# pH Measurements in Ionic Liquids

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By

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#### Abstract

### pH Measurements in Ionic liquids

Deep eutectic solvents (DESs) and ionic liquids (ILs) have been significantly used in a variety of applications and one of the challenges is to understand the behaviour of protons in these non-aqueous media. The aim of this study is to investigate pH scales in DESs and ILs and to use the values to understand processes which occur in these media. The first stage of the study involved the development of a spectroscopic analytical method for measuring effective proton activity in IL media. Its  $pK_{In}$  data for bromophenol blue as an indicator were obtained in DESs and ionic liquids and it was found that the  $pK_{In}$  was influenced by the amount of the salt in the system. The value of  $pK_{In}$  was lower in DESs and ILs than in water.  $pK_{In}$  values were used to obtain  $pK_a$  values for different organic acid in variety of DESs and in two different imidazolium-based ILs containing different anions. The order of acidity is controlled by the element of the anion within it and it was found that  $F^- > HSO_4 > CI^- > Ac^-$  suggesting some correlation with hydrogen bond strength. In the second stage of this study a glass membrane electrode was used for the first time in DESs and ILs. The investigation successfully measured the pH scales of different DESs. It was shown that the response of a glass electrode was almost Nernstian in a DES with minimal water incorporated. The Nernstian slope increased as more water was added to the DES. A new, non-aqueous glass electrode was also made using Ag/AgCl in Ethaline reference electrodes. It was shown that this also had a Nernstian response showing that the glass membrane could function with only the traces of water naturally incorporated in the DESs. In the final part of this study the pH values of DESs were used to investigate the solubility of metal oxides in different DESs and the solubility was found to correlate well with the pH of the liquid. The formation of polyaniline was invetgated in solutions of differing pH both with and without water. The data showed the effect of both pH and mass transport on the rate of film growth. It was found that pH was not directly related to polymer growth rate but it showed that polymer only grew when an emulsion of monomer formed in solution. This significant discovery was only enabled by quantification of solution pH.

### **Publications**

#### **A-Papers**

 Abbott, A.P., Alabdullah, S.S., Al-Murshedi, A.Y. and Ryder, K.S., 2018. Brønsted acidity in deep eutectic solvents and ionic liquids. *Faraday discussions*, 206, pp.365-377.

#### 2- Conferences

#### (1) Talk

- 1- Sahar S. Alabdullah, Andrew P. Abbott and Karl S. Ryder, Bronsted acidity in Deep Eutectic Solvents and Ionic liquids, Leicester University for the 21st meeting of the ELECTROCHEM conference series, 17<sup>th</sup> -19<sup>th</sup> August 2016, Stamford Court, Manor Rd, Leicester LE2 2LH, UK.
- 2- Sahar S. Alabdullah, Andrew P. Abbott and Karl S. Ryder, Bronsted acidity in Deep Eutectic Solvents and Ionic liquids 4th July 2017, Leicester University Postgraduate Research Day, Department Of Chemistry, University of Leicester, Leicester, UK.

#### (2) Poster

- Sahar S. Alabdullah, Andrew P. Abbott and Karl S. Ryder, Bronsted acidity in Deep Eutectic Solvents and Ionic liquids, 26<sup>th</sup> EUCHEM conference on molten salts and ionic liquids, 3<sup>rd</sup> -8<sup>th</sup>, 2016, Vienna.
- 2- Sahar S. Alabdullah, Andrew P. Abbott and Karl S. Ryder, Bronsted acidity in Deep Eutectic Solvents and Ionic liquids, Leicester University for the 21st meeting of the ELECTROCHEM conference series, 17<sup>th</sup> -19<sup>th</sup> August 2016, Stamford Court, Manor Rd, Leicester LE2 2LH, UK.

### Statement

The work explained in this thesis for the degree of Ph.D. entitled "pH measurements ionic liquids" was carried out by the author in the Department of Chemistry at the University of Leicester between July 2014 and June 2018.

In this thesis, the work recorded was original except where acknowledged or referenced. None of the work has been submitted for another degree at this or any other university.

Signed ..... Date.....

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#### Dedication

I would like to dedicate this thesis to:

*My dearly loved father*, who strived for my comfort and well-being, and he inspired me to succeed.

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Abbreviations	Full name (unit)
DES	Deep eutectic solvent
IL	Ionic liquid
$pK_{In}$	Dissociation constant of indicator
QAS	Quaternary ammonium salt
DMSO	Dimethyl sulfoxide
HBD	Hydrogen bond donor
UV-Vis spectroscopy	Ultraviolet-visible spectroscopy
CV	Cyclic voltammetry
E	Electrode potential (V)
$E_{pa}$	Anodic peak potential (V)
$E_{pc}$	Cathodic peak potential (V)
F	Faraday constant (96 486 C mol <sup>-1</sup> )
i	Current (A)
$i_p$	Peak current
A	Absorbance
Q	Charge (C)
t	Time (s)
PANI	polyaniline
$pK_a$	Dissociation constant
LJP	Liquid junction potential
CE	Counter electrode
RE	Reference electrode
WE	Working electrode
[Emim] [OAC]	1-Ethyl-3-methylimidazolium acetate
[Bmim] [BF4]	1-Butyl-3-methylimidazolium tetrafluoroborate
[Emim] [HSO <sub>4</sub> ]	1-Ethyl-3-methylimidazolium ethyl sulfate

### List of abbreviations

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#### Introduction

#### 1.1 pH in Aqueous Solutions

Most chemical processes involve the transfer of an electron or a proton and so the concept of proton activity is central to most fields of chemistry. The concept of acidity could first be credited to Boyle who noted that acids tasted sour, were corrosive and could change the colour of vegetable dyes. Lavoisier proposed that acids were substances that contained oxygen. This was quickly discredited when it was shown that many bases also contained oxygen. The idea was later replaced by that of Davy who defined acids as substances that contained hydrogen that could be replaced totally or partly by metals and this was demonstrated by the liberation of hydrogen when acids reacted with many metals. Arrhenius extended this concept to define acids as substances that ionised in solution to produce hydrogen ions.<sup>1</sup> Indicators of acidity can be traced back to the 19<sup>th</sup> century where litmus paper was probably the first formally produced sensor for acidity. It can be produced from a variety of lichens all of which have 7-hydroxyphenoxazone as the chromophore. This is colourless in neutral solutions, red in acidic and blue in alkaline solutions.

