks all increase.

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To keep the peak heights inside of the range of the detector, several standards were run using lauric acid, as to determine the correct concentration of each sample needed, and it was determined that each sample vial would contain 0.02 g of product in 1.25 mL of THF. The temperature of the column was set at 40 °C. The optimum flow rate was 1.0 mL/min. It should be noted that the ratio of peak areas does not alter by varying the concentration of the sample.

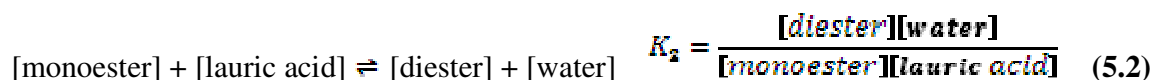
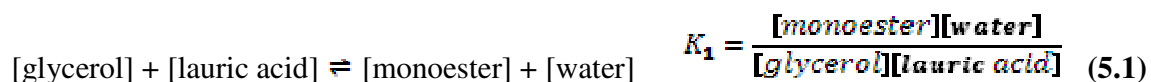
The estimated error in the data is believed to be of the order of +/-1% for all measurements so error bars have not been included in the following plots as these error bars are very close in size to the data markers.

5.3. Results and Discussion

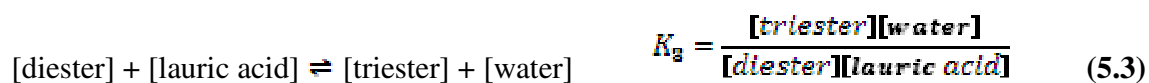
The data in the following pages outlines the effect of initial acid concentration in mixtures containing various concentrations of ChCl. The aim of this work is to determine the effect of hydrogen bonding of Cl⁻ to the OH moieties on glycerol. It is envisaged that the strength of the H-bonding will affect the reactivity of glycerol and this could change the product distribution and/or the kinetics of the reaction.

The esterification of the triol can be broken down into three elementary steps each of which is an equilibrium. Analysis of such a complex process is clearly complicated and therefore only a simple quantitative analysis of the first step is carried out. Attempts to fit all of the data were unsuccessful due to the inaccuracy associated with the analytical technique.

The scheme for this reaction is as follows:



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The plots shown in Figure 5.5 show the progression of the esterification of lauric acid in various ChCl: glycerol DES mixtures and also pure glycerol. In each system, 60 cm³, (0.82 mol) of glycerol was used and corresponding molar amount of ChCl needed to make up the desired ratio was added. It should be noted that the addition of ChCl changes the volume of the system and so the data have not been analysed in terms of the concentration, but rather the number of moles of each reagent. In each case the acid catalyst added was trifluoroacetic acid, 6 cm³, which was chosen as it is a monoprotic acid that has been shown previously to form a DES with ChCl and does not appear to react with ChCl. In these systems 0.1 moles of lauric acid was added to systems. The reactions were all carried out at 150 °C, in a sealed vessel. As lauric acid and the respective esters are insoluble in glycerol and the glycerol based DES's, aliquots were taken of the top organic layer, which at this temperature was liquid. The isomeric form of the mono- and di-esters were not investigated in the analysis. Only the formation of the mono- and di-esters were investigated. The ChCl: glycerol 1:3 data set is not available for the 0.1 moles data.

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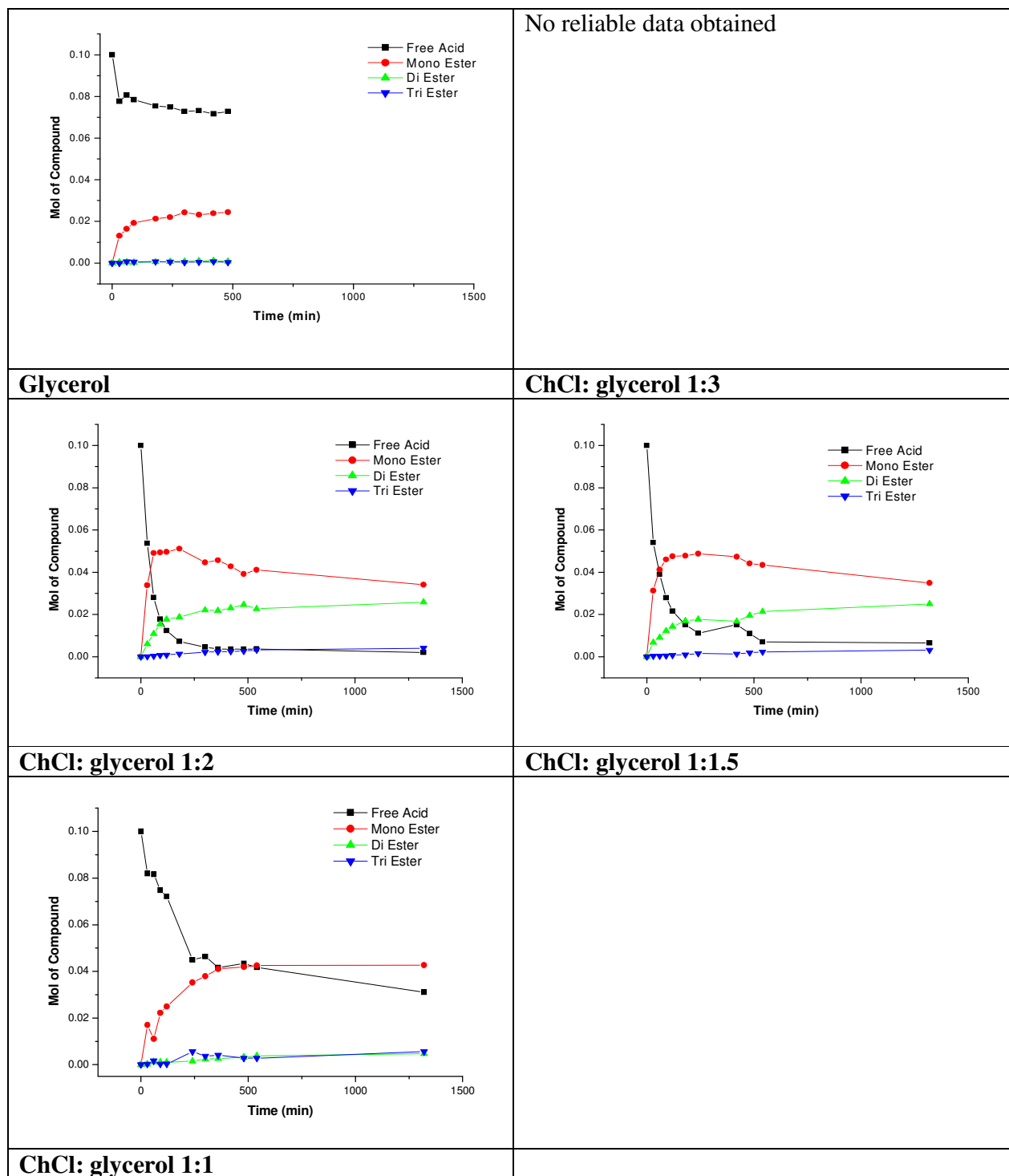


Figure 5.5: Esterification Data of 0.1 moles of Lauric Acid in Various ChCl: Glycerol DES Mixtures

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The data in Figure 5.5 show the addition of ChCl does have a marked effect on the product distribution of the reaction. These systems are operating in large excess of glycerol, with a greater than 8:1 ratio of glycerol: lauric acid. The mono-ester would be the most abundant product predicted due to the large excess of glycerol. This is indeed the case with pure glycerol where negligible amounts of di- and tri-esters formed. It also shows that after 8 hours there is still approximately 70% of the free acid remaining. This is a surprising result since there is such a large amount of glycerol available for the lauric acid to react with but this could be due to the high viscosity of the system.

The 1:1 ChCl: glycerol mixture shows a faster consumption of the lauric acid than the pure glycerol system, resulting in a much greater formation of the mono-ester. It should be noted that twice as many moles of products are made when ChCl is added which clearly negates any effect of dilution. The 1:1.5 and 1:2 systems show similar overall conversion to the monoester but noticeably the monoester concentration goes through a maximum due to its use in reaction (5.2). The concentration of the diester is significantly increased with respect to both the pure glycerol and the 1:1 ChCl systems. The rate of consumption of the lauric acid follows $1:2 \approx 1:1.5 > 1:1 > \text{glycerol}$. This could be due to the *pseudo* site inhibition, but a more logical explanation is that the process is mass transport controlled.

This is an oversimplification because the system is in effect an emulsion, however because the catalyst, glycerol and ChCl are in one phase while the lauric acid is in the other it is still important to consider the mass transport of species to and from the interface. Another issue that cannot be overlooked is the activity of the catalyst. In aqueous solutions pH will be dependent upon ionic strength. This should also be the case in an ionic liquid although it is an area that has not been significantly studied.²¹

The results shown in Figure 5.5 indicate that the addition of choline chloride alters the product distribution of the esterification of glycerol and lauric acid. The 1:2 mixture shows that it is possible to form the di-ester product in relatively large amounts considering that initial ratio of glycerol: lauric acid is very high. Deviating slightly to a ratio of 1:1.5 barely alters this product distribution, however increasing to a ratio of 1:1 the product

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distribution more closely resembles that of the pure glycerol system. There are likely to be many factors governing how these reactions progress. On one hand the addition of ChCl to glycerol results in a lower viscosity, which would increase the mass transport in the system.

This section has shown that at low acid concentrations and high ChCl concentrations the monoester can be selectively produced at a significantly higher rate than in pure glycerol.

An additional point worth discussing at this juncture is that the choline cation contains an OH moiety which in principle could be esterified. Despite numerous experiments no such esters were observed. Bell *et al.* also studied esterification reactions in choline based ionic liquids and deep eutectic solvents. The choline cation was found to be very unreactive and it was only when strong Lewis acids such as ZnCl_2 were present with acetic anhydride that any significant acylation took place.²²

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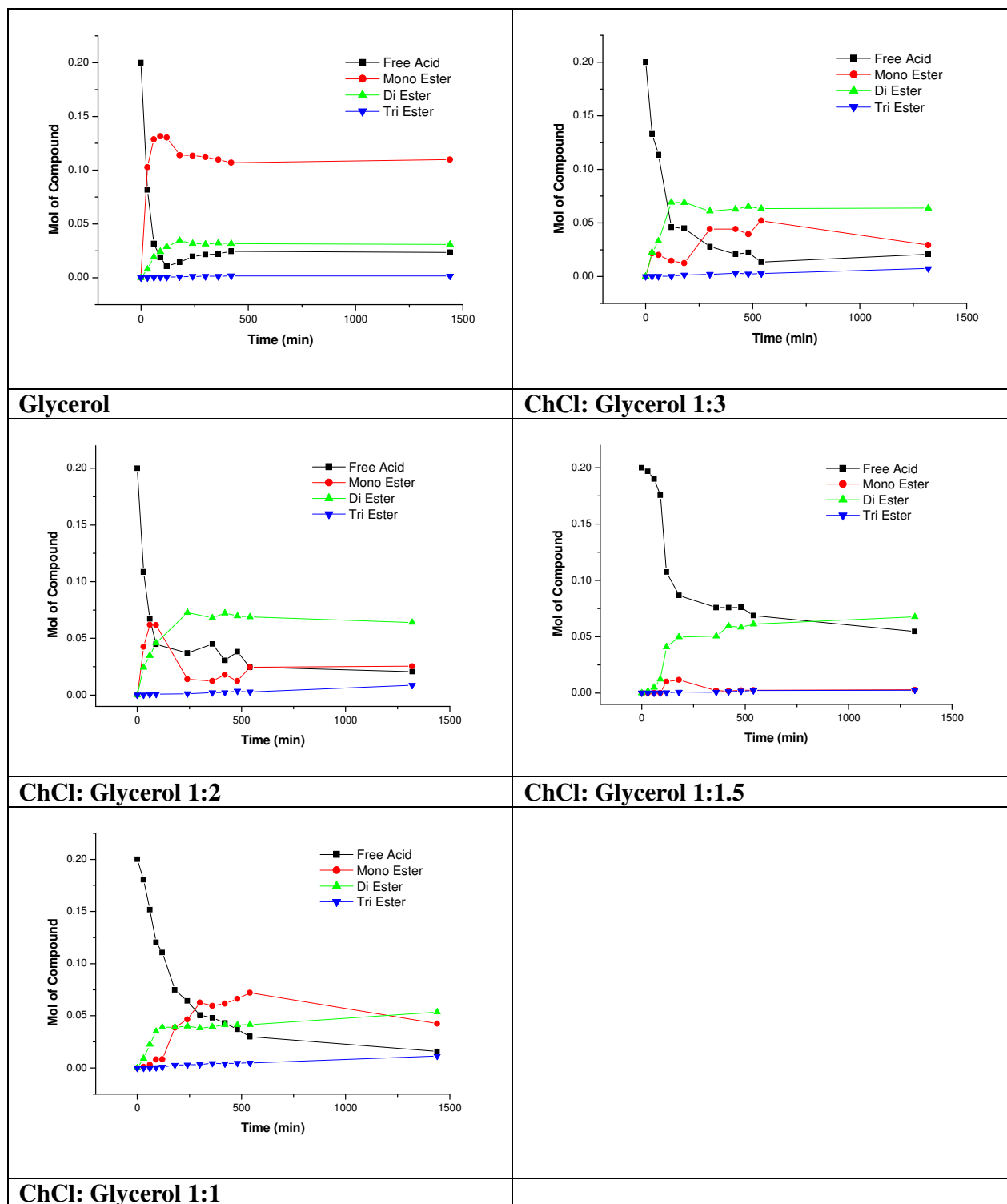


Figure 5.6: Esterification Data of 0.2 M Lauric Acid in Various ChCl: Glycerol DES Mixtures

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The data shown in Figure 5.6 is directly comparable to that in Figure 5.5, but with twice the concentration of lauric acid added. The first point to note is that in the pure glycerol system the rate at which lauric acid is used up is considerably faster than in the previous case. It is also noteworthy that the free acid concentration reaches a minimum before reaching a constant value of c.a. 0.02 moles. This is characteristic of system at equilibrium *i.e.* the back reaction of equation (5.1) becomes significant. It can also be seen that almost no tri-ester forms. The addition of 0.33 eq. of ChCl causes a decrease in the rate of acid usage, a decrease in the yield of mono-ester but a significant increase in the concentration of di-ester and tri-ester. The same trends are observed for the 1:2 and 1:1.5 mole ratio mixtures. Most importantly in the 1:1.5 mixture the di-ester was effectively the only product produced. This shows that the aim of this section of the work is possible, namely that selective alkylation can be achieved. The isomerisation of the product was not one of the issues of the project although other groups have elucidated this using nmr spectroscopy.¹⁻¹⁰ It is also evident from the data in Figure 5.6 that the ChCl systems have not reached equilibrium within the timescale of the experiment. The reason appears to be that the tri-ester is still being formed, albeit at a slow rate.

In the equimolar ChCl: glycerol mixture the rate of conversion decreases and the monoester is the favoured product. The same trend was observed using 0.1 moles of free acid. This hints at the possibility that the *pseudo* site inhibition may occur at high ChCl concentrations.

Overall the results show a different set of trends than the data seen in Figure 5.5 *i.e.* the trends can not simply be explained by mass transport. As would be expected more di-ester products are formed as a direct result of more lauric acid being available. In this experiment, the pure glycerol system shows a much faster consumption of lauric acid than any of the ChCl based systems which is in direct contrast to the trend shown in Figure 5.5. It should be noted that while the reaction reaches equilibrium rapidly the product distribution is not selective for the mono-ester as seen above.