The quantification of proton activity was firstly defined in 1909 by Sorensen as a logarithmic scale which was termed pH.<sup>2</sup> The study described the hydronium and hydroxide ion concentrations in aqueous solutions. The International Union of Pure and Applied Chemistry (IUPAC) extended the concept of hydronium ion concentration to a pH scale in water.<sup>2</sup> Their definition is;<sup>3</sup>

$$pH = -\log a_{H+(aq)}$$

(1.1)

Where  $a_{H^{+}(aq)}$  is the activity of hydrogen ions in an aqueous solution. The equilibrium constant  $K_w$  for the self of ionization of water at 298 K is 10<sup>-14</sup> meaning that the concentrations of both hydronium and hydroxide ions is 10<sup>-7</sup>mol kg<sup>-1</sup>. For pure water the neutral point is therefore pH 7. The acidity scale is usually quoted between pH 0 (fully dissociated) to pH 14 (fully associated).<sup>4</sup>

Cremer first reported in 1906 that when a glass membrane was used to separate solutions of different acidity an electrical potential was built up across that membrane which was a measure of the pH difference. Michaelis *et al.* <sup>5, 6</sup> set up the first cell which was to all

intents and purposes the current commercial glass pH electrode. It was made up of the cell

#### Ag|AgCl|HClaq|| Analyte|KClaq|Hg2Cl2|Hg

The analyte compartment was titrated with an acid and the cell potential was shown to be proportional to the pH of the solution. The difficulties with developing a commercial pH electrode were associated with being able to produce a suitably robust and sufficiently conducting glass. MacInnes and Dole produced a glass from 72% SiO<sub>2</sub>, 6% CaO and 22% Na<sub>2</sub>O although subsequent improvements were based around a mixture with 63% SiO<sub>2</sub>, 28% Li<sub>2</sub>O, 5% BaO, and 2% La<sub>2</sub>O<sub>3</sub>. It is ions such as sodium and barium which are critical to the stability of the glass.

While the glass electrode is the most commonly used method of determining pH in aqueous solutions the IUPAC primary standard is based on a cell without a liquid junction; which is called the Harned cell: <sup>3</sup>

$$Pt |H_2 \text{ standard buffer, } Cl^{-}|AgCl |Ag$$
(1.2)

The use of a Harned Cell depends on the potential of Ag/AgCl electrode which is fixed to the molality of hydrochloride solution. Where Pt  $|H_2$  is the hydrogen electrode, Cl<sup>-</sup> ion is the solution of potassium or sodium chloride and the acidity function  $p(a_H + \gamma_{Cl})$  of the Harned Cell is:<sup>2</sup>

$$p(a_H \gamma_{Cl}) = -\log(a_H + \gamma_{Cl})$$
(1.3)  
= [(E - E°) F/ (RT ln 10)] + log (m<sub>Cl</sub>/m°) (1.4)

Here  $\gamma_{Cl}$  is the activity coefficient of the chloride ion and it measures the differences between the molalities, *m*, of chloride ions in solution in the cell. *F*, *R* and *T* are the Faraday constant, gas constant and the absolute temperature respectively. *E* is the potential difference of the cell, and  $E^{\circ}$  is the standard potential difference of the cell.

The procedure of pH measurements with cell 1 always needs some standard conditions; firstly,  $E^{\circ}$  of the silver-silver chloride couple in a Harned cell needs to be maintained by using a constant molality of hydrochloric acid. The mean activity coefficient of HCl, at different temperatures can be kept relatively constant by using a molality of 0.01 mol kg<sup>1</sup>. The next step is by using a buffer solution to maintain the required pH of the solution. Then, the last step is the extrapolation of the pH function to zero chloride molality. Linear extrapolation of the measurements is useful to know the potential of the acidity function to calculate the pH of the solution. However, it is quite possible that errors can affect the Harned cell method such as the electrode preparation method and the calibration of solutions. The operation of Harned cell is very time-consuming because of the calibration needed with each measurement.<sup>7</sup>

The Baucke cell is also a method that can be used to measure pH scales. The cell depends on the determination of a secondary standard pH which originates from primary standards. The pH electrode cell is designed as two buffers with a liquid junction potential. The liquid junction potential is at a phase boundary between the two electrolytes solutions which causes a small change in the measured voltage. The cell is defined as:

$$Pt (1) | H_2| standard buffer (1) || standard buffer (2) | H_2| Pt (2)$$
(1.5)

Here the cell contains two identical electrodes Pt (1) and Pt (2) and it consists of two identical buffers (S1) and (S2), where these buffers have pH values pH (S1) and pH (S2). The potential of  $E_{cell}$  is written as:

$$E_{cell} = E(2) - E(1) + E_j \tag{1.6}$$

Here  $E_j$  is the liquid junction potential. The standard buffer solutions of the cell are identical if the cell contains the comparable concentrations on both sides of the liquid junction. However, the pH scales could be determined according to the equation below, when the liquid junction potential is less than 0.01 values:

$$pH(S2) = pH(S1) - E_{cell}/K$$
(1.7)

Here *K* is the equilibrium constant. The differential pH cell is straightforward and easier to use compared with the Harned cell.<sup>8, 9</sup> The considerable dissimilarity between the standard buffers could cause inaccuracy in measuring the acidity of the solution. **Figure 1.1** shows the metrological traceability for pH measurements in different types of electrode.



Figure 1.1: Metrological traceability scheme for pH.<sup>10</sup>

In terms of chemical reactions, the definition of pH is an important parameter in liquids but the knowledge of equilibrium acidity ( $pK_a$ ) in solutions is sometimes more useful rather than pH. The  $pK_a$  is important for understanding the tendency of the solvent to donate or accept hydrogen ions.<sup>11</sup>

The concept of chemical equilibrium was first proposed in 1864 by Guldberg and Waage.<sup>12</sup> The idea was extended by van't Hoff in his studies of osmotic pressure and conductivity of solutions to determine the degree of dissociation for an electrolyte.<sup>13</sup> Then 1907 Henderson provided the first explaining of the relation between the composition of buffer and hydrogen ion and together with Hasselbalch suggested their famous equation (1.8).<sup>14-17</sup>The equation relates acidity values and the equilibrium constant of dissociated acid and non-dissociated acid.<sup>18</sup>

$$pH = pKa + \log_{10} ([A^{-}]/[HA])$$
(1.8)

The dissociation constant for weak acid HA in aqueous solution can be found by the following expression:

$$HA_{(aq)} + H_2O \iff H_3O^+_{(aq)} + A^-_{(aq)}$$
(1.9)

$$K_a = \frac{[H_3O^+(aq)][A-(aq)]}{[HA(aq)]}$$
(1.10)

For strong acids the equilibrium in equation 1.9 lies to the right whereas for a weak acid it lies to the left.<sup>19, 20</sup>

#### **1.2** Techniques for determining pH

There are numerous methods to determine the effect of proton activity on a system and these are briefly described below. For the purposes of the current study it is the first two; potentiometry and spectroscopy which will be studied in detail. This is because they are the two most commonly used and they provide two fundamentally different ways of assessing activity *i.e.* a bulk measurement and an interfacial measurements.<sup>21</sup>

#### 1.2.1 Potentiometric pKa determination

It is one of the simplest quantitative techniques in analytical chemistry. Potentiometric titration considers the most commonly used method for pKa calculations. The method was founded in 1893, when Beherend titrated potentiometrically potassium bromide, potassium iodide and potassium chloride with a mercury electrode along with mercurous nitrate. <sup>22-24</sup> In the early of the 20th century, there has been increased interest in understanding the potentiometer method.<sup>25</sup> In 1908, Denham et al. found development potentiometric method by studying the behaviour of a hydrogen electrode in solutions of lead and univalent thallium salts with a platinum working electrode. They established the reduction potential of hydrogen electrode as 0 V, which was the first potentiometer setup to determine equilibrium constants during that time.<sup>26, 27</sup> Shortly after the hydrogen electrode was replaced with the glass electrode. When Haber firstly noticed the voltage of a glass membrane changed with hydrogen activity of solution. In 1906, Max Cremer reported that an electrical potential which develops across a glass membrane is proportional to the pH difference across that membrane.<sup>28</sup> A good discussion for the various errors of the electrode measurements is given by Gardiner.<sup>29</sup> However, Benett<sup>27</sup> reviews the common ways to quantify *pKa* from the measured potential.