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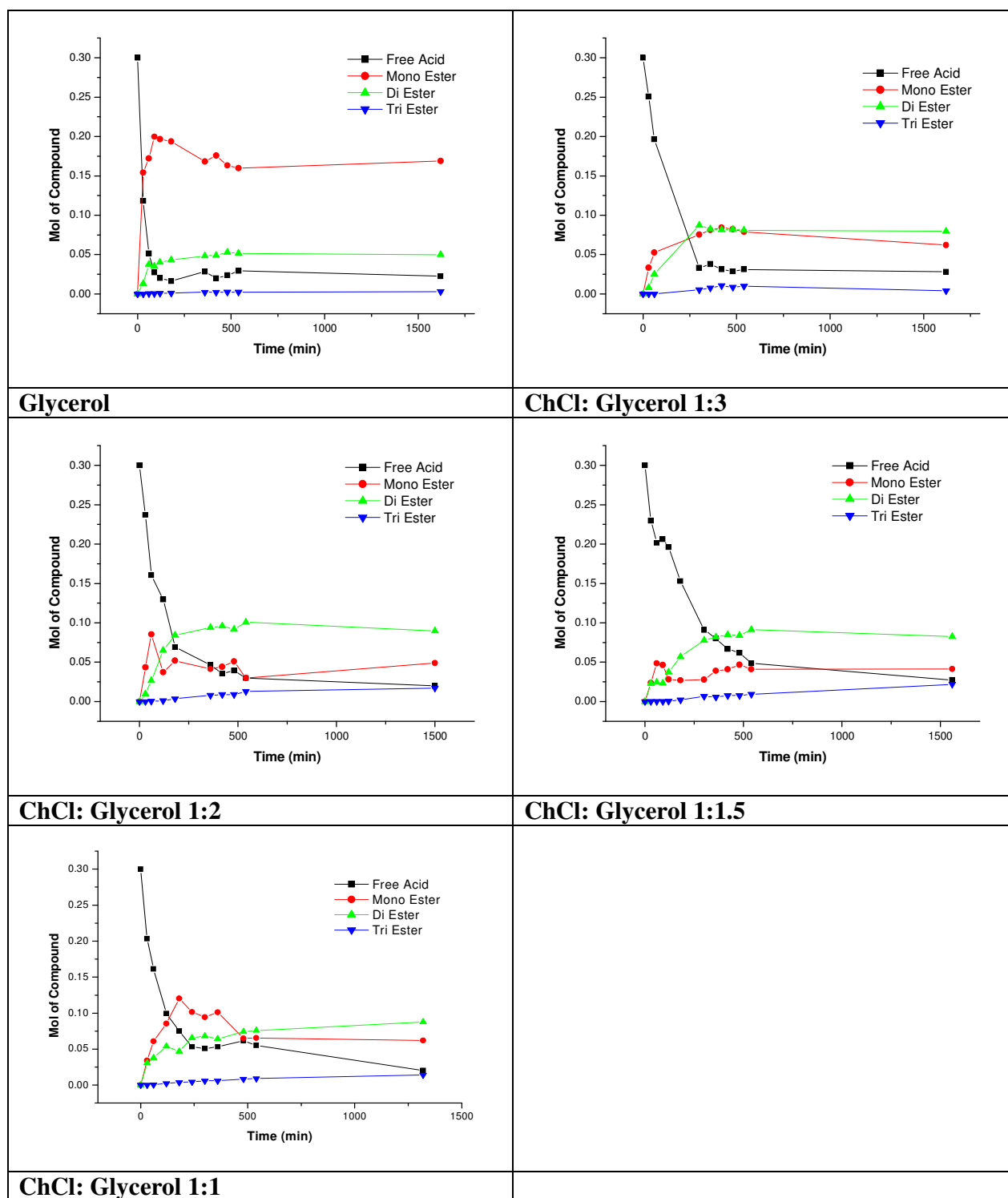


Figure 5.7: Esterification Data of 0.3 M Lauric Acid in Various ChCl: Glycerol DES Mixtures

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The data in Figure 5.7 are all carried out using 0.3 M lauric acid. The data for the pure glycerol system shows similar trends to that seen in Figure 5.6 with the trend in the product distribution mono- > di- > tri-ester. The product distribution also appears to reach a constant value rapidly. If this is a true equilibrium then the equilibrium constants should be independent of acid concentration. Table 5.1 lists the equilibrium constants, K_1 , K_2 and K_3 as a function of concentration.

Table 5.1.: Equilibrium constants for the esterification reaction in pure glycerol

Lauric acid/ moles	K_1	K_2	K_3
0.2	1.58	0.41	0.02
0.3	2.43	0.79	0.04
0.4	2.24	0.62	0.04
0.6	2.14	1.11	0.15

Table 5.1 shows that with the slight exception of 0.2 molar data, the values for K_1 are very close and suggest that in each reaction the system has reached equilibrium. The values for K_2 are less accurate but do hint at having reached equilibrium, as do the K_3 data. While these reactions qualitatively appear to be equilibria, it is difficult to gain any quantitative information from the data.

The 1:1 system shows a faster rate of formation of the mono-ester than in the 0.2 M system, as would be expected since the amount of lauric acid is greater. In all of the ChCl containing systems the amount of di-ester formed is approximately constant (0.01 moles). This is significantly higher than the pure glycerol system. All of the systems containing ChCl do not appear to have reached equilibrium, again because the tri-ester appears to form slowly and removes di-ester from the system.

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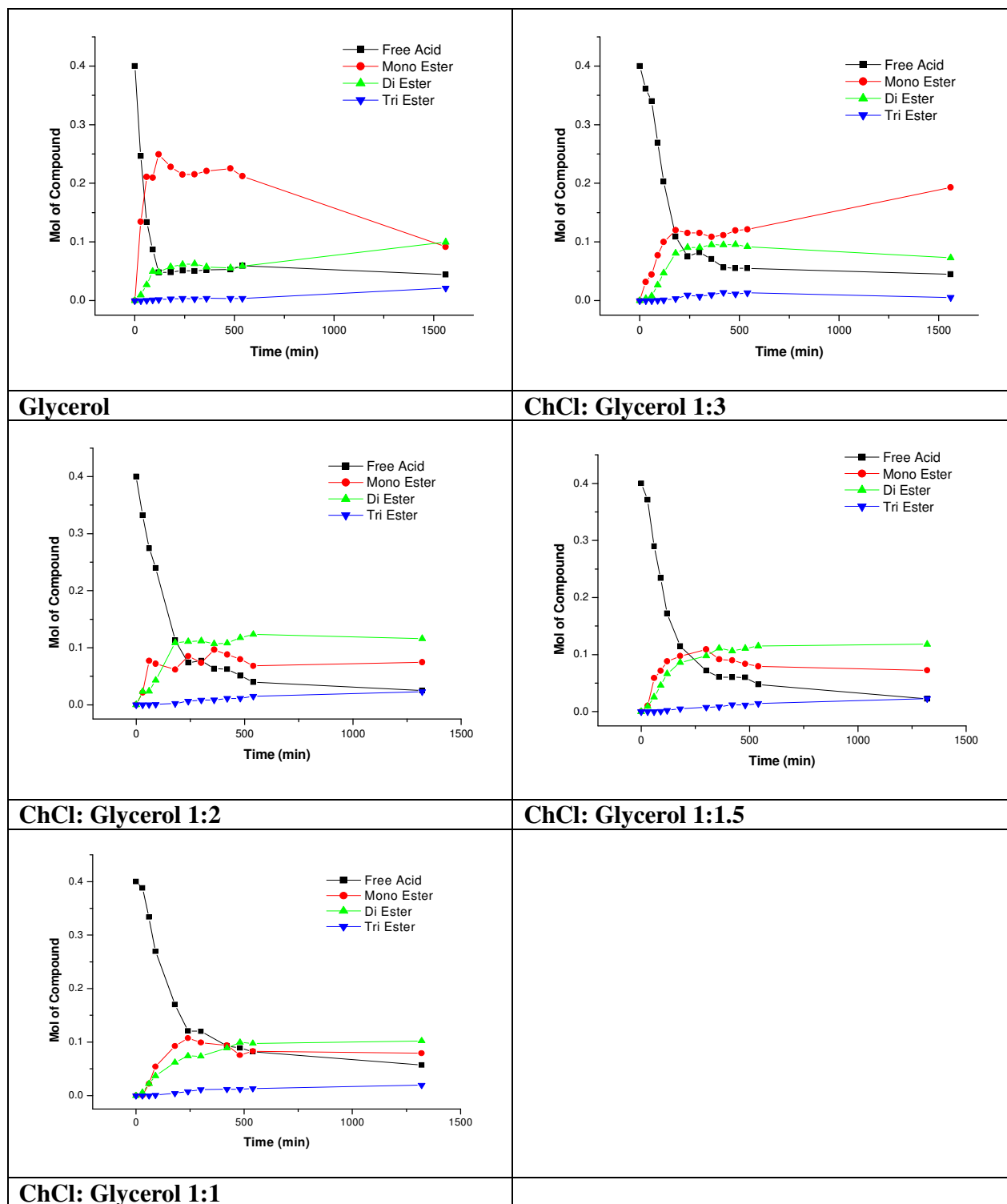


Figure 5.8: Esterification Data of 0.4 M Lauric Acid in Various ChCl: Glycerol DES Mixtures

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Increasing the lauric acid concentration to 0.4 moles results in a similar product distribution to that found in the 0.3 moles and as Table 5.1 shows the equilibrium constants for pure glycerol remain relatively similar. As the lauric acid concentration increases the data for the ChCl containing systems approach equilibrium. The equilibrium constants are shown in Table 5.1 In all of the pure glycerol systems the equilibrium constants are in the order $K_1 > K_2 > K_3$ whereas for the ChCl containing mixtures the order is $K_2 > K_1 > K_3$. The only way in which the equilibrium can be driven to the right is if one of the components is removed or more accurately if it decreases its activity in the system. One possible explanation for the data observed in Tables 5.1 and 5.2 is that the presence of ChCl causes a decrease in the activity of water due to hydrogen bonding between the chloride anion and the water molecules.

One complication is that the reaction is carried out at 150 °C which would normally be enough to drive the water from the reaction vessel however in these experiments the reaction vessel was closed and so the ChCl would only affect the concentration of water vapour in the headspace. Nevertheless, inspection of the data in Table 5.2 suggests that both K_2 and K_3 increase as the ChCl concentration increases which supports this idea. Furthermore the central premise of this work was that ChCl could act as a pseudo-site inhibitor. This could either prevent esterification, which is clearly not the case, or it could reduce the activity of glycerol in equation (5.1). If this were the case, then di- and tri-esterification would be preferred, which is indeed what appears to occur.

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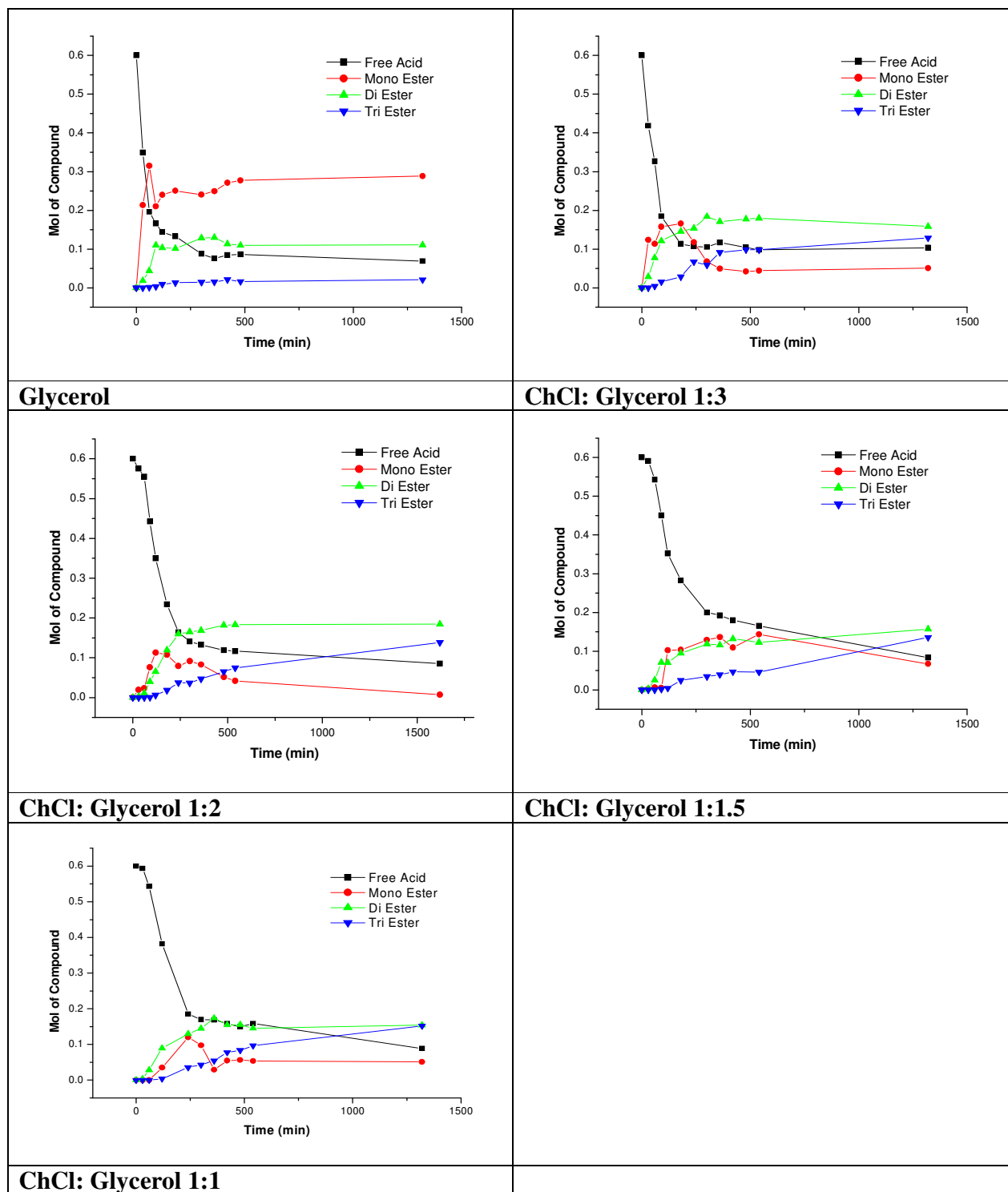


Figure 5.9: Esterification Data of 0.6 M Lauric Acid in Various ChCl: Glycerol DES Mixtures

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The results for the system containing 0.6 moles of ChCl superficially support all of the discussions above. The concentration of the mono-ester is up to ten times larger than that observed in some of the ChCl containing systems. Given that glycerol is still present in a large excess it is important to notice that the overall lauric acid concentration is approximately the same at the end of each experiment. While this could be viewed in terms of decreased glycerol activity in the ChCl an alternative view could be that the ChCl breaks up the structure of the glycerol and therefore actually enables further reaction on the OH moieties that could normally be inter-molecularly hydrogen bonded. It is probably a mixture of both effects that lead to the observed product distribution.

Table 5.2.: Equilibrium constants for the formation of the mono-, di- and tri- esters for all ChCl based systems shown in Figures 5.5 -5.9

Ratio of ChCl:Glycerol	Lauric acid/ moles	K₁	K₂	K₃
1:3	0.2	1.038	1.26	0.053
	0.3	1.053	1.080	0.13
	0.4	1.28	0.97	0.14
	0.6	0.64	2.58	1.41
1:2	0.1	1.43	0.79	0.11
	0.2	0.24	0.66	0.026
	0.3	0.40	1.36	0.174
	0.4	1.01	1.83	0.22
	0.6	0.44	1.91	0.78
1:1.5	0.1	0.48	0.21	0.021
	0.2	0.006	0.16	0.005
	0.3	0.31	0.70	0.070
	0.4	0.97	1.40	0.17
	0.6	0.90	0.77	0.290
1:1	0.1	0.077	0.007	0.005
	0.2	0.58	0.34	0.040
	0.3	0.44	0.50	0.061
	0.4	0.52	0.61	0.082
	0.6	0.41	1.11	0.74

Equilibrium constants have been calculated for the ChCl based systems, and are shown in Table 5.2.

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Attempts were made to analyse the initial rate data using both integrated rate equations and the initial rate method, however the scatter of both the pseudo-first order analysis and the log rate vs. initial concentration plots were such that the results were statistically meaningless.

5.4 Conclusions

In this Chapter the solventless esterification of glycerol with the addition of ChCl has been studied for the first time. This work has shown that the addition of ChCl to glycerol can significantly affect the product distribution for the esterification of glycerol with lauric acid. Specific mono-esters and di-esters can be achieved by varying the liquid components. This site specific esterification is thought to occur due to the ability of ChCl to break up the hydrogen bonding in glycerol, but also to interact with water molecules produced in the reaction. The ChCl also decreases the viscosity of the liquid and at low acid concentrations when the system has not reached equilibrium, it is suggested that the process is mass transport controlled.

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CHAPTER 6

Conclusions and Future Work

6.1 Introduction

6.1.1 Physical Properties of Alcohol Based Deep Eutectic Solvents

6.1.2 Investigation of Intramolecular Interactions in Deep Eutectic Solvents Using Solvatochromic Probes

6.1.3 Esterification of Glycerol in a Choline Chloride Based Deep Eutectic Solvents

6.2 Future Work

6.1 Summary

This study has brought about a better understanding in the relatively novel area of alcohol based Deep Eutectic Solvents (DES). Several physical properties were investigated and the data was applied to several models to explain the behaviour of the systems.

6.1.1 Physical Properties of Alcohol Based Deep Eutectic Solvents

A series of polyol systems containing various concentrations of ChCl were investigated. The physical properties viscosity, conductivity, surface tension and density were investigated. For all diol systems, an increase in the ChCl concentration resulted in an increase in the viscosity of the system, whereas in the triol system, glycerol, the addition of ChCl caused a marked reduction. It was therefore shown that ChCl could be used to break up larger intermolecular structures, granting more degrees of freedom throughout the structure. This is also backed up by the density data which decreases as ChCl is added, where this is not true for the diol systems.