The principles of classical potentiometric titrations are simple to operate for evaluating the *pKa* of solute, the method mainly depends on the plotting  $\Delta V/\Delta E$  vs. When, the potential vs. volume titration between acids and bases a sigmoid curve observed. The inflection point of the potential signals the end point. With the use of known pH solutions in this case potential can be linearly converted into a pH, equalling *pKa*.<sup>27, 30</sup> This method was firstly reported by Gran in 1950. Then, in 1951 Sørensen noticed a similar curve happened for neutralization titrations of silver ions with chloride ions. Later Gran described another titration system which relies on Sorensen's method but with more complicated titration. Gran used titrations of ion combinations containing ions of different valences. Since then, Sorensen and Gran's method has been considered the appropriate procedure for measuring potentiometric titration curves.<sup>30</sup>

Potentiometric titration is an accurate technique for determining pKa values. It is widely used due its reliable and readily available to automated instruments. However, the potentiometry has limited application for determination of second dissociation constants. Inaccurate measurements of classical potentiometric titrations sometimes happen especially for measurements at high pH, To prevent the errors, in this case carbonate-free solutions should be prepared.<sup>23</sup>

#### **1.2.2 Conductometry**

One of the first attempts to measure acid dissociation constants was in 1896 using conductometry technique where Whitney described the conductimetric end point titration of free sulfuric acid in solutions of chromium sulfate complexes.<sup>31</sup> Later, Kolthoff summarised the applications of conductmetric end point detections.<sup>32</sup> The development of the conductimetric methods was subsequently carried out. The study was the first to discover ion migration of sodium and potassium salts in solutions containing different anions. The study proposed the independent migration of ions such that the limiting molar conductivity of an electrolyte was the summation of the contribution of the individual ions,

$$\Lambda^0 = \Sigma \,\lambda_i^0 \tag{1.12}$$

Where,  $\Lambda^0$  is the limiting molar conductivity of an electrolyte and  $\lambda_i^0$ , is the limiting molar conductivity of an ionic species. The study also found that a strong electrolyte is completely dissociated at all concentrations, while for weak electrolytes, complete dissociation can only happen at infinite dilution.<sup>33</sup> This enables the limiting molar conductivity of a weak acid to be determined by Equation (1.13)

$$\Lambda^{0}_{\rm HA} = \Lambda^{0}_{\rm NaA} + \Lambda^{0}_{\rm HCl} - \Lambda^{0}_{\rm NaCl}$$
(1.13)

Ostwald derived an expression to determine the dissociation constant for a weak electrolyte

$$K_{d} = \Lambda_{c}^{2} c / (\Lambda^{0} (\Lambda^{0} - \Lambda_{c}))$$
(1.14)

Where, *c* is the concentration and  $\Lambda_c$  is the molar conductivity at a given concentration. The conductimetric method can be a reliable method of *pKa* measurements and has an accuracy in the range  $\pm 0.01-0.03$  units.

#### 1.2.3 UV/Vis spectrometry

It has long been known that acidity leads to colour changes of many natural substances. Spectrometry with visible light is an easy way to measure *pKa* values of acid/base indicators. The principle of UV-Visible spectroscopy is the absorption of electromagnetic radiation from the 180–900 nm range in which the electrons are excited to higher energy states.<sup>21</sup> A requirement for UV-vis/ pH measurement is to have a chromophore close to the ionization site in the molecule. In this case the spectra of the non-dissociated and dissociated species can probably be expected to differ from each other. This method later was developed by using the absorption measurements of two different wavelengths at different pH values. The *pKa* is the inflection point from a plot of absorption peak ratio against pH.<sup>27</sup> It is imperative that the absorbance peaks are not overlapping and there are no interfering absorbances. The method has been used by a variety of groups to characterise the *pKa* values for a variety of protic solutes in a range of media.<sup>34 35 36, 37 38, <sup>39 40, 41</sup> This method will be used extensively in Chapter 3 and is described in detail there.</sup>

#### 1.2.4 Calorimetry

Isothermal Titration Calorimetry (ITC) has been used to measure *pKa*. A regular acidbase titration takes place inside a calorimeter while the energy required to keep the temperature constant is measured.<sup>42</sup> The first application of the ITC method was by Lavoisier and Laplace.<sup>43</sup> In the last few years, the ITC method has been applied to determine the *pKa* of peptides and finding the effects of binding on the specific ionisation groups.<sup>44</sup> The method also can be used to measure the *pKa* from the enthalpy change by plotting the maximum or the minimum values against pH and using the sigmoidal curve to determine the inflection point which shows the *pKa*. The accuracy of this method ranges from 0.05 to 0.15 *pKa* units depending on the calorimetric method used.<sup>21,45</sup>

#### **1.2.5 Partition coefficients**

The first systematic discussion of distribution constant or partition coefficient was by Berthelot and Jungleisch in 1872.<sup>45</sup> The study investigated the distribution between

systems of two immiscible liquids in equilibrium, and found that the ratio of the concentrations in each phase was constant. Also, the relative amounts of solvents does not affect the distribution. Based on this research, in 1891, Nernst reported that the partition coefficient (P) was only a constant if a single substance was considered.<sup>46</sup>

In the development of the partition coefficients of ionisable compounds it was found that the partition coefficients depended on the pH of the aqueous phase and the knowledge of the *pKa* of the solute is required.<sup>45</sup> Vezin *et al* calculated dissociation constants of phenothiazine derivatives of low aqueous solubility between water and organic solvents. The partition coefficients showed a clear pH dependency and the *pKa* values were repeatable to less than 0.03 units.<sup>47</sup> The method has not been widely used except for the determination of poorly water soluble pharmaceutical reagents.<sup>21</sup>

#### 1.2.6 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) spectroscopy has been used for the determination of acid dissociation constants.<sup>48</sup> It is well known, any changes in ionisation state lead to changes in the chemical shifts of nuclei in close proximity to the ionisable group.<sup>49, 50</sup> Generally, any changes in pH values lead to chemical exchange, and the observed chemical shift of a resonance based on a weighted average of the chemical shifts of the two species. The *pKa* values in this case, can be calculated by plotting the chemical shifts against pH. An early <sup>1</sup>H NMR spectrometer operating at 30 MHz was produced by Varian in 1953.<sup>48</sup> Grunwald *et al* calculate the *pKa* of mono, di and trimethyl amine based on the chemical shift of the protons in the CH<sub>3</sub> groups of the amines as a function of pH. A sigmoid curve was obtained between the chemical shift and the acid-base ratio. The *pKa* was determined from the linear correlation observed at constant temperature.<sup>27</sup>

Silva *et al* estimate the *pKa* values for the hydroxyl group in lactic acid, malic acid and citric acid at high pH values and studied the effect of a-carbon substitution in these hydroxyl groups by <sup>13</sup>C NMR techniques. The experimental information explained the comparison of the *pKa* values for the three acids. The study found a reliable value for the deprotonation constant of the alcohol group. The *pKa* of the hydroxyl group of these acids are higher than that previously reported in the literature for citric acid .<sup>51</sup>

In summary, the application of <sup>1</sup>H NMR for *pKa* determinations is not commonly used in *pKa* of a high diluted acid systems. A small or dilute sample will give a weak signal, and doubling or tripling the sample concentration increases the signal strength proportionally.

For instance, if the samples take for NMR spectrum of equal molar amounts of benzene and cyclohexane in carbon tetrachloride solution, the resonance signal from cyclohexane will be twice as intense as that from benzene because cyclohexane has twice as many hydrogens per molecule. This is an important relationship when samples incorporating two or more different sets of hydrogen atoms are examined, since it allows the ratio of hydrogen atoms in each distinct set to be determined. The limitation of this techniques around in most samples around 250 ppb , However, the method has been efficiently used in biology areas such as measuring the *pKa* of amino acids.<sup>52, 53</sup>

#### 1.2.7 Kinetic method

In this method, the dissociation constant for an acid is determined by measuring the rate of reaction of a control experiment which is influenced by pH of its reaction medium. Szwarc reported the method for determining the dissociation energies in small hydrocarbon molecules.<sup>54</sup> Bordwell *et al.* reported the kinetics of neutralization of simple ketones by direct methods in dipolar aprotic solvents.<sup>55</sup> The study found the *pKa* values on going from dipolar aprotic solvent to water,<sup>55, 56</sup> and was later followed by the determination of the equilibrium acidities of a range of nitrocycloalkanes.

#### 1.2.8 Density functional theory (DFT) method

Density functional theory (DFT) uses quantum mechanical modelling to calculate the ground state electron distribution in molecules. The electronic distribution can be used to predict properties such as structure and ionisation potentials of molecules accordingly it can be used to determine dissociation constants for molecules. Zevatskii *et al.* calculated the dissociation constants of 15 carboxylic acids in DMSO, methanol, and water by empirical and quantum-chemical DFT methods. Delgado also calculated the dissociation constants of dimethoxy pyrimidinylsalicylic-based herbicides by a using DFT method.<sup>57</sup> The method is useful for determining *pKa* values for small molecules, but tends to only give accurate predictions in the range 1-5 molecules in the samples .The limitation of the method for higher than 5 molecules is due to the electrostatic nature of hydrogen bond formed by proton with proton accepter sites of molecules to produces the acid- base equilibrium. <sup>58</sup>

The above methods are just a selection of those which have been applied to determining pH and *pKa* values. Others include capillary electrophoresis,<sup>59</sup> high performance liquid chromatography,<sup>60</sup> hyper Rayleigh scattering, displacement ELISA,<sup>61</sup> solvation

modelling,<sup>62</sup> thermal lensing spectroscopy,<sup>38</sup> surface tension and interfacial tension<sup>63</sup> and mass spectroscopy.<sup>64</sup> A more in-depth review of other method is given by van Hoof *et al.*<sup>27</sup>

#### 1.3 Classification of non-aqueous solvents

There are a variety of ways of characterising non-aqueous solvents including in terms of their polarity or functional groups.<sup>65</sup> One classification is according to the characterisation of the chemical bonding formed between them.<sup>66</sup> molecular liquids are formed covalent bond at near room temperature, ionic liquids a class of liquids consist of ionic bond and atomic liquids which contains metallic bond of low melting metals like liquid sodium or liquid mercury. A wide range of solvents/solutions can be produced by mixing these three basic solvent types together.<sup>66</sup> This idea is shown schematically in **Figure 1.2**.



**Types of solvents** 

Figure 1.2: Classification of solvents in terms of chemical bonds.<sup>66</sup>

Molecular liquids as solvents are commonly classified into ionizing solvents (usually more polar molecules) and non-ionizing solvents (usually a polar) enabling them to be classified in terms of their relative permittivity or acid/base properties.<sup>67</sup> In 1925, Brønsted made a classification of solvents using their acid and base properties. He devised eight types of solvents by measuring the dielectric constant (which is a measure of the

ability of the medium to reduce the force between two electric charges).<sup>66</sup> In 1974, Kolthoff refined the Brønsted classification according to the fundamental prototypic properties. Kolthoff's classification includes two groups of solvents; amphoteric and aprotic solvents. The amphoteric solvents have both acid and basic properties. However, the solvents which behaved like acids were called protic solvents. These solvents can be ionised and participate in hydrogen bonding because they have N-H or O-H bonds, with strong intermolecular forces. Furthermore, these O-H or N-H bonds can provide sources of protons. While, the aprotic solvents, may have hydrogens in their chemical structure, but the lack of O-H or N-H bonds, which cannot take part in hydrogen bonding.<sup>68</sup>

#### 1.4 pH windows in non-aqueous solvents and pH scales for multi-solvents

The activity of protons mostly depends on the type of the liquid. The tendency of protons to ionise in non-aqueous solvents depends on the relative acidity/basicity of the solvent.<sup>66,</sup> <sup>67</sup> The ionisation of an acidic solvent is increased by the basicity of substances dissolved in it e.g. acetic acid is an acidic compound in water however it behaves as a base in liquid HCl. The ionisation of an acids relies on the basicity of the solvent. Thus, it seems difficult to account which type of solvents belongs to a specific number some non-aqueous solvents can act as acids. To compare the differences in acid-base properties in various solvents, it is essential to determine a pH scales that are valid in different solvents. **Figure 1.3** shows the pH scales of different non-aqueous solvents reported in the literature.<sup>69</sup>



Figure 1.3: Common pH scales with pH windows in different solvents.<sup>69</sup>

Here, pH scales refer to the water as a reference. The values in the figure represent the width of the pH window in the different solvents; these expanded pH windows decided various chemical possibilities. In solvents with a wide pH region on the left, the solvated protons have a very strong acidity and some acids which behave as strong acids in water, tend to behave as weak acids of different strengths. For instance, in most aprotic solvents which have weak proton donor capacities like DMSO (dimsyl ion, CH<sub>3</sub>SOCH<sub>2</sub><sup>-</sup>) is somewhat stable for their ions however, alkali metal dimsyl in DMSO are more strongly basic and have used as a titrant. In protophobic aprotic solvents, the pH window expands in both sides. While, in solvents with a wide pH region on the right the solvated protons have very strong basicity and some bases which behave as strong bases in water tend to behave as weak bases of different strengths. If the density of the solvent is between 0.8 and 1.2 g cm<sup>-1</sup>, then the differences between the pH on molality and that the molality within 0.1. The shifted in pH values shows that the solvent is more basic than water, the pH extends to the left and when it is more acidic it extends to the right side.<sup>70</sup>

The importance of solvent - solute interactions on the change of the pH /pKa values has been emphasized in literature.<sup>71, 72</sup> It was found that a difference in specificities of interaction of the solute with two component solvents can be occurred. These can lead to preferential solvation of the solute where the local composition of the solvent shell

surrounding the solute is different from the average solvent composition. Kenndler *et al.* reported that the impact of the solvent on the ionization constants is interpreted based on the free energy of transfer applied to all particles involved in the ionization reaction of acids and bases, and the concept of the 'medium effect' on these species.<sup>73</sup> They also concluded that organic solvents are such poor solvators for anions that the overall effect to the p $K_a$  value for neutral acids of type HA is dominated by the large positive medium an effect on the anion. For cation acids the ability to stabilize the proton (the basicity of the solvents) goes parallel with its ability to solvate (and stabilize) the cation HB.