Conductivity data for the diol systems has shown that the point at which the system becomes a saturated salt solution is at 20 mol% ChCl, because at higher concentrations the conductivity decreases despite the increase in number of charge carrying species. This would suggest that the additional ChCl molecules are causing a hindrance to the flow of ions throughout the system

It was shown that it is possible to form eutectic mixtures from many different types of alcohols. A mono alcohol, phenol, was used to form an extremely fluid eutectic at a ratio of 4:1 phenol to ChCl. This eutectic offers some of the lowest viscosity data seen for any DES. This is most likely due to the delocalised π -electron system on the benzene ring which is increasing the amount of charge delocalisation on ChCl. On the other hand, polyols, with more than 3 OH moieties were also investigated and were shown to form DES's with ChCl. Sugars such as erythritol, xylitol, D-(-) fructose and D-glucose all formed stable DES's which opens up the potential for creating benign and possibly edible liquids from naturally occurring salts and sugars.

6.1.2 Investigation of Intramolecular Interactions in Deep Eutectic Solvents Using Solvatochromic Probes

In this work several parameters, E_T^N , α , β and π^* have been obtained for the first time for several alcohol based DESs. The data has given information on the relative polarity of these systems, which suggests that they are similar to RNH_3^+X^- , $\text{R}_2\text{NH}_2^+\text{X}^-$ and imidazolium ionic liquids. It was also shown that the effect of ChCl on these systems is very much dependent upon the nature of the hydrogen bond donor. Whilst the addition of ChCl gave an increase in the E_T^N value for every system, the degree to which it was altered was not the same in each case. The greatest changes were seen in the 1,3- and 1,2-butanediol systems.

The addition of ChCl has slightly different effects on the values for the hydrogen bond acceptor parameter β . In the diol cases, with the exception of 1,4-butanediol, the β value decreases when ChCl is added, which would be expected since the Cl^- will be interacting with the OH moieties, reducing the ability to further accept hydrogen bonds. In the glycerol systems, there is no change. This would perhaps indicate that the number of free OH groups for the indicator probe to interact with does not change when ChCl is added, despite its addition increasing the degree of freedom throughout the system. This could indicate that one OH moiety is always free in both glycerol and the eutectic mixture. The addition of ChCl shows an increase in the values for hydrogen bond donor α .

It has been proposed that there is a correlation between the values for $E_T(30)$, α and β with regards to the molar volume per OH moiety. There are distinct trends, distinguishing between the pure alcohol systems and the eutectic systems. This is not surprising since the OH moiety is a hydrogen bond donor/acceptor. There was no such trend observed for the π^* data.

6.1.3 Esterification of Glycerol in a Choline Chloride Based Deep Eutectic Solvents

Solventless esterification of glycerol and lauric was carried out using ChCl with the intention of using its hydrogen bonding interaction with glycerol to behave a

potential site inhibitor as to selectively form mono- or di-ester products. The work has shown that the addition of ChCl to the system actually encourages the reaction to progress further towards the di-ester product, as opposed to the pure glycerol system encouraging only mono-ester formation. It is thought that because ChCl breaks up the 3-D structure of glycerol, this actually works in favour of the esterification reaction as it can further react with glycerol molecules already esterified. It is also possible that ChCl is interacting with water molecules produced in the reaction, effectively removing them from the equilibrium, which in turn helps drive the reaction forward. The ChCl also decreases the viscosity of the liquid and at low acid concentrations when the system has not reached equilibrium, it is suggested that the process is mass transport controlled.

6.2 Future Work

There is still a great deal that could be learnt from these systems with some further work. In a continuation of the physical properties of the alcohol based DES's, additives could be added to the system and the changes in these properties could be investigated. The addition of water would be interesting to investigate because the hygroscopic nature of ChCl means that these systems are constantly absorbing moisture from the atmosphere over time. Mixed systems containing alcohols with dicarboxylic acids/diamides could also be investigated.

The technique EXAFS (Extended X-Ray Absorption Fine Structure) could be employed to gather information on the interaction between the Cl and OH moieties and see how this interaction changes in each of the systems investigated in this thesis. The technique has been used to help understand the local structure in many systems such as glass, amorphous and liquid systems, organometallic compounds, metal clusters. This interaction between the chloride anion and hydroxyl group is crucial in the formation of DES's but has not been fully investigated due to the inherent difficulties of being able to do so.

A more sensitive method for investigating the phase transitions of the systems described throughout this thesis would be to use a DSC (Differential Scanning Calorimetry), which would give a more accurate account of the melting and glass

CHAPTER 6 – Conclusions and Future Work

transitions, for example. The DSC measures energy or heat capacity changes and so would give further qualitative data on these systems.

While it would be expected that the Lewis basicity would change with the addition of ChCl to the alcohol systems, none of the parameters determined in Chapter 4 highlight this. It is proposed that a new scale of chloride activity could be developed by using an indicator that is sensitive to Cl^- ions. Some transition metal hydrate salts are well known to change colour when heated or in the presence of ligands stronger than H_2O because they lose waters of hydration from their coordination sphere. Examples of this include $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue to yellow) or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (blue to pink). In an endeavour to develop a chloride activity scale for chloride eutectics $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ could be added to the liquids and the ratio of the two absorbance bands ($[\text{Cu} \cdot 4\text{H}_2\text{O}]^{2+}$ and CuCl_3^-) could be measured by UV-Vis spectroscopy.

Appendix

7.1 Physical Properties Raw Data

7.1.1 Choline Chloride : 1,2-Ethenediol

7.1.2 Choline Chloride : 1,4-Butanediol

7.1.3 Choline Chloride : 1,6-Hexanediol

7.1.4 Choline Chloride : 1,2 Butanediol

7.1.5 Choline Chloride : 1,3 Butanediol

7.1.6 Choline Chloride : 2,3 Butanediol

7.1.7 Choline Chloride : Glycerol

7.2 Esterification Raw Data

7.2.1 Pure Glycerol

7.2.2 ChCl : Glycerol 1:3

7.2.3 ChCl : Glycerol 1:2

7.2.4 ChCl : Glycerol 1:1.5

7.2.5 ChCl : Glycerol 1:1

7.3 Publications

7.1 Physical Properties Raw Data**7.1.1 Choline Chloride : 1,2-Ethenediol***Table 7.1: Raw data for 1,2-ethenediol with 5% choline chloride*

Temperature (°C)	4	6	8	10	12	14	16	18	20
Viscosity (cP)	43	35	30	26	23	21	19	17	15
Conductivity (mS)	2.59	2.68	2.82	2.99	3.14	3.29	3.45	3.71	3.93
Surface Tension (n/nM)	48.0	47.8	47.4	47.1	46.8	46.4	46.2	45.8	45.7

Table 7.2: Raw data for 1,2-ethenediol with 10% choline chloride

Temperature (°C)	4	6	8	10	12	14	16	18	20
Viscosity (cP)	45	37	32	28	25	23	21	19	17
Conductivity (mS)	4.31	4.43	4.57	4.72	4.89	5.09	5.33	5.58	5.83
Surface Tension (n/nM)	49.5	49.3	48.9	48.6	48.3	48.0	47.8	47.6	47.5

Table 7.3: Raw data for 1,2-ethenediol with 15% choline chloride

Temperature (°C)	4	6	8	10	12	14	16	18	20
Viscosity (cP)	48	40	35	31	28	25	23	21	19
Conductivity (mS)	5.27	5.37	5.52	5.71	5.96	6.28	6.62	6.98	7.35
Surface Tension (n/nM)	51.4	51.2	51.0	50.7	50.4	50.2	49.9	49.7	49.6

Table 7.4: Raw data for 1,2-ethanediol with 20% choline chloride

Temperature (°C)	4	6	8	10	12	14	16	18	20
Viscosity (cP)	53	46	40	36	31	28	25	23	21
Conductivity (mS)	5.68	5.79	5.93	6.11	6.35	6.59	6.84	7.13	7.56
Surface Tension (n/nM)	50.6	50.2	50.0	49.8	49.7	49.4	49.3	49.2	49.0

Table 7.5: Raw data for 1,2-ethanediol with 25% choline chloride

Temperature (°C)	4	6	8	10	12	14	16	18	20
Viscosity (cP)	68	60	54	49	44	40	36	32	29
Conductivity (mS)	5.40	5.51	5.63	5.77	5.98	6.24	6.61	6.97	7.44
Surface Tension (n/nM)	50.8	50.4	50.0	49.6	49.4	49.2	48.9	48.6	48.3

Table 7.6: Raw data for 1,2-ethanediol with 30% choline chloride

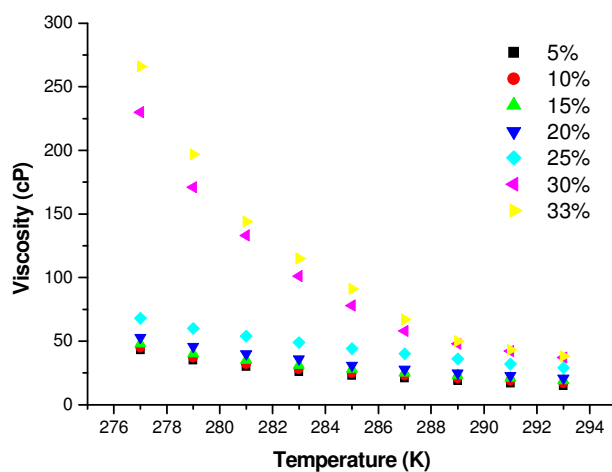
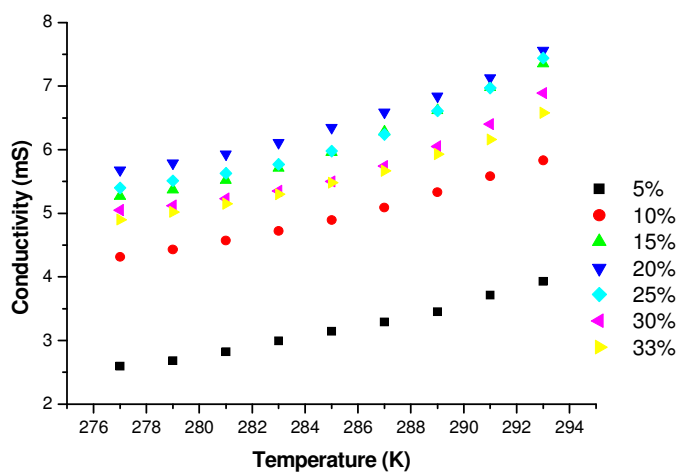
Temperature (°C)	4	6	8	10	12	14	16	18	20
Viscosity (cP)	230	171	133	101	78	58	48	42	37
Conductivity (mS)	5.05	5.12	5.23	5.35	5.50	5.74	6.05	6.40	6.89
Surface Tension (n/nM)	49.6	49.2	48.9	48.7	48.4	48.2	48.0	47.7	47.5

Table 7.7: Raw data for 1,2-ethanediol with 33% choline chloride

Temperature (°C)	4	6	8	10	12	14	16	18	20
Viscosity (cP)	266	197	144	115	91	67	50	43	38
Conductivity (mS)	4.90	5.02	5.15	5.30	5.48	5.67	5.93	6.16	6.58
Surface Tension (n/nM)	50.0	49.8	49.4	49.2	49.1	48.6	48.3	47.9	47.7

Table 7.8: Raw data for density of the 1,2-ethanediol systems choline chloride at 293K

ChCl %	0	5	10	15	20	25	30	33
Density (gcm^{-3})	1.113	1.114	1.115	1.115	1.117	1.118	1.118	1.120

**Figure 7.1:** Plot of temperature versus viscosity as a function of choline chloride composition for the 1,2-ethanediol system**Figure 7.2:** Plot of temperature versus conductivity as a function of choline chloride composition for the 1,2-ethanediol system

7.1.2 Choline Chloride : 1,4-Butanediol*Table 7.9: Raw data for 1,4-butanediol with 5% choline chloride*

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	78	68	60	54	48	44	40	36	32	29
Conductivity (μS)	593	617	640	671	708	746	784	824	865	910
Surface Tension (n/nM)	46.4	46.3	46.1	46.0	45.9	45.8	45.7	45.6	45.4	45.3

Table 7.10: Raw data for 1,4-butanediol with 10% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	84	72	60	54	48	44	40	36	33	30
Conductivity (μS)	923	948	974	1009	1068	1144	1209	1308	1422	1563
Surface Tension (n/nM)	46.8	46.7	46.6	46.4	46.3	46.3	46.2	46.1	46.0	45.8

Table 7.11: Raw data for 1,4-butanediol with 15% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	78	68	62	55	49	44	40	37	34	31
Conductivity (μS)	1271	1323	1378	1443	1529	1610	1719	1845	1990	2170
Surface Tension (n/nM)	46.9	46.8	46.8	46.7	46.5	46.4	46.3	46.1	46.0	46.0

Table 7.12: Raw data for 1,4-butanediol with 20% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	88	76	68	61	55	50	46	42	38	35
Conductivity (μS)	1606	1664	1739	1829	1947	2080	2230	2360	2500	2710
Surface Tension (n/nM)	47.4	47.3	47.1	47.0	46.9	46.8	46.6	46.6	46.3	46.2

Table 7.13: Raw data for 1,4-butanediol with 25% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	176	136	98	76	66	58	52	47	42	38
Conductivity (μS)	1654	1683	1748	1865	1998	2130	2280	2410	2630	2880
Surface Tension (n/nM)	47.6	47.5	47.4	47.4	47.3	47.3	47.2	47.1	47.1	47.0

Table 7.14: Raw data for density of the 1,4-butanediol systems choline chloride at 293K

ChCl %	0	5	10	15	20	25
Density (gcm⁻³)	1.017	1.021	1.026	1.036	1.046	1.052

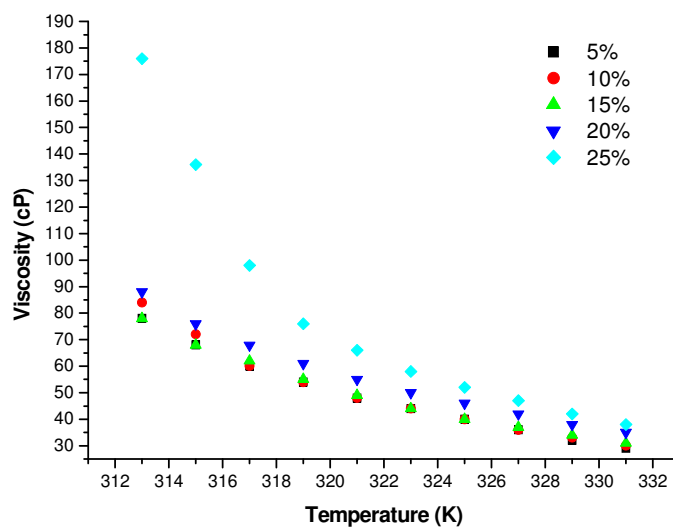


Figure 7.3: Plot of temperature versus viscosity as a function of choline chloride composition for the 1,4-butanediol system

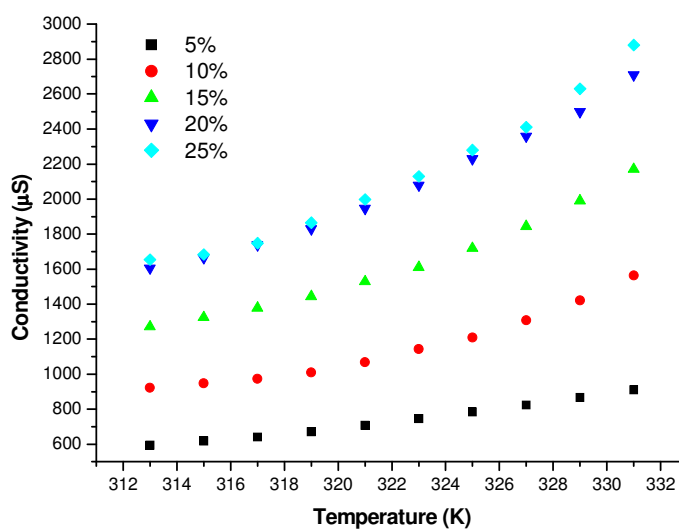


Figure 7.4: Plot of temperature versus conductivity as a function of choline chloride composition for the 1,4-butanediol system

7.1.3 Choline Chloride : 1,6-Hexanediol*Table 7.15: Raw data for phase diagram plot of choline chloride : 1,6-hexanediol*

Molar Ratio (1,6-Hexanediol: Choline Chloride)	Freezing Point (°C)
1:1	165
2:1	72
3:1	31
4:1	27
5:1	28
6:1	29
7:1	30
8:1	31

Table 7.16: Raw data for 1,6-hexanediol with 5% choline chloride

* note surface tension is measured at a different temperature than viscosity and conductivity

Temperature (°C)	45	47.5	50	52.5	55	57.5	60	62.5
Viscosity (cP)	43	36	33	29	26	24	22	20
Conductivity (μS)	317	333	349	370	393	417	440	466
Temperature (°C)	43.5	46	48.5	51	53.5	56	58.5	61.5
Surface Tension (n/nM)	42.3	42.1	41.9	41.5	41.3	41.2	41.1	41.0