#### **1.5 Ionic liquids**

Ionic liquids are generally defined as low temperature molten salts usually with a melting point of less than 100°C.<sup>74-76</sup> The initial description stated that it should just be composed of an organic cation most typically derivatives of pyridinium, imidazolium or tetraalkylyammonium cations with a variety of inorganic or organic anions such as [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], [BF<sub>4</sub>]<sup>-</sup>, [CH<sub>3</sub>CO<sub>2</sub>] and halides. <sup>77, 78</sup> This concept has been extended by Abbott to include the equilibria:<sup>79</sup>

cation + anion + complexing agent  $\rightleftharpoons$  cation + complex anion (1.10)

cation + anion + complexing agent  $\longrightarrow$  complex cation + anion (1.11)

As this encompasses classes of liquids such as eutectic ionic liquids, deep eutectic solvents and protonic ionic liquids which contain molecular components but which are largely ionic.

One of the first ionic liquids was ethylammonium nitrate  $[C_2H_5NH_3]NO_3$  which was described by Walden in 1914 and has a melting point of 12 °C. It was synthesized by reacting concentrated nitric acid with ethylamine.<sup>80</sup> In 1951, Hurley and Weir<sup>81</sup> reported that mixtures of aluminium chloride with ethylpyridinium bromide had a melting point at the eutectic composition of -40°C. In 1992 Wilkes *et al* showed a decrease in the viscosity and an increase in the conductivity of these mixtures at room-temperature for AlCl<sub>3</sub> contents between 67 and 33 mol % when imidazolium salts were used in place of pyridinium ones.<sup>82</sup> These eutectic based ionic liquids were found to be applicable to a variety of other metal halides such as ZnCl<sub>2</sub> as they formed complex anions such as ZnCl<sub>3</sub><sup>-</sup> and Zn<sub>2</sub>Cl<sub>5</sub><sup>-</sup>.<sup>83</sup>

#### **1.5.1 Discrete anion ionic liquids**

The so-called second generation ionic liquids were developed to have discrete anions such in  $[NTf_2^-]$ ,  $[BF_4^-]$  and  $[PF_6^-]$ .<sup>84</sup> Wilkes and Zarotwoko are attributed with producing the first air- and water-stable ionic liquids. They synthesised 1-ethyl-3-methylimidazolium tetra fluoroborate [EMIM][BF4] and acetate [EMIM][OAc] liquids for the first time.<sup>85</sup> Hagiwara *et al.* described that fluorohydrogenate anions can be utilized to form room temperature liquids with N,N'- dialkylimidazolium cations.<sup>86</sup> The anions  $[PF_6^-]$  and  $[BF_4^-]$  were initially used because of their useful wide electrochemical windows;<sup>87, 88</sup> although they are now less popular as they were found to slowly hydrolyse in the presence of water producing HF.

Fluorinated anions decreased the interionic interactions and so decreased the viscosity and increased the conductivity of the liquids. **Figure 1.4** shows some of the anions and cations commonly used to form ionic liquids.



N,N'-dialkylimidazolium N-alkylpyridinium Alkyammonium Alkylphosphonium



Figure 1.4: Common cations and anions used to make ILs.

Despite there being a large number of anions and cations prepared in the literature, a common selection of cationic ionic liquid used in most chemical processes is N, N'-dialkylimidazolium. The most commonly studied N, N'- dialkylimidazolium species are 1-butyl-3-methylimidazolium [BMIM] and 1-ethyl-3- methylimidazolium [EMIM] cations **Figure 1.5** as these have the lowest viscosities and highest conductivities.



**EMIM** 

BMIM

Figure 1.5: Structures of 1-ethyl-3-methylimidazolium [EMIM] and 1-butyl-3methylimidazolium [BMIM].

#### **1.5.2 Properties of ionic liquids**

The physical and chemical properties of ionic liquids can be changed by the selection of different cations or anions. Moisture can change the physical and chemical properties of ILs e.g. hydrolysis of [BF<sub>4</sub>] can release HF and moisture tends to significantly decrease the viscosity of ILs.<sup>89</sup> More stable ionic liquids have been developed by using more hydrophobic anions such as bis- (trifluoromethanesulphonyl) imide [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and trifluoromethanesulfonate [CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>].<sup>89</sup>

The densities of ionic liquids are influenced primarily by the identity of anions. For instance, the densities of 1-butyl-3-methylimidazolium type with different anions, in ionic liquids such as  $[BF_4]$ ,  $[PF_6]$  and  $[Tf_2N]$ . The order of increasing density for ionic liquids composed of a single cation is:  $[BF_4] < [CF_3CO_2] < [CF_3SO_3] < [C_3F_7CO_2] < [(CF_3SO_2)_2N].^{89}$  This is mostly dominated by the number of heavier atoms e.g.  $[PF_6^-]$  liquids are more dense than  $[BF_4^-]$  liquids.

The melting point of an ionic liquid defines the lower temperature limit of the liquidphase in which they can be used as solvents and thermal decomposition often marks the upper limit of the range. The phase behaviour of these systems is affected by the size of the ions, their charge distributions and ionic geometries.<sup>82</sup> Increasing the ion symmetry leads to a higher melting point. This is because of it is easier for ions to pack in to the crystal lattice.<sup>90</sup> However, salts with unsymmetrical cations have lower melting points as they reduce the coulombic interactions. By reducing the symmetry of the ions, distortion of the ideal close-packing of ionic charges in the solid state lattice can be generated, which in turn leads to a reduction in the lattice energy of the crystal and, hence, a depression of the melting point. For example, 1-ethyl-2-methylimidazolium chloride has a higher melting point than 1-ethyl-3- methylimidazolium chloride.<sup>91, 92</sup> The cationic component is not the only important factor in the melting point of the system, the anion also has a significant effect on the melting point. By keeping the cation constant, in this case  $[EMIM]^+$  the effect of altering the size of the anion whilst maintaining the same charge alters the melting point e.g. [EMIM]Cl has a melting point of 87 °C, but the melting point of [EMIM][NO<sub>3</sub>] is 38 °C.<sup>82</sup>