Table 7.17: Raw data for 1,6-hexanediol with 10% choline chloride

* note surface tension is measured at a different temperature than viscosity and conductivity

Temperature (°C)	45	47.5	50	52.5	55	57.5	60	62.5
Viscosity (cP)	43	38	34	30	27	24	22	20
Conductivity (μS)	549	576	607	639	680	713	759	808
Temperature (°C)	43.5	46	48.5	51	53.5	56	58.5	61.5
Surface Tension (n/nM)	42.6	42.4	42.3	41.8	41.7	41.6	41.5	41.3

Table 7.18: Raw data for 1,6-hexanediol with 15% choline chloride

* note surface tension is measured at a different temperature than viscosity and conductivity

Temperature (°C)	45	47.5	50	52.5	55	57.5	60	62.5
Viscosity (cP)	43	38	34	31	28	25	22	20
Conductivity (μS)	867	882	929	978	1035	1095	1187	1304
Temperature (°C)	43.5	46	48.5	51	53.5	56	58.5	61.5
Surface Tension (n/nM)	42.8	42.6	42.5	42.4	42.2	42.2	42.0	42.0

Table 7.19: Raw data for 1,6-hexanediol with 20% choline chloride

* note surface tension is measured at a different temperature than viscosity and conductivity

Temperature (°C)	45	47.5	50	52.5	55	57.5	60	62.5
Viscosity (cP)	48	43	38	34	31	29	26	23
Conductivity (μS)	1090	1126	1186	1250	1332	1446	1565	1699
Temperature (°C)	43.5	46	48.5	51	53.5	56	58.5	61.5
Surface Tension (n/nM)	43.2	43.1	43.0	42.9	42.6	42.6	42.5	42.3

Table 7.20: Raw data for 1,6-hexanediol with 25% choline chloride

* note surface tension is measured at a different temperature than viscosity and conductivity

Temperature (°C)	45	47.5	50	52.5	55	57.5	60	62.5
Viscosity (cP)	48	43	38	34	31	28	25	22
Conductivity (μS)	1325	1367	1428	1497	1589	1693	1823	1968
Temperature (°C)	43.5	46	48.5	51	53.5	56	58.5	61.5
Surface Tension (n/nM)	43.6	43.5	43.4	43.3	43.1	42.9	42.7	42.7

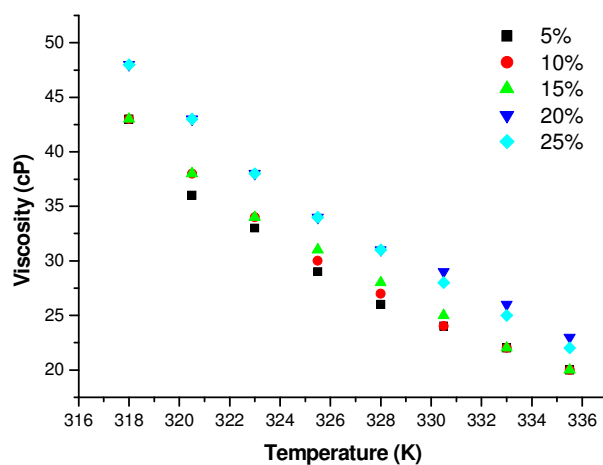


Figure 7.5: Plot of temperature versus viscosity as a function of choline chloride composition for the 1,6-hexanediol system

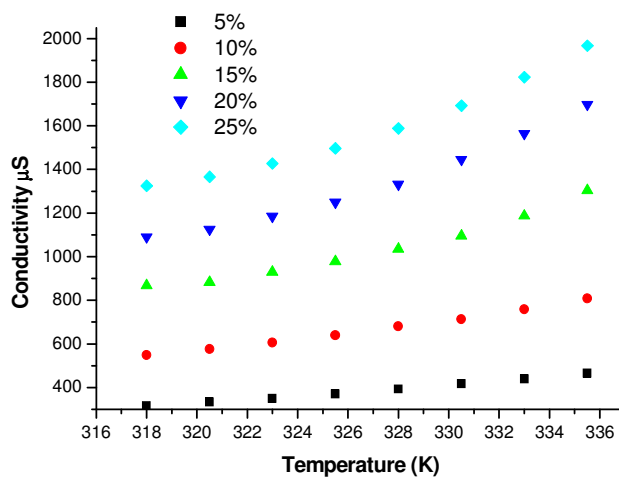


Figure 7.6: Plot of temperature versus conductivity as a function of choline chloride composition for the 1,6-hexanediol system

7.1.4 Choline Chloride : 1,2 Butanediol*Table 7.21: Raw data for 1,2-butanediol with 5% choline chloride*

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	62	55	48	41	34	31	26	22	19	17
Conductivity (μS)	459	489	524	564	606	645	685	730	775	820
Surface Tension (n/nM)	32.9	32.8	32.5	32.3	32.1	31.9	31.7	31.6	31.3	31.1

Table 7.22: Raw data for 1,2-butanediol with 10% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	67	53	45	41	36	31	26	22	19	17
Conductivity (μS)	811	877	937	1010	1071	1143	1226	1291	1364	1441
Surface Tension (n/nM)	33.7	33.4	33.2	33.0	32.8	32.6	32.2	32.0	31.9	31.7

Table 7.23: Raw data for 1,2-butanediol with 15% choline chloride

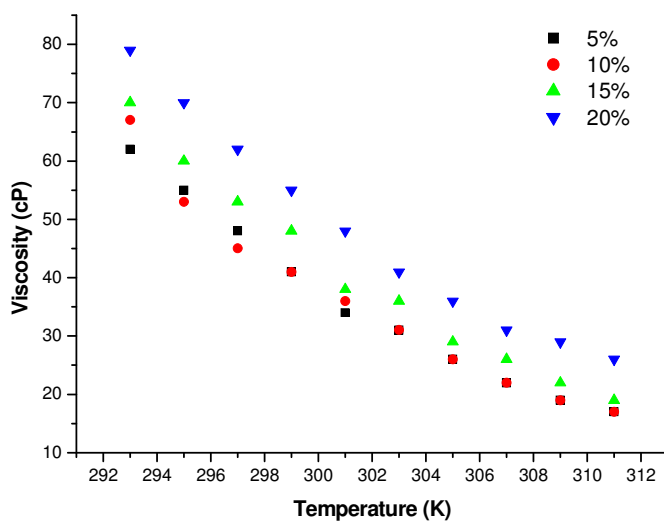
Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	70	60	53	48	38	36	29	26	22	19
Conductivity (μS)	1078	1167	1245	1309	1415	1508	1674	1770	1870	1988
Surface Tension (n/nM)	34.2	33.9	33.7	33.4	33.3	33.2	33.1	33.0	32.9	32.6

Table 7.24: Raw data for 1,2-butanediol with 20% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	79	70	62	55	48	41	36	31	29	26
Conductivity (μS)	1358	1429	1524	1623	1716	1920	2030	2150	2260	2380
Surface Tension (n/nM)	34.7	34.5	34.3	34.2	34.1	33.9	33.7	33.5	33.4	33.2

Table 7.25: Raw data for density of the 1,2 -butanediol systems choline chloride at 293K

ChCl %	0	5	10	15	20
Density (gcm ⁻³)	1.006	1.009	1.013	1.022	1.030

*Figure 7.7: Plot of temperature versus viscosity as a function of choline chloride composition for the 1,2-butanediol system*

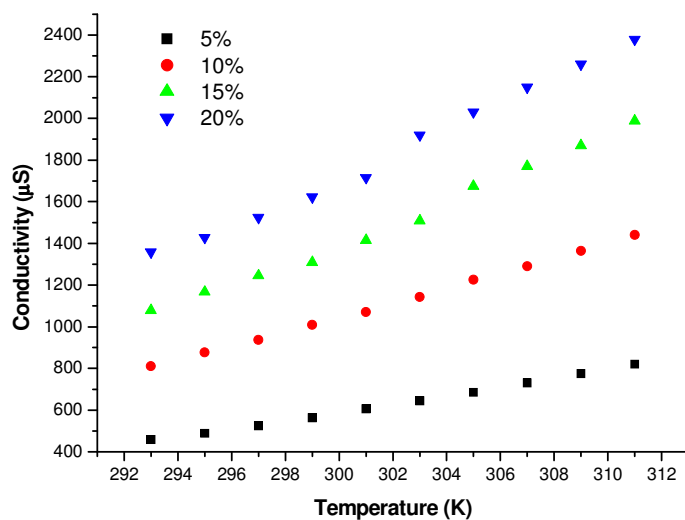


Figure 7.8: Plot of temperature versus conductivity as a function of choline chloride composition for the 1,2-butanediol system

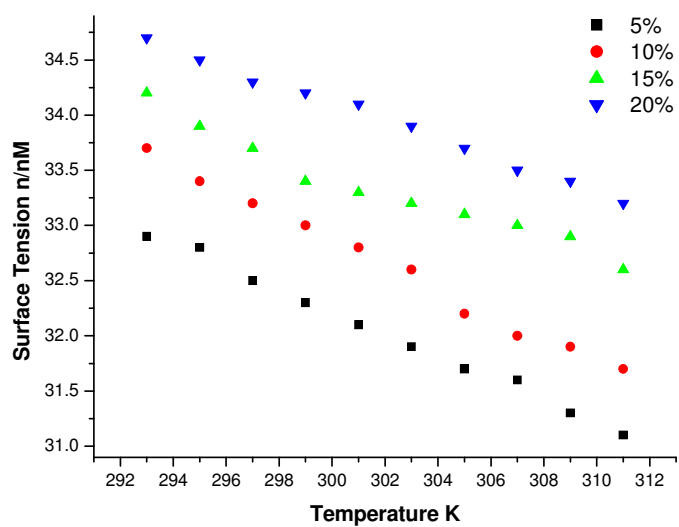


Figure 7.9: Plot of temperature versus surface tension as a function of choline chloride composition for the 1,2-butanediol system

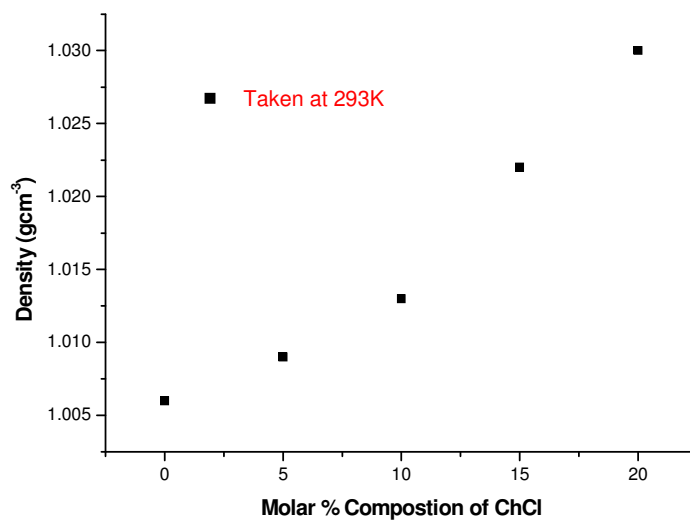


Figure 7.10: Plot of choline chloride composition versus density for the 1,2-butanediol system taken at 293 K

7.1.5 Choline Chloride : 1,3 Butanediol

Table 7.26: Raw data for 1,3-butanediol with 5% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	98	86	77	67	60	53	46	41	36	31
Conductivity (μS)	351	375	403	431	460	489	521	554	587	622
Surface Tension (n/nM)	34.4	34.2	34.0	33.9	33.7	33.4	33.0	32.6	32.3	31.9

Table 7.27: Raw data for 1,3-butanediol with 10% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	101	89	79	70	62	55	48	43	38	34
Conductivity (μS)	645	693	741	792	846	900	953	1014	1069	1120
Surface Tension (n/nM)	38.2	37.9	37.8	37.5	37.5	36.9	36.5	36.2	35.9	35.7

Table 7.28: Raw data for 1,3-butanediol with 15% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	106	94	82	72	62	53	48	43	36	31
Conductivity (μS)	934	987	1051	1118	1190	1264	1335	1406	1480	1616
Surface Tension (n/nM)	39.0	38.9	38.6	38.3	38.3	38.2	38.0	37.6	37.2	36.9

Table 7.29: Raw data for 1,3-butanediol with 20% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	113	101	89	77	70	60	53	48	43	39
Conductivity (μS)	1152	1228	1309	1380	1475	1565	1652	1824	1923	2070
Surface Tension (n/nM)	40.1	39.8	39.6	39.6	39.2	39.2	38.9	38.5	38.3	38.1

Table 7.30: Raw data for density of the 1,3 -butanediol systems choline chloride at 293K

ChCl %	0	5	10	15	20
Density (gcm ⁻³)	1.005	1.008	1.015	1.026	1.034

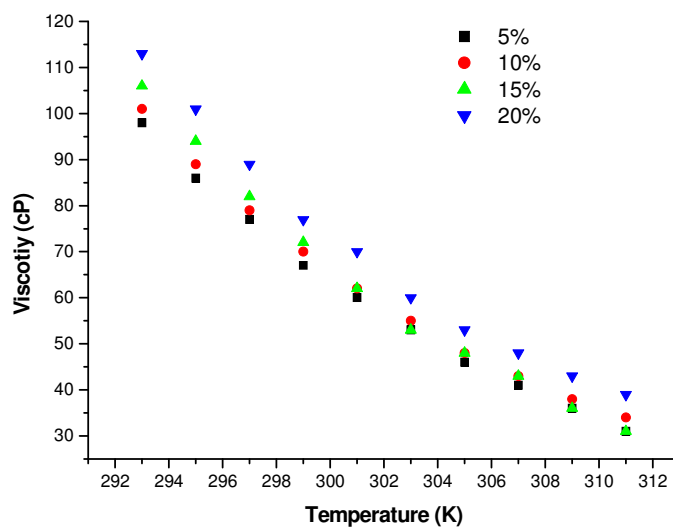


Figure 7.11: Plot of temperature versus viscosity as a function of choline chloride composition for the 1,3-butanediol system

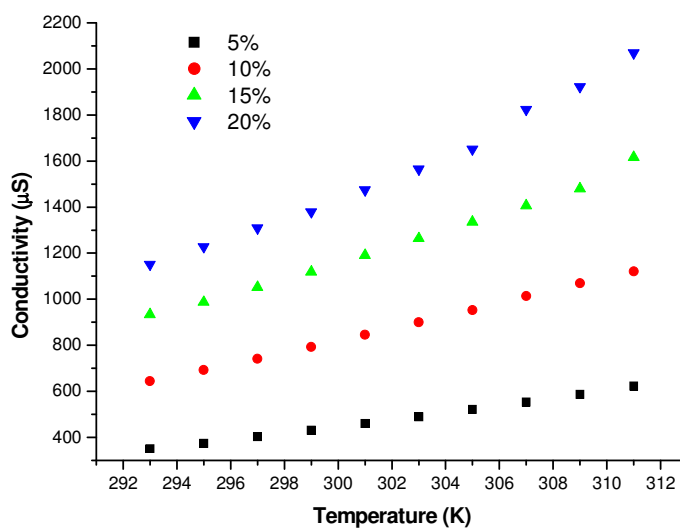


Figure 7.12: Plot of temperature versus conductivity as a function of choline chloride composition for the 1,3-butanediol system

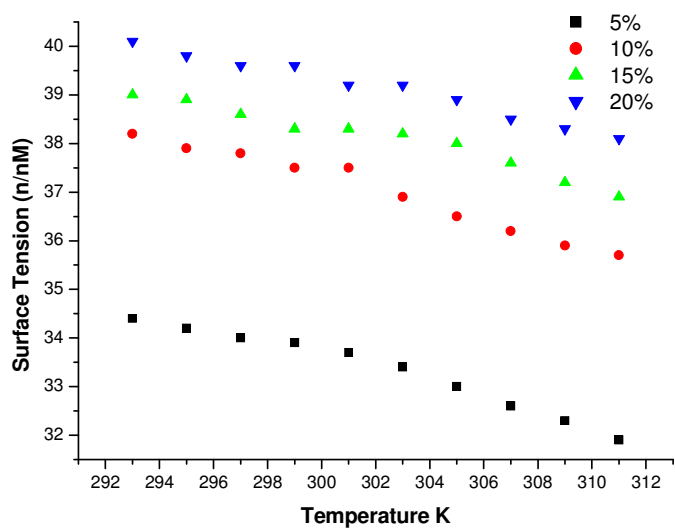


Figure 7.13: Plot of temperature versus surface tension as a function of choline chloride composition for the 1,3-butanediol system