Ionic liquids have relatively low vapour pressure compared to most common molecular solvents. It has been commonly described that ionic liquids have no measurable vapour pressure. This means that it is possible to efficiently separate the products from a reaction mixture by distillation. There is no azeotrope formation between the product and the ionic liquids.<sup>72</sup> Vapour pressure are often conditioned on the thermal stability of the liquid and most ionic liquids exhibit a high thermal stability, with decomposition temperatures commonly being reported as greater than 400°C. <sup>93</sup> [EMIM][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N] has a liquid range of 400 °C<sup>94</sup> and [EMIM][BF<sub>4</sub>] has a liquid stability range of 300 °C.<sup>95</sup> This has allowed ionic liquids to be applied in ultra-high vacuum techniques.<sup>96</sup>

#### 1.5.3 Synthesis of ionic liquids

Ionic liquids can be prepared by either an ion exchange reaction between halide and ammonium salts of a required anion or via acid-base neutralisation reactions.<sup>72</sup> Synthesis of ionic liquids usually needs the quaternisation of amine or an imidazole with an alkyl halide to form the cationic component.<sup>82</sup> Several ionic liquids can be designed directly via quarternisation reactions; ionic liquids that can be prepared by direct quaternisation for example are [EMIM] CF<sub>3</sub>SO<sub>3</sub> and [BMIM] Cl.<sup>97</sup> It is not always possible to synthesise the desired anion directly by such a process, and another step is often required. This second step in the preparation of ionic liquids is mostly a solid phase synthesis, which is prepared by the reaction between the metal halide with the quaternary salt. This mechanism is shown schematically in **Figure 1.6**.



*Figure 1.6*: *Scheme for synthesis of ILs, exemplified for an ammonium salt.* 

The synthesis of these ionic liquids should proceed at low temperature and under a moisture free environment. **Figure 1.6** shows the synthesis of an ammonium salt, where "R" is an alkyl group and "X" is a halide group. From this point the ammonium halide can be reacted with a Lewis acid MX<sub>y</sub>, to form an ionic liquid as  $[R'R_3N]^+$   $[MX_{y+1}]^-$  which is described in Step IIa and equation (1.12) . In this stage different anion species are formed in equilibrium. The proportion of species present lies upon the ratio of the two mixtures, in this  $[R'R_3N]^+$  X<sup>-</sup> and MX<sub>y</sub>. Chloroaluminate melts are the best known example of this reaction. As the ratio of chloride to AlCl<sub>3</sub> ratio changes, thus the anionic species changed. When the ratio of Cl: AlCl<sub>3</sub> the only anionic species formed is AlCl<sub>4</sub><sup>-</sup>. However, if the molar fraction of AlCl<sub>3</sub> is at x (AlCl<sub>3</sub>) > 0.5 the chloroaluminate anions become multi-nuclear.<sup>97</sup>

$[R'R_3N]^+X^- + MX_y $	$[R'R_3N]^+ [MX_{y+1}]^-$	(1.12)
$[R'R_3N]^+ AlCl_4 + AlCl_3$	$[R'R_3N]^+ [Al_2Cl_7]^-$	(1.13)
$[R'R_3N]^+Al_2Cl_7 + AlCl_3$	$[R'R_3N]^+ [Al_3Cl_{10}]^-$	(1.14)

Chloroaluminates are not the only ionic liquids that can prepared by this reaction. Many examples can be generated by the reaction of a halide with a Lewis acid. An anion can be

substituted using an anion exchange resin (synthesis step IIb, Scheme 2). Anion exchange methods however could result in impurities from residual halide species. These halide ions may react with solute materials and it is therefore essential to remove them. Unlike traditional solvents, purification cannot be by distillation.<sup>97</sup>

#### **1.6 Deep eutectic solvents**

Eutectic based ionic liquids were some of the first systems studied as described above. They were initially confined to quaternary ammonium salts with metal halides. It was later found that similar eutectic mixtures could be formed using metal salt hydrates. In 2003, Abbott *et al.* discovered eutectic mixtures with large depressions of freezing point could be obtained by heating mixtures of quaternary ammonium salts and hydrogen bond donors such as urea. These were termed deep eutectic solvents (DESs) are now widely acknowledged as a separate class of ionic liquid.<sup>98</sup> DESs are formed from between a variety of hydrogen bond donors, such as amides, acids, alcohols, and a quaternary ammonium halide salt. **Table 1.1** show the general descriptions of compounds that can be used to form DESs.

Туре	General formula	
1	$Cat^{+}X^{-}zMCl_{x}$	M= Zn, Sn, Fe, Al, Ga, In
2	Cat <sup>+</sup> X <sup>-</sup> zMCl <sub>x</sub> .yH <sub>2</sub> O	M= Cr, Co, Cu, Ni, Fe
3	Cat <sup>+</sup> X <sup>-</sup> zRZ	Z= CONH <sub>2</sub> , COOH, OH
4	$MCl_x + RZ = MCl_{x-1}^+ RZ + MCl_{x+1}$	$M = Zn$ , Al and $Z = CONH_2$ , OH

Table 1.1: Classification of deep eutectic solvents<sup>98</sup>

Where X is a halide anion (usually  $Cl^{-}$ ). The formation of DESs depends on equilibria set up between X<sup>-</sup> and a Lewis or Brønsted acid, Cat<sup>+</sup> is generally an ammonium or phosphonium salt.



*Figure 1.7:* The eutectic point on a two component phase diagram<sup>98</sup>.

Type 3 DESs are the most commonly used because they are easy to form, generally inexpensive, versatile and tuneable. Numerous quaternary ammonium and imidazolium cations have been used to form DESs but choline chloride, [ChCl,  $HOC_2H_4N^+$  (CH<sub>3</sub>)<sub>3</sub>Cl] is the most common due to its ease of manufacture and lack of toxicity. Choline chloride is a pro-vitamin (B4) and has a daily human allowance of 500 mg.<sup>99</sup> Common hydrogen bond donors include carboxylic acids (malonic acid, oxalic acid, citric acid), renewable polyols (glycerol), urea and amino acids.<sup>100</sup> Abbott *et al.* showed that monofunctional HBDs such as phenylpropionic acid and urea had eutectic compositions of 67 mol% HBD, whereas difunctional HBDs such as in oxalic acid and malonic acid had eutectic compositions at 50 mol% HBD. For citric acid the eutectic was at 33 mol% HBD.<sup>101</sup> Figure 1.7 shows how the freezing point at the eutectic composition in a binary mixture of A + B is compared with a theoretical ideal mixture those are correlate, with  $\Delta T_f$  which refers to the magnitude of the interaction between A and B, it seems that the larger the interaction is related to the larger  $\Delta T_f$ . In case of carboxylic acids, it was found that the lower the molecular weight of the HBD the higher was the depression of freezing point.<sup>102</sup> <sup>103</sup> Figure 1.8 shows the chemical structure of some of the most commonly used hydrogen

bond donor and halide salts for the preparation of deep eutectic solvents.98, 103, 104



*Figure 1.8*: *Typical structures of the hydrogen bond donor and quaternary ammonium salts used in deep eutectic solvents.*<sup>98</sup>

The formation of hydrogen bonds between the halide anion of the salt and the HBD play a significant role in type 3 DESs; where these HBDs are multifunctional, the eutectic point tends to be found around a 1:1 molar ratio of salt and HBD.<sup>98</sup> It also was reported that the depression in freezing point is related to the mass fraction of HBD in the mixture.