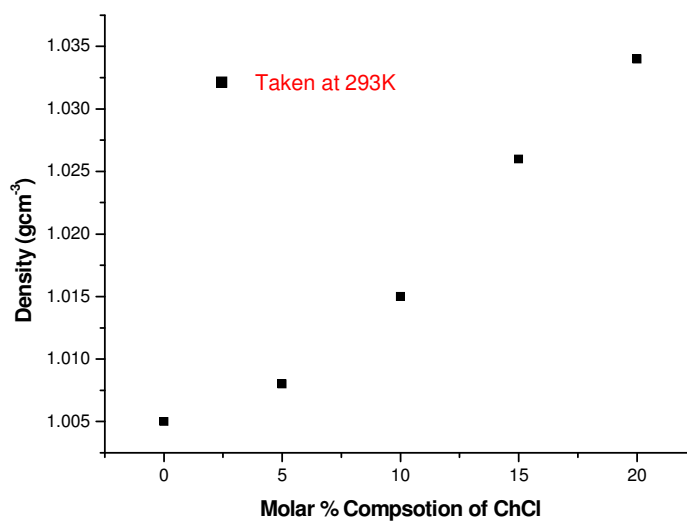


Figure 7.14: Plot of choline chloride composition versus density for the 1,3-butanediol system taken at 293 K

7.1.6 Choline Chloride : 2,3 Butanediol*Table 7.31: Raw data for 2,3-butanediol with 5% choline chloride*

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	120	96	82	69	58	48	41	36	31	26
Conductivity (μS)	246	277	302	328	356	389	422	457	491	526
Surface Tension (n/nM)	34.2	34.0	33.7	33.7	33.5	33.2	33.0	32.9	32.6	32.3

Table 7.32: Raw data for 2,3-butanediol with 10% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	122	101	86	72	62	53	46	38	34	31
Conductivity (μS)	476	530	575	623	672	734	788	840	898	958
Surface Tension (n/nM)	34.5	34.3	34.1	33.9	33.4	33.3	33.2	33.1	32.8	32.8

Table 7.33: Raw data for 2,3-butanediol with 15% choline chloride

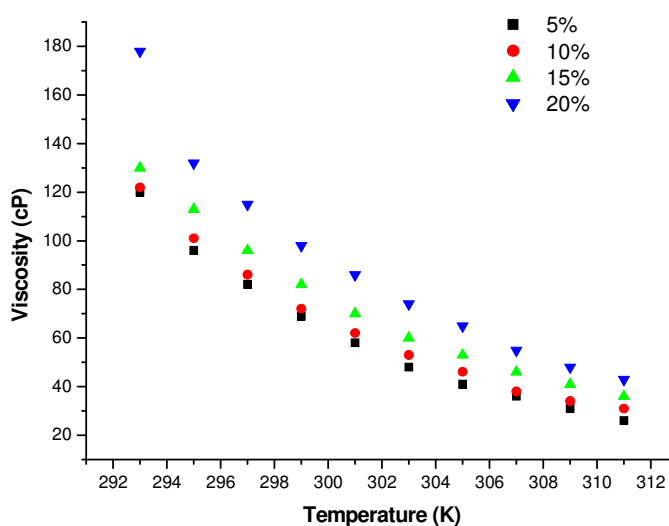
Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	130	113	96	82	70	60	53	46	41	36
Conductivity (μS)	776	839	916	996	1076	1163	1237	1321	1403	1495
Surface Tension (n/nM)	35.1	34.9	34.6	34.4	34.2	34.0	33.7	33.5	33.3	33.0

Table 7.34: Raw data for 2,3-butanediol with 20% choline chloride

Temperature (°C)	20	22	24	26	28	30	32	34	36	38
Viscosity (cP)	178	132	115	98	86	74	65	55	48	43
Conductivity (μS)	895	956	1026	1108	1190	1281	1372	1467	1566	1751
Surface Tension (n/nM)	35.6	35.4	34.9	34.7	34.7	34.5	34.3	34.0	33.7	33.5

Table 7.35: Raw data for density of the 2,3 -butanediol systems choline chloride at 293K

ChCl %	0	5	10	15	20
Density (gcm ⁻³)	0.995	1.001	1.015	1.024	1.032

*Figure 7.15: Plot of temperature versus viscosity as a function of choline chloride composition for the 2,3-butanediol system*

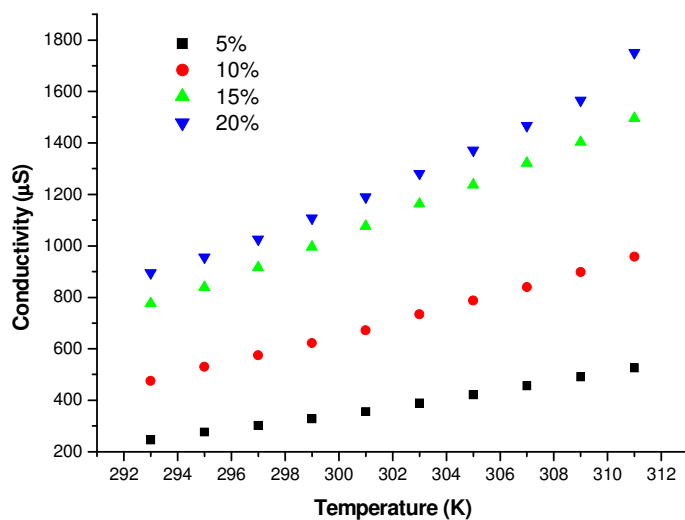


Figure 7.16: Plot of temperature versus conductivity as a function of choline chloride composition for the 2,3-butanediol system

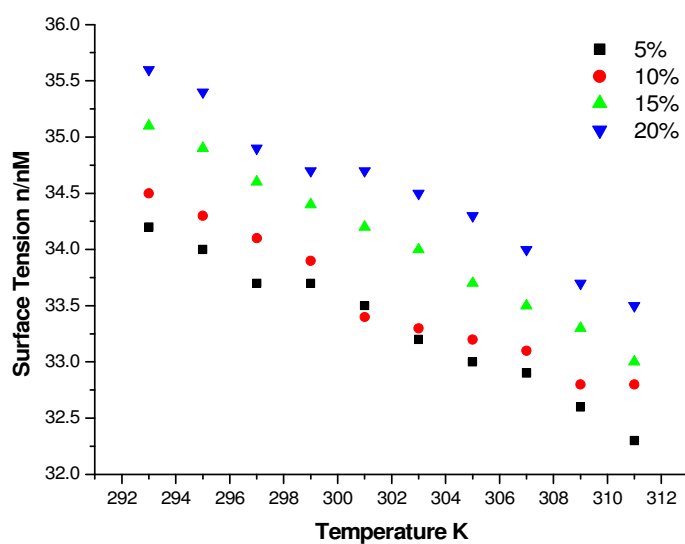


Figure 7.17: Plot of temperature versus surface tension as a function of choline chloride composition for the 2,3-butanediol system

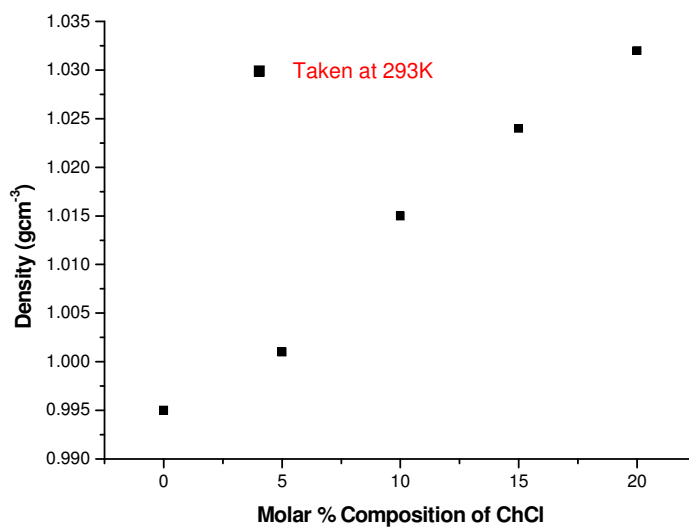


Figure 7.18: Plot of choline chloride composition versus density for the 2,3-butanediol system

7.1.7 Choline Chloride : Glycerol

Table 7.36: Raw data for glycerol with 5% choline chloride

Temperature (°C)	20	25	30	35	40	45	50	55
Viscosity (cP)	998	654	450	314	222	163	120	90
Conductivity (μS)	106.4	143.3	190.1	252	320	394	479	568
Surface Tension (n/nM)	63.7	62.8	62.0	61.3	60.5	59.8	59.3	58.7

Table 7.37: Raw data for glycerol with 10% choline chloride

Temperature (°C)	20	25	30	35	40	45	50	55
Viscosity (cP)	790	503	349	247	180	132	98	74
Conductivity (μS)	243	297	374	483	601	759	980	1245
Surface Tension (n/nM)	61.6	61.0	60.3	59.5	59.0	58.4	57.9	57.5

Table 7.38: Raw data for glycerol with 15% choline chloride

Temperature (°C)	20	25	30	35	40	45	50	55
Viscosity (cP)	548	380	270	194	140	107	80	60
Conductivity (μS)	470	555	666	798	963	1114	1403	1788
Surface Tension (n/nM)	60.8	60.2	59.7	59.1	58.7	58.1	57.6	57.3

Table 7.39: Raw data for glycerol with 20% choline chloride

Temperature (°C)	20	25	30	35	40	45	50	55
Viscosity (cP)	503	350	246	178	132	98	86	57
Conductivity (μS)	580	739	930	1140	1362	1609	1923	2250
Surface Tension (n/nM)	57.4	57.0	56.6	56.1	55.7	55.2	54.8	54.4

Table 7.40: Raw data for glycerol with 25% choline chloride

Temperature (°C)	20	25	30	35	40	45	50	55
Viscosity (cP)	450	320	229	169	126	95	73	58
Conductivity (μS)	850	1030	1244	1490	1835	2140	2480	2930
Surface Tension (n/nM)	50.8	50.3	49.9	49.3	48.9	48.4	48.0	47.6

Table 7.41: Raw data for glycerol with 30% choline chloride

Temperature (°C)	20	25	30	35	40	45	50	55
Viscosity (cP)	401	295	213	160	120	91	71	55
Conductivity (μS)	964	1165	1410	1750	2080	2430	2800	3260
Surface Tension (n/nM)	48.5	48.0	47.5	47.1	46.7	46.4	46.0	45.6

Table 7.42: Raw data for glycerol with 33% choline chloride

Temperature (°C)	20	25	30	35	40	45	50	55
Viscosity (cP)	376	259	188	140	104	82	64	52
Conductivity (μS)	1047	1298	1636	1947	2320	2710	3110	3560
Surface Tension (n/nM)	55.8	55.4	55.0	54.7	54.2	53.8	53.4	53.0

Table 7.43: Raw data for density of the glycerol systems choline chloride at 293K

ChCl %	0	5	10	15	20	25	30	33
Density (gcm ⁻³)	1.261	1.242	1.234	1.219	1.210	1.203	1.192	1.181

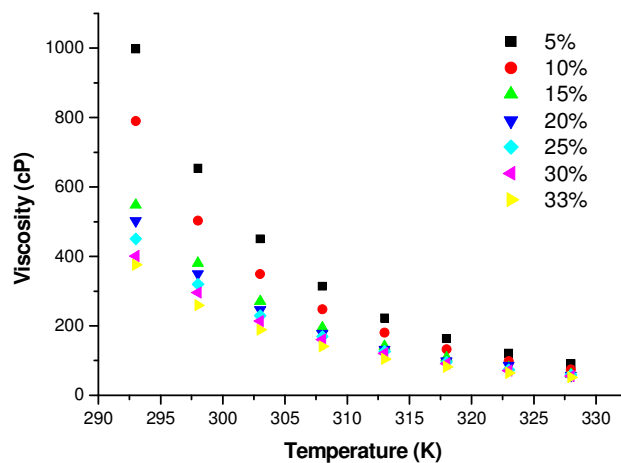


Figure 7.19: Plot of temperature versus viscosity as a function of choline chloride composition for the glycerol system

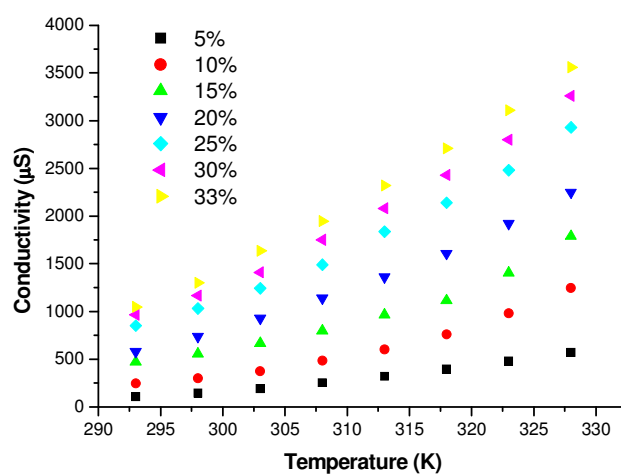


Figure 7.20: Plot of temperature versus conductivity as a function of choline chloride composition for the glycerol system

7.2 Esterification Raw Data

7.2.1 Pure Glycerol

Table 7.44: Raw data for concentrations of products and reagents in pure glycerol with 0.1 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.1	0	0	0
30	0.0777	0.0131	4.6E-4	0
60	0.08064	0.01644	4.3E-4	6.87E-4
90	0.07845	0.01923	3.05E-4	5.7E-4
180	0.07542	0.02132	5.44E-4	7.25E-4
240	0.07495	0.02203	6.72E-4	5.6E-4
300	0.07283	0.02428	8.53E-4	3.95E-4
360	0.07319	0.02322	0.00112	4.49E-4
420	0.07166	0.02389	0.00117	7.03E-4
480	0.07282	0.02445	8.31E-4	3.54E-4

Table 7.45: Raw data for concentrations of products and reagents in pure glycerol with 0.2 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.2	0	0	0
30	0.08163	0.1027	0.00783	0
60	0.0317	0.12862	0.01913	2.58E-4
90	0.01876	0.13147	0.02421	4.54E-4
120	0.01063	0.1303	0.02885	4.56E-4
180	0.01446	0.11393	0.03457	8.25E-4
240	0.01967	0.11352	0.03163	0.00118
300	0.02151	0.11229	0.03117	0.00128
360	0.02217	0.1098	0.03209	0.00129
420	0.02457	0.10701	0.03166	0.0017
1440	0.02348	0.1099	0.03086	0.00163

Table 7.46: Raw data for concentrations of products and reagents in pure glycerol with 0.3 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.3	0	0	0
30	0.11832	0.15416	0.01323	0
60	0.05133	0.17224	0.03764	3.8E-4
90	0.0274	0.19973	0.03552	6.09E-4
120	0.02016	0.19667	0.04021	9.16E-4
180	0.01635	0.19374	0.04314	0.00121
360	0.02841	0.16824	0.04838	0.0022
420	0.01995	0.17575	0.04909	0.00205
480	0.02369	0.16323	0.05291	0.00242
540	0.02944	0.15989	0.05161	0.00248
1620	0.02259	0.16888	0.04992	0.0029

Table 7.47: Raw data for concentrations of products and reagents in pure glycerol with 0.4 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.4	0	0	0
30	0.2466	0.13435	0.00952	0
60	0.13384	0.21112	0.02698	3.6E-4
90	0.08704	0.20952	0.04983	0.00126
120	0.04818	0.24949	0.04855	0.00174
180	0.04839	0.22793	0.0577	0.00275
240	0.05138	0.21491	0.06153	0.00355
300	0.05047	0.21519	0.0626	0.00305
360	0.05221	0.22125	0.05743	0.0039
480	0.05299	0.22522	0.05554	0.00357
540	0.05928	0.21212	0.05875	0.00371
1560	0.04436	0.09188	0.0998	0.02139

Table 7.48: Raw data for concentrations of products and reagents in pure glycerol with 0.6 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.6	0	0	0
30	0.34933	0.21333	0.01867	0
60	0.19603	0.31514	0.04367	0.00149
90	0.16588	0.21038	0.11025	0.00324
120	0.1439	0.23983	0.10356	0.00916
180	0.13291	0.25063	0.10158	0.01329
300	0.08773	0.24058	0.12859	0.01452
360	0.07565	0.24928	0.13001	0.01504
420	0.08421	0.27116	0.11362	0.0212
480	0.08642	0.27738	0.10989	0.01643
1320	0.06887	0.28838	0.11083	0.02109

7.2.2 ChCl : Glycerol 1:3*Table 7.49: Raw data for concentrations of products and reagents in ChCl: glycerol 1:3 with 0.2 M lauric acid*

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.2	0	0	0
30	0.1331	0.02163	0.02253	6.93E-5
60	0.11367	0.02002	0.03306	5.96E-5
120	0.04601	0.01456	0.06924	3.15E-4
180	0.04506	0.01245	0.0691	0.00143
300	0.02781	0.04424	0.06103	0.00197
420	0.02083	0.04427	0.06289	0.00304
480	0.02234	0.03951	0.06539	0.00245
540	0.01339	0.05209	0.0633	0.00264
1320	0.02074	0.02931	0.06381	0.00744

Table 7.50: Raw data for concentrations of products and reagents in ChCl: glycerol 1:3 with 0.3 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.3	0	0	0
30	0.25082	0.03344	0.00787	0
60	0.19644	0.05257	0.02527	0
300	0.03325	0.07539	0.08718	0.00535
360	0.03793	0.08118	0.08246	0.00751
420	0.03123	0.08443	0.08166	0.01041
480	0.02866	0.08225	0.08221	0.00846
540	0.03123	0.07894	0.08087	0.00987
1620	0.02808	0.06211	0.0797	0.00398

Table 7.51: Raw data for concentrations of products and reagents in ChCl: glycerol 1:3 with 0.4 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.4	0	0	0
30	0.36124	0.03173	0.00351	0
60	0.34009	0.04465	0.00763	0
90	0.26924	0.07708	0.02663	1.38E-4
120	0.20308	0.09983	0.04718	9.12E-4
180	0.10922	0.11996	0.08057	0.00322
240	0.0755	0.11552	0.0906	0.00926
300	0.08249	0.11516	0.09048	0.00713
360	0.07082	0.10865	0.09524	0.01002
420	0.05658	0.11159	0.09509	0.01388
480	0.05527	0.11975	0.09557	0.01128
540	0.05521	0.12128	0.09202	0.01316
1560	0.04494	0.19324	0.07296	0.0053

Table 7.52: Raw data for concentrations of products and reagents in ChCl: glycerol 1:3 with 0.6 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.6	0	0	0
30	0.41837	0.12392	0.02885	0
60	0.32682	0.11362	0.07769	0.00418
90	0.18465	0.15757	0.12113	0.01551
180	0.11359	0.16602	0.14592	0.02854
240	0.10677	0.11793	0.15394	0.06741
300	0.10547	0.0678	0.1839	0.05893
360	0.117	0.04945	0.17108	0.09139
480	0.10411	0.04219	0.17753	0.09863
540	0.09803	0.04448	0.17973	0.09803
1320	0.10363	0.05078	0.15855	0.12877

7.2.3 ChCl : Glycerol 1:2

Table 7.53: Raw data for concentrations of products and reagents in ChCl: glycerol 1:2 with 0.1 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.1	0	0	0
30	0.05366	0.03384	0.00608	1.15E-4
60	0.02809	0.04905	0.01092	3.4E-4
90	0.01789	0.04937	0.01537	6.73E-4
120	0.0124	0.04959	0.01768	8.84E-4
180	0.00726	0.05115	0.01881	0.00132
300	0.0046	0.0446	0.02207	0.00222
360	0.00367	0.04566	0.02186	0.00232
420	0.00363	0.04275	0.02306	0.0025
480	0.00363	0.03918	0.02465	0.00263
540	0.00369	0.04114	0.0227	0.00326
1320	0.00204	0.03409	0.0258	0.00409

Table 7.54: Raw data for concentrations of products and reagents in ChCl: glycerol 1:2 with 0.2 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.2	0	0	0
30	0.10859	0.04249	0.02437	6.25E-5
60	0.06714	0.06194	0.03475	4.73E-4
90	0.04468	0.06164	0.04578	7.02E-4
240	0.03707	0.0139	0.07272	0.00119
360	0.04504	0.01243	0.06803	0.00216
420	0.03053	0.01794	0.07237	0.00226
480	0.03813	0.01243	0.06966	0.00338
540	0.02454	0.02454	0.0689	0.00271
1320	0.02065	0.0254	0.06401	0.00865

Table 7.55: Raw data for concentrations of products and reagents in ChCl: glycerol 1:2 with 0.3 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.3	0	0	0
30	0.237	0.04362	0.00969	0
60	0.16051	0.08532	0.02657	3.4E-4
120	0.1297	0.03721	0.06506	9.92E-4
180	0.06917	0.05188	0.08417	0.00354
360	0.0466	0.04138	0.09399	0.00801
420	0.03552	0.04425	0.09605	0.00877
480	0.03938	0.05097	0.09162	0.0088
540	0.02973	0.02973	0.10092	0.0129
1500	0.0199	0.0489	0.08988	0.01714

Table 7.56: Raw data for concentrations of products and reagents in ChCl: glycerol 1:2 with 0.4 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.4	0	0	0
30	0.33232	0.02134	0.02317	0
60	0.27443	0.07717	0.02399	1.4E-4
90	0.23959	0.07197	0.04308	7.63E-4
180	0.11314	0.06171	0.10897	0.0024
240	0.07384	0.08528	0.11087	0.00638
300	0.07723	0.07377	0.11205	0.0083
360	0.06339	0.09649	0.10704	0.00868
420	0.06249	0.08808	0.10811	0.01107
480	0.0511	0.07971	0.11758	0.01137
540	0.03979	0.06822	0.12342	0.01501
1320	0.02507	0.07455	0.11588	0.02287

Table 7.57: Raw data for concentrations of products and reagents in ChCl: glycerol 1:2 with 0.6 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.6	0	0	0
30	0.57519	0.01969	0.00256	0
60	0.5548	0.02338	0.01091	0
90	0.44246	0.07632	0.04022	7.74E-4
120	0.34982	0.11307	0.06537	0.00636
180	0.23439	0.10794	0.11951	0.01864
240	0.16365	0.07944	0.15979	0.03733
300	0.14104	0.09176	0.16517	0.03687
360	0.13273	0.08296	0.16863	0.04706
480	0.11917	0.05164	0.18182	0.06555
540	0.11683	0.04221	0.18317	0.07462
1620	0.08547	0.00718	0.18444	0.13846

7.2.4 ChCl : Glycerol 1:1.5*Table 7.58: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1.5 with 0.1 M lauric acid*

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.1	0	0	0
30	0.05403	0.03127	0.00675	3.99E-4
60	0.03901	0.04122	0.00913	3.91E-4
90	0.02791	0.04605	0.01221	5.43E-4
120	0.02157	0.04754	0.01428	7.77E-4
180	0.01513	0.0478	0.01703	0.001
240	0.01113	0.0488	0.01772	0.00154
420	0.01519	0.04732	0.01678	0.00131
480	0.01097	0.04417	0.01955	0.00192
540	0.00705	0.04345	0.02133	0.00228
1320	0.00651	0.03491	0.02496	0.00316

Table 7.59: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1.5 with 0.2 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.2	0	0	0
30	0.19667	0	0.00167	0
60	0.18998	0	0.00501	0
90	0.17559	0	0.0122	0
120	0.1073	0.01003	0.0409	2.93E-4
180	0.0867	0.01164	0.04964	7.92E-4
360	0.07585	0.00212	0.05039	7.08E-4
420	0.0757	0.00172	0.05943	0.00124
480	0.07611	0.00238	0.05831	0.00163
540	0.06872	0.00248	0.06118	0.00215
1320	0.05465	0.00277	0.06766	0.00242

Table 7.60: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1.5 with 0.3 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.3	0	0	0
30	0.2297	0.02379	0.02306	1.27E-4
60	0.20146	0.04854	0.02477	1.42E-4
90	0.20625	0.04639	0.02345	1.51E-4
120	0.1961	0.02816	0.0373	3.79E-4
180	0.15292	0.02691	0.05695	0.00209
300	0.0911	0.02779	0.07781	0.00676
360	0.08007	0.03909	0.08192	0.00566
420	0.06677	0.04097	0.08474	0.00759
480	0.06198	0.04673	0.08397	0.00779
540	0.04851	0.04105	0.09145	0.00918
1560	0.02742	0.04135	0.08273	0.02193

Table 7.61: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1.5 with 0.4 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.4	0	0	0
30	0.37128	0.01034	0.00919	0
60	0.28968	0.05891	0.02561	6.43E-5
90	0.23405	0.07155	0.04616	6.92E-4
120	0.17208	0.08839	0.06648	0.00219
180	0.11478	0.09746	0.08609	0.0052
300	0.07199	0.10911	0.09775	0.0078
360	0.06067	0.0915	0.11119	0.00849
420	0.06042	0.09005	0.10645	0.01223
480	0.05998	0.08376	0.11091	0.01148
540	0.04762	0.07954	0.11497	0.0143
1320	0.0227	0.07252	0.11823	0.02277

Table 7.62: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1.5 with 0.6 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.6	0	0	0
30	0.59103	0.00245	0.00326	0
60	0.54251	0.00648	0.02551	0
90	0.45042	0.00538	0.07109	0.00217
120	0.35196	0.10226	0.07067	0.00443
180	0.28226	0.10341	0.09492	0.02448
300	0.19993	0.12899	0.11824	0.03461
360	0.19264	0.13634	0.1158	0.03939
420	0.18019	0.1094	0.13193	0.04655
540	0.16525	0.14338	0.12272	0.04593
1320	0.08326	0.06712	0.15705	0.13553

7.2.5 ChCl : Glycerol 1:1

Table 6.63: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1 with 0.1 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.1	0	0	0
30	0.08198	0.017	2.02E-4	2.02E-4
60	0.0816	0.01104	0.00123	0.00164
90	0.07479	0.02222	0.00105	2.92E-4
120	0.07211	0.0249	0.00101	3.21E-4
240	0.04492	0.03522	0.00153	0.0056
300	0.04636	0.03787	0.00243	0.00364
360	0.04159	0.04106	0.00262	0.00404
480	0.04336	0.04191	0.00321	0.00277
540	0.04173	0.04248	0.00376	0.00276
1320	0.03108	0.0427	0.00473	0.00559

Table 7.64: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1 with 0.2 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.2	0	0	0
30	0.1804	0.00115	0.00922	0
60	0.15172	0.00318	0.02255	0
90	0.12051	0.00809	0.03508	4.13E-4
120	0.11071	0.00842	0.03899	9.63E-4
180	0.07484	0.03857	0.03915	0.00276
240	0.06427	0.04658	0.04009	0.00299
300	0.05058	0.06266	0.03821	0.00345
360	0.0481	0.05962	0.03946	0.00445
420	0.04314	0.06171	0.04134	0.00415
480	0.03706	0.06622	0.04131	0.0047
540	0.03001	0.07213	0.04155	0.00492
1440	0.0159	0.04252	0.05367	0.01141

Table 7.65: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1 with 0.3 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.3	0	0	0
30	0.20344	0.0342	0.03069	3.25E-4
60	0.16131	0.06089	0.03796	6.33E-4
120	0.0995	0.08545	0.05393	0.00239
180	0.07517	0.12034	0.04689	0.00357
240	0.05322	0.10153	0.06575	0.00458
300	0.0509	0.09447	0.06829	0.00602
360	0.05316	0.1012	0.06425	0.00606
480	0.06161	0.06494	0.07418	0.00837
540	0.05514	0.06565	0.07582	0.00919
1320	0.02023	0.06205	0.08779	0.01405

Table 7.66: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1 with 0.4 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.4	0	0	0
30	0.38799	2.65E-4	0.00587	0
60	0.33362	0.02189	0.02224	0
90	0.26945	0.05422	0.03697	7.99E-4
180	0.17017	0.09265	0.06198	0.00441
240	0.12087	0.10744	0.07417	0.00778
300	0.12013	0.09901	0.07354	0.01126
420	0.09282	0.09409	0.08881	0.01183
480	0.0891	0.07563	0.09946	0.01212
540	0.08197	0.0831	0.09763	0.01323
1320	0.05714	0.0792	0.10226	0.01972

Table 7.67: Raw data for concentrations of products and reagents in ChCl: glycerol 1:1 with 0.6 M lauric acid

Time (min)	[Free Acid]	[Mono Ester]	[Di Ester]	[Tri Ester]
0	0.6	0	0	0
30	0.59354	0	0.00323	0
60	0.5431	0	0.02845	0
120	0.38201	0.03488	0.08969	0.00374
240	0.18514	0.11973	0.12971	0.0357
300	0.16968	0.09756	0.14493	0.04289
360	0.16869	0.02907	0.17388	0.0545
420	0.15867	0.05459	0.15464	0.07745
480	0.14941	0.05644	0.15534	0.08348
540	0.15876	0.05365	0.14562	0.09635
1320	0.08865	0.05096	0.15418	0.15203

7.3 Publications

Application of Hole Theory to Define Ionic Liquids by their Transport Properties,

Andrew P. Abbott, Robert C. Harris, Karl S. Ryder, *J. Phys. Chem. B*, **2007**, *111*, 4910

4910

J. Phys. Chem. B **2007**, *111*, 4910–4913

Application of Hole Theory to Define Ionic Liquids by their Transport Properties[†]

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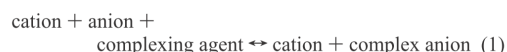
Eutectic mixtures of quaternary ammonium salts with Lewis or Brønsted acids have been described as ionic liquid, but doubt exists over the compositional range for which this description is valid. In the current work, the conductivity, viscosity, density, and surface tension of a number of glycolic mixtures with choline chloride are measured over the mole fraction range 0 to 0.33. The data are fitted to hole theory, and it is proposed that the composition at which the measured conductivity matches the theoretical value is the point at which hole mobility becomes the dominant mechanism for charge mobility. For the mixtures of ethylene glycol and butanediol, this occurs at a ChCl mole fraction of approximately 0.2.

Introduction

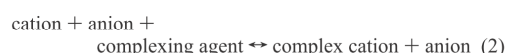
Ionic liquids are without doubt in their hiatus at the beginning of the 21st century, and yet there is significant confusion about what an ionic liquid actually is. The recognized definition as an ionic material that is liquid below 100 °C leaves significant question as to what constitutes an ionic material. Some authors like to limit the definition to cations and so-called discrete anions, e.g., BF₄[−] and NO₃[−], although this is unsatisfactory, as it excludes the original research in the area on chloroaluminate systems. These are less easy to categorize as ionic, as they depend upon complex equilibria and consist of a variety of anionic species. The concentrations of the ionic species are strongly influenced by the composition of the different components.

Others have classified ionic liquids into first and second generation ionic liquids,¹ where first generation liquids are those based on eutectics and second generation have discrete anions.² We have sought to further divide the first generation liquids into a variety of types depending on the nature of the Lewis or Brønsted acid that complexes the halide anion to form an ionic complex.³ While there is some dispute whether eutectics with Brønsted acids constitute ionic liquids at all, there are others who seek to widen the description of ionic liquids to include materials such as salt hydrates.⁴

What is clear is that all ionic liquids form due to delocalisation of charge and this can be described by an equilibrium



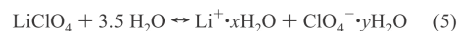
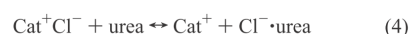
or potentially



with the vast majority focusing on the former case.

The confusion arises from the magnitude of the equilibrium constant. For discrete anions such as BF₄[−] and even ((CF₃SO₂)₂N)[−], the equilibrium lies clearly to the right of eq 1. For eutectic based liquids, the equilibrium constant depends

upon the strength of the Lewis or Brønsted acid such that a variety of complex anions are possible. Hence, all of the following could be described as ionic liquids



but there must be a point where the Lewis or Brønsted acid is in considerable excess and the system becomes a solution of salt in the acid. A similar scenario also exists with the incorporation of diluents or impurities. Many ionic liquids with discrete anions are hydrophilic, and the absorption of water is found to sometimes have a significant effect upon the viscosity and conductivity of the liquids.^{5–7} What is required is a simple method of distinguishing the properties of ionic liquids from those of a concentrated solution.

In the current work, we will present physical data on mixtures formed between quaternary ammonium halides and a variety of glycol hydrogen bond donors as a function of salt concentration. These will provide evidence for the change in properties from those of an ionic liquid to those of a solution.

Experimental

Choline chloride (ChCl) (Aldrich 99%) was recrystallized from absolute ethanol, filtered, and dried under vacuum. Ethylene glycol (EG), 1,4-butanediol (butylene glycol, BG), and glycerol (all Aldrich >99%) were used as received. The eutectic mixtures were formed by stirring the two components at 100 °C until a homogeneous colorless liquid was formed. The liquids were cooled at a rate of 1 °C min^{−1}, and the freezing point was taken as the temperature at which the first solid began to form. The viscosity was determined using a Brookfield DV-E viscometer fitted with a thermostated jacket. The conductivity and its temperature dependence were determined using a Jenway 4071 conductivity meter with temperature and conductivity probes. A Kruss K11 tensiometer equipped with a thermostatted jacket, was used for the surface tension experiments. The equilibrium geometry and volumes of the ions and hydrogen

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bond donors were calculated using a Hartree–Fock method utilizing an STO-3G model provided by commercially available software.⁸

Results

Angell⁹ has shown that for ionic liquids with discrete anions the molar conductivity is inversely proportional to the viscosity of the liquid and this correlation is virtually independent of the cation and anion. This has been used as a method of defining the properties of an ionic liquid. We have recently used hole theory to show that Angell's observation is due to a different mechanism of charge transfer in ionic liquids from that encountered in ionic solutions or high-temperature molten salts.^{10,11} Hole theory was initially developed by Fürth¹² as an alternate view of the liquid state and later expanded by Bockris et al. for use with molten salts.¹³ The model was found to have serious limitations in molten salts because ionic association significantly affects ionic activity. A discussion of the various models for pure fused salts is given by Stillinger.¹⁴ However, in ionic liquids the large ion size and low temperatures mean that hole sizes are comparatively small. The probability of ions being able to move is several orders of magnitude smaller than in molten salts and so the role of ionic association can be ignored for charge transfer. Under these conditions Hole theory is an excellent model for the mobility of charged species.