#### 1.7 Properties of deep eutectic solvents

Although ionic liquids and DESs have different chemical formulations, they have similar physical properties.<sup>105-107</sup> Thermophysical properties have been extensively characterised including density, conductivity, viscosity and melting point.<sup>108, 109</sup> The physical properties of the liquid are dependent upon the hydrogen bond donor and can be tuned for a given application.<sup>98</sup> DESs are comparatively highly conducting solvents, <sup>101</sup> and have properties which are similar to most imidazolium liquids.<sup>72</sup> Mjalli *et al* measured the density of different deep eutectic solvent as a function of temperature and composition.<sup>110</sup> Physical properties of various types of DESs, ionic liquids with discrete anions at 298 K are reported in **Table 1.2**.

Table 1.2: Physical Properties of different DESs and Ionic Liquids at 298 K

Salt (mole eq.)	HBD (mole	Viscosity	Conductivity	Density
	<b>eq.</b> )	/ cP	/ mS cm <sup>-1</sup>	/ g cm <sup>-3</sup>
ChCl (1)	Urea (2)	632	0.75	1.24
ChCl (1)	Ethylene glycol(2)	36	7.61	1.12
ChCl (1)	Glycerol (2)	376	1.05	1.18
ChCl (1)	Malonic acid	721	0.55	
[C4mim][Cl]	AlCl <sub>3</sub>	19	9.2	1.33
[C4mim][BF4]		115	3.5	1.14
[C4mim][(CF3CO2)2N]		69	3.9	1.43

The values in **table 1.2** show that DESs are more viscous than molecular solvents. The reason of this disparity is associated with the large size of the ions and relatively low free volume in the ionic systems resulting from a high surface tension. Previously, it was found that there is a good correlation between the fluidity (1/viscosity ( $\eta$ )) and the molar conductivity  $\Lambda$  of ILs.<sup>91, 98</sup> The same observation has been found for DESs. This has been explained in terms of hole theory where the small amount of holes which are large enough to allow ionic mobility is effectively limiting charge transport. The holes are effectively at infinite dilution and so the Nernst-Einstein equation is valid.

The effective polarity of choline chloride combined with four HBDs, 1,2-ethanediol, glycerol, urea, and malonic acid, has been measured using solvatochromic polarity indicators, and all four liquids were found to be fairly dipolar.<sup>98</sup> DESs are easy to prepare, they have low vapour pressures, are generally non-flammable and have relatively wide potential windows.<sup>101, 102</sup>

#### 1.8 Acidity/ basicity of ionic liquids

Ionic liquids can be classified into two approaches depending on their constituents.<sup>111</sup> One is the organic approach and the other is inorganic. As previously mentioned, the organic approach subdivides the liquids into protic and aprotic. Aprotic ionic liquids have organic molecular-ions such as alkyl pyridinium and dialkyimidazolium cations.<sup>84</sup> Protic ionic liquids are defined as those able to transfer a proton to a Brønsted base.<sup>112</sup> Ohno <sup>84</sup> established the nature and reversibility of proton potentials in ionic liquids by neutralizing different acids with five alkylimidazoles to prepare several salts. Various methods have been used to determine the acidity of protic ionic liquids.<sup>113</sup> Li *et al.* labelled a series of functional ionic liquids with some acid sites and tested their ability to act as catalysts for chemical reaction.<sup>114</sup> The study used acidic cations in the same context, Gerhard *et al.* found that trialkylsulfonium cations are also acidic.<sup>115</sup> **Figure 1.9** shows some approximate classifications of cations and anions in ionic liquid according to the Lewis acid /base properties.<sup>116</sup>



Figure 1.9: Classification of cations and anions used in ionic liquids.<sup>116</sup>

#### 1.9 Acidity measurement in ionic liquids and its limitation

The activity of protons in non-aqueous media has been studied and it is known to affect the behaviour some properties such as density, conductivity and viscosity.<sup>69, 78, 117</sup> The
concept of acidity can be dealt with in a similar manner to that in aqueous solutions but the nature of the base is different in each liquid. The concentration of the base form of the molecule (non-protonated) is important to understand. <sup>117-119</sup>

In ionic liquids, the activity of protons in ionic liquids can be affected by the ability of the anion and/or cation to act as proton donors or acceptors in the same way that any molecular solvent can. While this may seem like a trivial issue to resolve, it is the lack of standard thermodynamic reference points that makes most of the usual methods difficult to apply to ionic liquids. The difficulties in ionic system are how to deal with equilibrium reaction in the system because of the unknown strength of the conjugate base or conjugate acid. The most basic species will generally be the anion of the salt but few studies have been carried out to quantify this aspect.<sup>120-122</sup>

Acidic ionic liquids can be prepared in one step by direct reaction between the base and the acid and sometimes it can be produced by distillation.<sup>123</sup> These significant properties make them attractive for large-scale in industrial uses.<sup>124-127</sup> The same is true for acid-based deep eutectic solvents.<sup>128</sup>

Numerous reviews of ionic liquids have highlighted the importance of anion-cation interactions in ionic liquids and many debate the importance of ionic dissociation (ionicity) in a system composed almost entirely of ions.<sup>117, 129</sup> Approximate measurements of pH have been made using with indicator papers such as bromophenol blue, methyl orange and phenolphthaleine.<sup>73</sup> MacFarlane *et al.*<sup>116</sup> studied traditional indicator molecules such as bromocresol purple and Alizarin red S to show that liquids such as C<sub>2</sub>mim acetate are relatively basic. The authors proposed that the *pK<sub>a</sub>* value of an acid (HX) in an ionic liquid (R<sub>4</sub>N<sup>+</sup>S<sup>-</sup>) containing a weak anion (S<sup>-</sup>) could be approximated by taking the ratio of the aqueous *pK<sub>a</sub>* values of the acid and salt in water i.e.

$$pK_a {}^{\text{R4NS}}_{\text{(HX)}} = pK_a {}^{\text{aq}}_{\text{(HX)}} / pK_a {}^{\text{aq}}_{\text{(HS)}}$$
(1.15)

Using this approach they showed that strong acids in water, such as HCl, HOTf, HNO<sub>3</sub> and HClO<sub>4</sub>, should be totally dissociated in ionic liquids. They also showed that ionic liquids acted as buffers when acids and bases were added to solution but they did not quantify  $pK_a$  or pH values.

Kanzaki *et al.*<sup>130</sup> used an electrochemical cell to measure the pH of the protonic ionic liquid ethylammonium nitrate (EAN) using the cell

#### Ag | AgCl | 0.1 M NaCl (aq) || EAN || sample EAN solution | H<sub>2 (g)</sub> | Pt

Where || was a glass membrane. They dissolved different organic acids in EAN and found that the *pK<sub>a</sub>* values were lower than in water. They also demonstrated that a potentiometric titration could be carried out by adding propylamine to EAN containing acetic acid.