We have shown that under these conditions the viscosity of a fluid, η , can be modeled by assuming it behaves like an ideal gas,¹⁰ but its motion was restricted by the availability of sites of the ions/molecules to move into. Hence, it was shown that

$$\eta = \frac{mc/2.12\sigma}{P(r > R)} \quad (6)$$

where m is the molecular mass (for ionic fluids this was taken as the geometric mean), \bar{c} is the average speed of the molecule ($= (8kT/\pi m)^{1/2}$), σ is the collision diameter of the molecule ($4\pi R^2$), and k is the Boltzmann constant. The probability of finding a hole of radius, r , greater than the radius of the solvent molecule, R , in a given liquid, ($P(r > R)$) is given by integration of eq 7¹⁰:

$$P \cdot dr = 0.601a^{7/2}r^2e^{-ar}dr \quad (7)$$

where $a = 4\pi\gamma/kT$ and γ is the surface tension. The good correlation obtained between the calculated and measured viscosities showed that it is valid to think of the viscosity of ionic fluids as being limited by the availability of holes. It therefore follows that charge transfer should occur in the same manner, hence ion motion depends on the migration of holes in the opposite direction. Since the fraction of suitably sized holes in ambient temperature ionic liquids is very low the holes can be assumed to be at infinite dilution and can be described by combining the Stokes–Einstein and Nernst–Einstein equations (eq 8)¹¹: where z is the charge on the ion and e is the electronic

$$\lambda_+ = z^2F e/6\pi\eta R_+ \quad (8)$$

charge. An expression can therefore be obtained for the molar conductivity of both ions: This explains Angell's observation

$$\Lambda = z^2F e/6\pi\eta(R_+ + R_-) \quad (9)$$

that all ionic liquids display a correlation between the molar conductivity and the fluidity.⁹ Although the size of the ion is also a variable in eq 9, in practice all of the ionic species that

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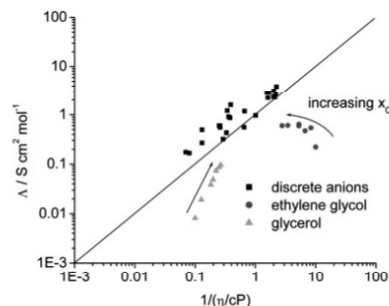


Figure 1. Plot of molar conductivity vs fluidity for a range of ionic liquids with discrete anions and mixtures of ChCl with glycerol and ethylene glycol at 20 °C.

form ionic liquids have relatively similar dimensions ($R \approx 3 - 4$ Å). Hole theory therefore potentially provides a method by which the dilution of ionic liquids can be quantified because eq 9 will no longer be valid when hole mobility does not limit conductivity.

Figure 1 shows a plot of molar conductivity versus fluidity ($1/\eta$) for the data presented in a recent review by Galinski et al. for ionic liquids with discrete anions.¹⁵ The scatter in Figure 1 is thought to be primarily due to the difference in size between the ions. It has previously been shown that eutectic mixtures of quaternary ammonium salts with hydrogen bond donors form liquids at ambient temperatures and the conductivity of these liquids obey eq 9.¹⁶ We have assumed that these liquids can therefore be classified as ionic liquids and Figure 1 shows some that these data fit the classification of Angell.⁹

The ability to vary the composition of Lewis or Brønsted acid adds an additional dimension to the tuneability of the eutectic-based ionic liquids. To test the hypothesis that an ionic liquid can become a solution is relatively difficult, as most complexing agents are solid at ambient temperature and hence a true test should be conducted at the melting point of the complexing agent. This adds the additional complexity that the interaction between the anion and the complexing agent will be significantly affected by the temperature. Lecocq et al.¹⁷ used ¹³C and ³⁵Cl NMR spectroscopy to show that at 110 °C 1BMMICl:1ZnCl₂ varies its structure with time from [BMMI]⁺[ZnCl₃]⁻ to [BMMI...Cl...ZnCl₂]. What is important, however, is the behavior of ionic liquids at ambient temperature. The only exceptions that we have found are with diols and triols which are liquid at ambient temperature and form relatively shallow eutectics when mixed with quaternary ammonium salts. These liquids have been shown to be very useful for electropolishing stainless steel as they are benign and simple to synthesize and recycle.^{18,19}

Table 1 shows the conductivity, viscosity, density, and surface tension of three glycolic mixtures with ChCl: ethylene glycol, 1,4-butanediol, and glycerol. An interesting phenomenon occurs in the different liquids. For EG and BG, the viscosity increases as salt is added to the mixture as would be expected for most salt solutions. For glycerol, however, the viscosity decreases when ChCl is added. This is because the diols form linear aggregates of hydrogen-bonded molecules, whereas glycerol with its three OH moieties is a three dimensionally hydrogen-bonded liquid imparting greater order, higher density, and higher surface tension than the other glycols. The addition of salt to glycerol breaks up this structure by complexing the OH moieties to the anion of the salt. This causes a significant decrease in

TABLE 1: Physical Properties of Various ChCl: Glycol Mixtures as a Function of Composition at 20.0 °C

ChCl: Ethylene Glycol							
% ChCl	5	10	15	20	25	30	33
density/gcm ⁻³	1.114	1.115	1.115	1.117	1.118	1.118	1.12
viscosity/cP	10	12	15	19	19	29	36
conductivity/mS cm ⁻¹	3.74	7.52	8.14	8.53	8.74	7.92	7.61
surface tension/mN m ⁻¹	48.1	47.3	45.3	47	45.4	47.2	49
ChCl: Glycerol							
density/gcm ⁻³	1.242	1.234	1.219	1.21	1.203	1.192	1.181
viscosity/cP	998	790	548	503	450	401	376
conductivity/μS cm ⁻¹	106.4	243	470	580	850	964	1047
surface tension/mN m ⁻¹	63.7	60.2	60.8	57.4	50.8	48.5	55.8
ChCl: 1,4Butanediol							
density/gcm ⁻³	1.021	1.026	1.036	1.046	1.052		
viscosity/cP	78	84	78	88	140		
conductivity/μS cm ⁻¹	593	923	1271	1606	1654		
surface Tension/mN m ⁻¹	46.4	46.8	46.9	47.4	47.6		

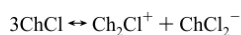
the surface tension opening up the free volume of the liquid, causing a decrease in the density and allowing greater movement of the ionic species.

Figure 2 shows the molar conductivity of choline chloride in a number of glycolic liquids. The molar conductivity was calculated by

$$\Lambda = \kappa M / \rho \quad (10)$$

where κ is the conductivity, ρ is the density, and M is the molar mass which is take as being the molar mass of the two components multiplied by their mole fraction in the mixture. The ionic radii were calculated using commercially available software assuming that each chloride ion is coordinated by one glycol molecule.⁸ The only other viable assumption is that two glycol molecules coordinate the chloride ion. The difference in radii between the two complexes is approximately 0.6 Å, and this causes a change in the calculated molar conductivity of approximately 10%. FAB-MS shows the presence of the chloride coordinated to both one and two glycol molecules, and presumably the composition of the two species will depend upon the composition of the two components in the mixture.

At low concentrations, most of the ions exist as ion pairs, and the molar conductivity is relatively low. As the concentration of salt increases, the molar conductivity increases as the concentration of triple ion increases according to This is well-



known to occur in nonaqueous solutions.^{20,21} As the salt concentration increases, the amount of free solvent decreases, and at some point there must be no free solvent molecules as

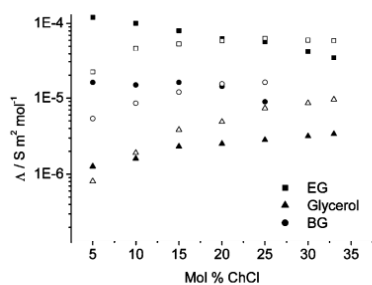


Figure 2. Plot of molar conductivity vs ChCl content for a variety of mixtures with different glycols at 20 °C. Open symbols are the measured values and filled symbols are the values calculated using eq 9.

they are all coordinated to the ions. At this point the movement of free “solvent” is prohibited, and it is only ionic species that can move. Under these conditions the mobility of the complex species is severely hindered due to their size and the decreased free volume of the liquid. For EG a maximum is observed in molar conductivity at approximately 25 mol % ChCl. According to eq 9, the limiting molar conductivity will be inversely proportional to the viscosity, and it would be expected that the molar conductivity would decrease as hole mobility replaced ion mobility as the dominant factor in charge transport. It is at this composition where hole mobility overtakes ion mobility as the dominant mechanism for charge-transfer that we propose an ionic liquid is formed.

Figure 1 shows the molar conductivity of the glycolic mixtures as a function of fluidity. It is clear that the molar conductivity values of the dilute solutions differ significantly from the Walden rule which is to be expected as the conductivity is dependent upon the number of charge carriers and the main mobile species which govern the fluidity of the liquid are the glycol molecules. Hence, the conductivity is greater than that predicted by eq 9. As the concentration of salt increases, the number of free solvent molecules decreases, and the conductivity approaches that of the other liquids where mobility is limited by hole mobility. Hence, the definition by Angell that all ionic liquids obey the same conductivity versus fluidity correlation is a good approximation to determining whether a material is an ionic liquid. A more rigid definition is possibly that an ionic liquid is a fluid where eq 9 is valid the justification being that in an ionic liquid the transport of charge is limited by hole mobility.

To determine the composition at which the eutectics in Figure 2 change from being ionic liquids to solutions of salt in glycols, the molar conductivity was calculated using eq 9 and plotted against the measured conductivity, and it can be seen that significant deviations are seen up to a composition of 20% EG and BG. Thereupon relatively good correlation was observed. BG could not be studied above 25 mol % because the temperature at which a homogeneous solution formed was above 20 °C. The other isomers of BG (1,2-, 1,3- and 2,3-) were also tested and showed similar trends to those observed for 1,4-BG, but these all reached supersaturation above 20 mol % at 20 °C and hence approached the properties of ionic liquids but could not exhibit the decrease in molar conductivity with concentration.

For glycerol the correlation between the values calculated from eq 9 and the measured values is closer at lower concentrations. This could be seen as an exception that shows the validity

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of the assumption, insofar as the very high viscosity of the pure fluid and the low free volume, as indicated by the high surface tension, mean that charge transport is still limited by hole transport, only in this exceptional case the mobility of the “solvent” molecules (i.e., glycerol) is not due to them all being complexed to the Cl^- but rather in this case they are hindered from moving by other solvent molecules.

If the mobility of charge is limited by the availability of suitably sized holes, then one diagnostic test for determining where most ionic liquids take on the properties of solutions would be that the molar conductivity passes through a maximum where ion mobility and hole mobility are at equilibrium.

Conclusions

It has been shown that mixtures of quaternary ammonium salts with glycols form homogeneous fluids with the properties of ionic liquids when the mole fraction of the salt exceeds 0.2. At higher salt concentrations, the dominant mode of charge transport is via the mobility of holes, and the mixture has the viscosity and conductivity characteristic of an ionic liquid, and below this concentration the properties can be described by the theories related to concentrated ionic solutions.

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Extraction of glycerol from biodiesel into a eutectic based ionic liquid

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A Lewis basic mixture of quaternary ammonium salts with glycerol has been used to extract excess glycerol from biodiesel formed from the reaction of triglycerides with ethanol in the presence of KOH. The effect of the cation on the partition coefficient of glycerol was determined, together with the time taken for the systems to reach equilibrium. Protocols were also investigated for the separation of glycerol from the quaternary ammonium salt mixtures.

Introduction

Biodiesel can be manufactured from a variety of natural product oil feedstocks, for example, sunflower oil, rapeseed oil, rubber seeds, and soy bean oil.^{1–8} Its synthesis from a natural product means biodiesel is a carbon-neutral fuel (*i.e.* carbon dioxide generated from its combustion is equal to or less than the carbon dioxide used up by the plants it is derived from) and it produces significantly fewer particulates¹ than conventional diesel fuel with no sulfurous emissions. It can be used pure or blended with mineral diesel in most modern compression-ignition engines.⁹

The manufacturing procedure for biodiesel is much the same, regardless of the feedstock used. The triglyceride oil extracted from the plant is transesterified into alkyl esters (usually methyl or ethyl) using a catalyst such as KOH, NaOH, or a lipase. This yields three moles of ester and one mole of glycerol per mole of triglyceride as shown schematically in Fig. 1.⁷

The liberated fatty acid esters comprise a mixture of C-18 products, such as stearic, linoleic, linolenic, and oleic acid, and C-16 derivatives, such as palmitic acid in varying compositions depending on the source. The glycerol is an unwanted by-product and must be removed before the ester biodiesel can be used as fuel, as the viscosity of the glycerol present in the mixture impedes the high-pressure injection system of a modern diesel engine and may cause damage.

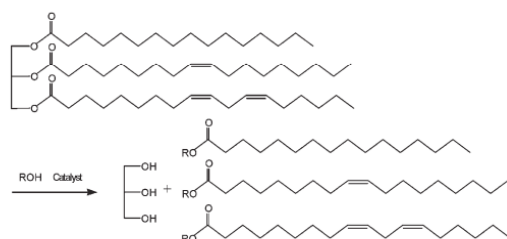


Fig. 1 Transesterification of triglycerides to alkyl esters of fatty acids and glycerol.

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Several methods have been used to remove glycerol from biodiesel and these include adsorption over silica,¹⁰ membrane reactors,¹¹ and the addition of lime and phosphoric acid.¹² There are numerous problems associated with the costs and complications of operating biodiesel synthesis on an industrial scale.⁷ Currently it is cheaper to drill and refine mineral diesel than to grow, extract, transesterify, and purify biodiesel, and methods to improve the economical feasibility of biodiesel production are sought.

The aim of this study is to design a system to separate glycerol and residual ethanol from some ethanol-esterified natural oils. We have previously shown that ionic liquids formed from eutectic mixtures of quaternary ammonium salts and hydrogen bond donors (HBDs) are an effective method of producing inexpensive, non-toxic, and environmentally benign solvent systems.^{13,14} These so-called deep eutectic solvents (DESs) are made from quaternary ammonium salts mixed with a small HBD molecule, of which glycerol is one example. These DESs have been shown to have practical use in applications such as electropolishing¹⁵ and metal oxide processing.¹⁶

The eutectic point (the composition of lowest freezing point and viscosity) of these solvents, that have so far been characterised, tends to occur at either 1 : 1 or 2 : 1 HBD : salt molar ratio.^{13,14} The components of the mixture have a high affinity for each other due to the strength of the hydrogen bonding interactions formed. The high affinity of the salt for glycerol should mean that if a Lewis basic mixture of salt and glycerol is mixed with a phase with a low affinity for glycerol, then the former should be able to extract the excess glycerol. The high affinity of the ionic liquids for alcohols should also allow excess ethanol to be extracted from the biodiesel layer.

The aim of this work is to characterise and optimise a eutectic extraction system capable of washing glycerol out of the biodiesel product. Five quaternary ammonium salts were studied and all formed eutectics with glycerol that were miscible with water and immiscible with oils.

Experimental

The alcoholysis of vegetable oils was studied using alkaline catalysts. Potassium hydroxide, 5 g (0.9 mol) was suspended in 1 L of absolute ethanol and shaken until dissolved. 1 g of this solution was mixed with 5 g of oil and shaken in a small

stoppered flask. The flasks were placed in an incubator shaker at 40 °C and 400 rpm for 24 h. After this time, they were allowed to stand for 1 h. Separation of the KOH-catalysed reaction in ethanol did not occur, but separation of the NaOH-catalysed reaction in methanol was observed. The molecular mass of soy bean oil was assumed to be 965.

A larger volume (10 ml oil and 2 ml 0.9 M KOH-ethanol) was produced under the same conditions and this was divided into 1 ml samples and used to test the eutectics and quaternary ammonium salts as extraction media. 1 mole equivalent of each salt was added to the oil samples and heated with agitation, but a lower layer was not seen to form. 1 : 1 eutectics of each quaternary ammonium salt were prepared and added to the solutions in a 1 : 1 salt : oil molar ratio.

For the larger scale experiments 500 g of oil (rapeseed or soy bean) and 150 g of 0.9 mol KOH in absolute ethanol were mixed in an incubator at 40 °C and 400 rpm for 24 h. After this period, a lower layer separated from the rapeseed oil reaction. This was collected and NMR analysis confirmed it to be predominantly glycerol. The soy bean oil reaction did not separate on standing.

The DES used for extraction was made by heating 46 g (0.5 mol) glycerol and 69.8 g (0.5 mol) of choline chloride on a hotplate at 50 °C until a homogenous transparent liquid formed. This was added to the homogeneous oil resulting from the soy bean oil reaction and the separated oil from the rapeseed oil reaction, shaken and allowed to stand for 30 min. Samples of the upper and lower layers were analysed by ¹H NMR in 1-butanol and dichloromethane, respectively, and a 10 µl sample of the upper layer was analysed by GC.

Removal of glycerol from a standard solution of ethyl caprate-glycerol was carried out using a standard solution of ethyl caprate-glycerol in a 3 : 1 molar ratio. To this 0.5% v/v solution, ethanol was added to aid miscibility. 10 ml of this solution was mixed with a 1 : 1 glycerol-acetylcholine chloride eutectic and samples were taken from the upper layer and analysed by FT-IR.

Viscosity and freezing point determination of deep eutectic solvents: viscosity was determined using a Brookfield DV-E viscometer according to the standard procedure. The freezing point was taken to be the glass transition temperature or crystallisation temperature as was measured with a Jenway 4071 temperature probe after gradual cooling in ice followed by dry ice-acetone.

The chloride ion concentration was determined using potentiometry with a silver chloride and calomel electrode.

In the cell



the change in potential with chloride ion concentration was found to follow a Nernstian behaviour.

Results and discussion

Soy bean oil was chosen as the feedstock of study because of its favourable cetane number, and also because it did not separate readily from glycerol at the end of the reaction, and therefore was useful for the principles to be studied. Fig. 2

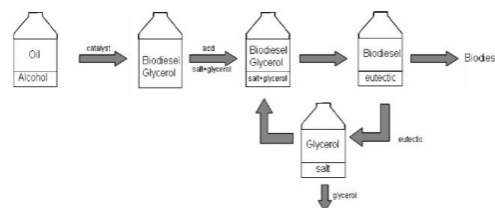


Fig. 2 Schematic diagram for the production of biodiesel and removal of excess glycerol using a sub-eutectic salt : glycerol mixture.

shows a schematic of a process that uses a choline chloride-glycerol mixture to draw out excess glycerol from biodiesel.

It was decided to concentrate on KOH and NaOH as the catalysts as these gave quantitative conversion of the oil to the methyl esters. Enzyme catalysed transesterification was also attempted, but of the fifteen lipases studied only *Candida antarctica* B gave a reasonable yield (38%) after a 24 h period of incubation. These data are comparable to the yields achieved with different oils published by Abigor *et al.*¹⁷

¹H NMR studies of the reaction products were undertaken using the solvent 1-butanol-*d*₁₀, as this was the only solvent in which glycerol, fatty acid esters, and unreacted soy bean oil were found to dissolve. The spectrum of the potassium hydroxide-catalysed reaction contained the glycerol signal but no discernible glyceride peaks (δ 4.15 and δ 4.3 ppm), which confirmed that the reaction had gone to completion.

Extraction of glycerol using sub-eutectic salt mixtures

Initially, pure quaternary ammonium salts were added to the crude biodiesel, to see if a deep eutectic would spontaneously form *in situ* extracting the glycerol and forming a separate layer. After the reaction was complete, the resulting oil was separated into 1 ml samples and each of these was shaken with a 0.5 mole equivalent of each of the quaternary ammonium salts chosen for the study. Upon shaking and heating, the salts all remained as solids and did not dissolve in the liquid phase, form a separate liquid phase, or effect any noticeable extraction of the glycerol from the biodiesel-glycerol mixture. This is probably due to the enthalpy of formation of the eutectic mixtures, and so an alternative approach was attempted.

Lewis basic mixtures of salt and glycerol (*i.e.* a 1 : 1 molar ratio) were made and heated until they formed homogeneous liquids. These were added to 1 ml samples of biodiesel in such quantity to ensure that the sum contents of both phases was a 1 : 2 salt : glycerol molar ratio. The mixtures were shaken, allowed to separate, and then analysed by ¹H NMR against the unwashed biodiesel product. A decrease in the glycerol signals (δ 3.55 and δ 3.45 ppm) in the oil phase was observed in all cases. No significant decrease in glycerol signals was observed when 1 : 2 salt : glycerol eutectics were added to the crude biodiesel in the same way, showing that the mixture is only effective at extracting glycerol when it is Lewis basic. No signal was detected for either ethanol or catalyst left in the biodiesel phase.

These initial results show that mixtures of salt and glycerol below the eutectic point can remove glycerol from crude

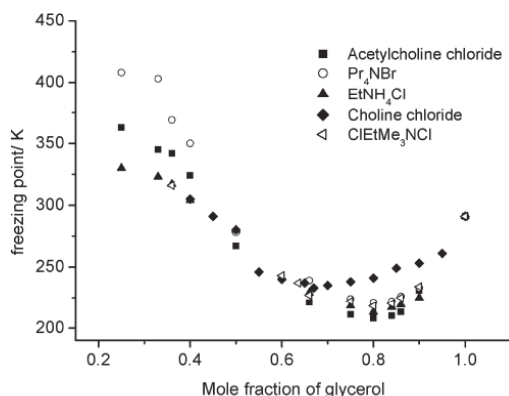


Fig. 3 Phase diagram of eutectics at different glycerol mole fractions.

biodiesel yields and suggests this extraction method to be suitable for more in-depth study.

Comparison of the physical properties of glycerol mixtures

The phase behaviour and viscosity of the salt : glycerol mixtures were characterised to identify which salts could be practically used to extract glycerol from biodiesel. The mixtures should preferably be liquid at ambient temperature and have viscosities that permit physical separation of phases by decantation or filtration. Five quaternary ammonium salts were used, and viscosities and freezing points of the mixtures were measured as a function of glycerol mole fractions in the range 0.35 to 1. The results obtained are shown in Fig. 3 and Fig. 4.

All of the eutectics studied showed their lowest viscosity at the mole fraction of approximately 0.75, whereas the freezing point minima tended to vary slightly depending on the salt. Choline chloride had a minimum freezing point at

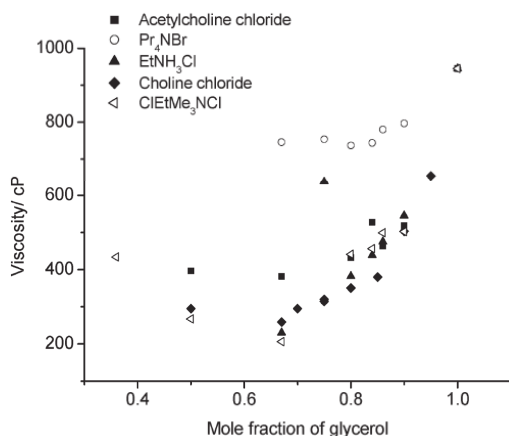


Fig. 4 Viscosity graph for eutectics at different glycerol mole fractions.

approximately 0.7, while the other salts had minima at mole fractions between 0.8 to 0.85. The freezing points at the eutectic point occurred between 210 and 235 K, meaning that all systems could be used effectively at ambient temperatures.

All the salts were also viable with respect to their viscosity. Since mixtures at the eutectic point were not found to be effective at removing glycerol from biodiesel, a Lewis basic mixture was needed. The 1 : 1 ratio of salt : glycerol mixture appeared to be the best compromise between viscosity and melting point and low mole fraction of glycerol. In this way, it is hoped that a 1 : 1 mixture of salt : glycerol could be used to extract one mole of glycerol from an equivalent 3 moles of biodiesel.

Quantification of glycerol extraction

The acetylcholine chloride eutectic was selected to study the extraction of glycerol from biodiesel as a function of time because the acetyl group on the cation and the OH group in glycerol have strong FT-IR resonances at 3330 and 1740–1730 cm^{-1} , respectively. These absorbances can be monitored over time to ascertain the time taken to reach equilibrium. By dividing the absolute intensity of the OH resonance by the absolute intensity of the acetyl resonance for studies of various molar ratios of the eutectic, a calibration curve was produced. A molar equivalent of 1 acetylcholine chloride eutectic to 1 glycerol was then used to wash a 1 ml sample of crude biodiesel. At various times, 10 μl samples of the eutectic layer were taken and analysed by FT-IR. The results are shown in Fig. 5.

This experiment revealed that the eutectic reached glycerol saturation after 10 min. Saturation corresponded to an approximate 1 : 2 molar ratio of acetylcholine chloride : glycerol and >99% removal of glycerol from the ester layer.

Effect of salt and initial composition of washing liquid

A standard mixture of 3 moles of ethyl caprate and 1 mole glycerol, with 5% v/v ethanol to aid miscibility, was mixed with

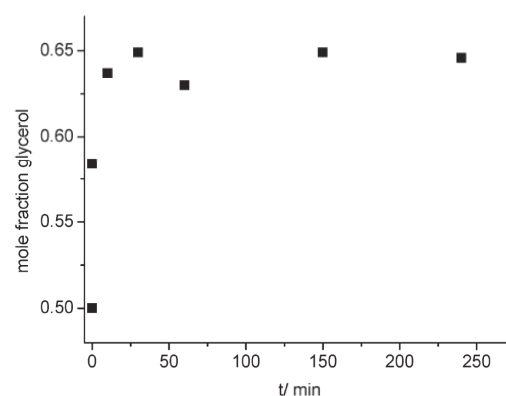


Fig. 5 Glycerol mole fraction in an acetylcholine chloride–glycerol mixture in contact with biodiesel containing glycerol as a function of time.

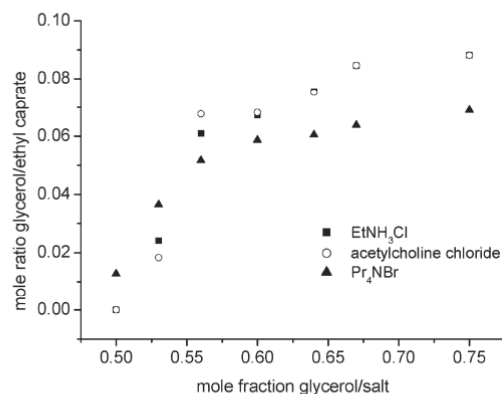


Fig. 6 Mole ratio of glycerol : ethyl caprate remaining in the biodiesel phase after washing with different salt–glycerol mixtures.

a variety of quaternary ammonium salt–glycerol mixtures of different molar ratios to determine their efficacy for glycerol removal. After shaking and warming the vials and allowing them to settle into two layers, the upper (ethyl caprate) layer was assayed by GC. The resulting glycerol–ethyl caprate mole fractions are shown in Fig. 6.

Fig. 6 shows similar profiles for the acetylcholine chloride and EtNH₃Cl eutectics. Pr₄NBr shows a slightly different profile with a better extraction of glycerol at higher mole fractions but a weaker extraction efficacy at the lower (0.5) mole fraction. From these results, it would appear the ability of the salt to draw glycerol out of the other phase may be dependent on the anion but is unaffected by the cation. The ability of chloride to extract glycerol at the 0.5 mole fraction is likely due to the higher electronegativity of the ion compared to bromide. Conversely, the lower ionic radius of chloride may become more of an issue at higher mole fractions of glycerol, and thus bromide is more effective at extracting glycerol at these mole fractions because its larger ionic radius simply means more moles of glycerol will fit around it spatially.

These results showed that the ability of the eutectics to remove glycerol from a standard system decreased with increasing glycerol concentration. The 1 : 1 molar ratio of glycerol : salt was found to be the most suitable in terms of its extraction ability and its ease of use. The three salts all gave very similar partition coefficients.

Extraction of glycerol from biodiesel into a eutectic solvent

The ideas developed with the ethyl caprate standard were applied to a practical sample of biodiesel produced using KOH, ethanol and soy bean oil. Mixtures of glycerol and salts were prepared in 1 : 1 molar ratios and used to extract 1 ml samples of crude biodiesel. The biodiesel layer was then analysed by GC to calculate the mole fraction of glycerol remaining. The results are shown in Table 1.

A significant decrease was observed in the mole fraction of glycerol remaining in the biodiesel layer after washing with all of the salt–glycerol mixtures. Particularly effective removal

Table 1 Mole fraction of glycerol in the biodiesel layer after washing with 1 : 1 glycerol : salt mixtures

Washing eutectic	X_{glycerol}
No wash	0.15
Pr ₄ NBr	0.08
EtNH ₃ Cl	0.00
ClEtMe ₃ NCl	0.00
Choline chloride	0.05
Acetylcholine chloride	0.03

was noted with EtNH₃Cl and ClEtMe₃NCl, with effectively complete removal of glycerol from the biodiesel. The least effective salt was Pr₄NBr, which confirms the earlier result using the standard ethyl caprate system in Fig. 6.

¹H NMR of the washed biodiesel and eutectic mixtures showed no traces of cross contamination of the two phases. However, the biodiesel yields showed impurities on the GC trace after washing with Pr₄NBr eutectic, thought to result from possible contamination with Pr₃N, and likewise after washing with acetylcholine chloride eutectics, the biodiesel layer showed evidence of impurities on the NMR spectrum, corresponding to the signals on the NMR spectra of the free amines of these salts which almost certainly comes from trace impurities in the original quaternary ammonium salts. No evidence of contamination, however, was seen when choline chloride, ClEtMe₃NCl, or EtNH₃Cl were used in washing solvents. Taking all these factors into account, ClEtMe₃NCl and EtNH₃Cl appear to be the most suitable quaternary ammonium salts for making eutectics for the extraction of glycerol from biodiesel, as they both remove almost all of it to practical detection limits in this system.

Separation of salt from glycerol mixture

To make the separation of glycerol from biodiesel using this method a viable process, a method of recovering the glycerol and the quaternary ammonium salt from the washing eutectic is necessary. In the system that has been developed here, the glycerol is recovered as a 2 : 1 mixture with a salt. In order to recycle the salt, it must be recovered or reduced to at least a 1 : 1 molar composition and the rest of the glycerol separated.

Possible purification methods include recrystallisation of the choline chloride, either by cooling or by addition of an antisolvent, and distillation of the glycerol. Distillation would be energetically difficult due to the high boiling point of glycerol (182 °C at 20 mm Hg) although vacuum distillation may be ultimately the easiest solution.

On cooling in ice, 1 : 2 mixtures of choline chloride : glycerol and acetylcholine chloride : glycerol both formed needle-like crystals. Filtration and analysis by the electrochemical method, however, showed that only about 4 wt% of the quaternary ammonium chloride could be recovered with either system. Further cooling of the solution in dry ice–acetone mixtures produced a glass-like material with no crystallisation.

Gas expansion of the mixtures was attempted using CO₂ at 50 bar as an antisolvent. The gas was soluble in the liquids as evidenced by opalescence of the solution on pressurisation and vigorous degassing on depressurisation, but no precipitation or crystal formation was observed over 24 h under pressure,

Table 2 Yield of biodiesel resulting from the transesterification of 550 g samples of two vegetable oils together with the amount of glycerol remaining after washing with a 1 : 1 glycerol : choline chloride mixture

Oil	Yield of biodiesel/g	Glycerol (wt%)
Soy bean	465	0.06
Rapeseed	471	0.02

and the potentiometric analysis showed the solution to be unchanged.

An alternative approach was attempted by adding a liquid co-solvent to aid the separation of the salt on cooling. 1-Butanol was added to the 1 choline chloride : 2 glycerol mixture, warmed to 50 °C to aid mixing and then cooled in ice. Significantly, more choline chloride formed as a precipitate than just by cooling the eutectic mixture. Analysis of the filtrate showed that 25% of the salt could be recovered by this method. While still unoptimised, the process shows that an anti-solvent could be added to recover the quaternary ammonium salt.

Scaled-up biodiesel synthesis with eutectic solvent extraction

To assess the suitability using salt–glycerol mixtures to purify biodiesel, a larger scale batch procedure was carried out. Both rapeseed and soy bean oil (500 g) were used with 150 g of KOH and ethanol for 24 h. Table 2 shows the yield of biodiesel produced from each experiment together with the amount of glycerol remaining after extraction with a 1 mole equivalent of 1 : 1 choline chloride : glycerol eutectic. After separation, the upper, biodiesel layer was analysed by ¹H NMR and GC-MS.

This shows that glycerol can be effectively removed from a biodiesel product on a moderate scale using a eutectic mixture.

Conclusions

Quaternary ammonium salt–glycerol mixture solvents were found to be successful as extraction media for glycerol from biodiesel product mixtures. A 1 : 1 glycerol : salt molar ratio was found to be the most effective for extracting glycerol from the biodiesel product. Of the salts studied, choline chloride, ClEtMe₃NCl, and EtNH₃Cl showed the best results in terms of effective glycerol removal. Choline chloride was recovered with some success from a 1 : 2 mixture with glycerol by

recrystallisation from 1-butanol, although this process was not optimised.

The process was scaled-up to a 500 ml batch process, with full alcoholysis of the triglyceride starting material and glycerol was successfully extracted by a choline chloride–glycerol washing solvent. Overall, the use of quaternary ammonium salt–glycerol DESs to remove glycerol by-products from the finished biodiesel reaction was found to be successful, but it is hoped further research will reveal a better method for recycling the salt and recovering the glycerol afterwards.

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