Gräsvik *et al.*<sup>131</sup> used the Hammett acidity scale to characterise the acidity of the BHim  $HSO_4-H_2SO_4$  system. This is a robust method which is able to measure a wide range of acidities with a single probe, however, it is less widely used than the *pH* scale. Xing *et al.* also measured Hammett acidity functions for sulfonic acid-functionalized ionic liquids and found that the acidity of the liquids were controlled by the nature of the anion. <sup>132</sup> Mihichuck *et al.* showed that there was a good correlation between the Hammett acidity scale and the pH for H[NTf<sub>2</sub>] in [C<sub>4</sub>mim][NTf<sub>2</sub>].<sup>133</sup>

Thomazeau *et al.* reported that some Brønsted acids are soluble in ionic liquids. The ionic liquids were used in the study were based on the 1-butyl-3-methylimidazolium cation, [BMIM]: [BMIM][NTf<sub>2</sub>], [BMIM][BF<sub>4</sub>], and [BMMIM]<sup>-</sup>[BF<sub>4</sub>] together with the strong acids such as HNTf<sub>2</sub> (NTf<sub>2</sub> = N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub><sup>-</sup>) and HOTf (OTf = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>).<sup>134</sup> The same authors extended the scope of their study to measure Brønsted acids in some ionic liquids using UV-Vis techniques to determine the Hammett acidity function ratio. A major deficiency of the paper is the lack of comparison of Hammett functions between different acids in ionic liquids and those in aqueous media. It is important to appreciate that the proton may behave differently in ionic liquids to other solvents.<sup>135</sup>

An investigation by Doherty *et al.* determined the absolute  $pK_b$  of N-centered bases in ionic liquids using an electrochemical method. However, the uncertainties in the results were quite large (± 0.4 -1.0 pK units) and the limitation of study was that it could only been applied to amines.<sup>136</sup> Additionally, Wang *et al* reported several series of dissociation constants of substituted benzoic acids in ionic liquids. The study examined the correlation between the *pKa* scales for different ionic liquids and showed a linear correlation with standard deviation (SD  $\leq \pm 0.05$ ) with those in aqueous media. The measurements also showed that both the anions and the cation in ionic liquids affected the acidity of benzoic acid. The study compared the acidity of four ionic liquid only and neglected the acidity of other carboxylic acids in the system.<sup>123, 137</sup>

An alternate method of describing proton activity is using an absolute scale making use of general thermodynamic considerations. These ideas were described for ionic liquids by Himmel *et al.*<sup>138</sup> and supported by quantum chemical calculations. They also characterised the super acidity of the HBr/AlBr<sub>3</sub> system using NMR spectroscopy and related this to other acids using the absolute pH scale.<sup>139</sup>

<sup>1</sup>H NMR has also been used to characterise acidity by correlating the shift in the NH signal to the Brønsted acidity of a liquid; the larger the change in chemical shift, the larger the Brønsted acidity.<sup>126, 140</sup> Hammett function has been be used for evaluating the acidity of non-aqueous solvents, where the ionization ratio of protonated and deprotonated of acid in a system is measured. The Hammett function can be defined by the following expression:

 $H_{-} = pK(\text{HI}) + \log_{10} ([\text{I}]/[\text{HI}])$ (1.16)

Where [HI] and [I] <sup>141</sup> are the molar concentrations of the neutral and anionic forms of an indicator, respectively and pK(HI) is the thermodynamic ionization constant. The data can be obtained using UV-Vis spectroscopy.

A large  $H_{-}$  value is strongly basic; therefore, the function possesses useful information for quantitative acidity comparison objectives.<sup>104</sup> The dissociation constant of an acid in water-ionic liquid mixtures was studied by some researchers to determine the acidity in ionic system. MacFarlane *et al.*<sup>116</sup> noted that Emim acetate has moderately strong base in pure water however, in water mixtures with ionic liquid the acid prefer to remain in the ionic liquid phase that means the basicity of the anion controls the proton activity .<sup>116, 142</sup> The pH value in pure ionic liquids are currently unknown. The first studies into a comparable *pKa* of organic acids in DESs are described in Chapter 3 of this thesis.

## 1.10 Uses of acidic ionic liquids AILs

Acidic ionic liquids (AIL) have been of significant interest for a variety of applications including polymer batteries, plasticizers, metal extraction and processing, electrophoresis, oil desulfurization, electrodeposition of metals and pharmaceutical ingredients.<sup>143</sup>

Acidic ionic liquids have been immobilised on polymer surfaces to act as proton transfer membranes e.g. calix resorcinarene was modified with imidazolium [HSO<sub>4</sub>] and polychlorostyrene was doped with pyridinium propanesulfonic acid.<sup>104</sup> Such materials have found use in membrane applications such as fuel cells.<sup>113</sup> Protic ionic liquids can be regarded as unique alternatives to the proton conductive membranes such as Nafion. The

membrane in water usually operates below 80°C to keep water inside it. However, the uses of protic ionic liquids enables an increase in temperature which increases the rate of the oxygen reduction reaction.<sup>111, 144, 145</sup> In a recent study Wu and co-workers reported the ionic conductivities of a series of PIL based on acetamide and Brønsted acids (HX, where X is  $HSO_4^-$ ,  $CF_3COO^-$ , or  $CH_3COO^-$ ). The ionic conductivities for most of the samples were in the range  $10^{-3}$  and  $10^{-1}$  S/m at room temperature. Most of the AILs studied possessed relatively moderate thermal stabilities due to this significant ionic conductivity properties make them beneficial liquids used in many reaction solvents and in organic synthesis.<sup>135, 143</sup>

#### 1.11 Project aim

The main objective of this project is to study the activity of protons in ionic liquids and deep eutectic solvents. In order to understand how the protons behave in these media. It is necessary to find a suitable analytical method that can be used to assess the pH scales in these solvents. It should be stressed at this point that the concept of pH is only valid in aqueous solutions so all the studies will only attempt to create relative acidity scales using the same definition of pH as shown in equation 1.1.

The relative acid/ base properties of ionic liquids has been discussed but no one has tried to quantify a pH scale.

The first part of the project was aimed to develop an analytical method to quantify the pH of an ionic liquid. This was using classical spectroscopic indicator solutes such as bromophenol blue to quantify proton activity. The issue would be to determine the pH of the indicator solute and this was achieved by a titration method. The main aim of the study was to compare the acid dissociation equilibrium constants of nine carboxylic acids in a deep eutectic solvents and compare them with the values obtained in aqueous solvents both by the same method and using literature values. The study was also aimed to investigate the effect of different hydrogen bond donors on the acidity of DESs. These values would be compared with ionic liquids with different anions to determine the effect of the anion on the pH of a liquid. The acidity of protic ionic liquids would also be analysed by the same technique to understand the effect of the anion in the acid base properties. Finally, the effect of water on the pH of ionic liquids and DESs would be determined.

The second part of the project was an attempt to develop an electrochemical pH sensor which can be used in ionic systems. The study addresses the effect of the linear response of cell potential vs. In  $a_{H+}$  and compares the slope for the correlation in aqueous solutions and DESs in glass electrode. As it already known that in aqueous solutions an Ag/AgCl electrode is commonly used, however this is not suitable for use in ionic liquid media due to liquid junction potentials. This chapter investigates the conditions which allow reliable and stable measurements of the cell potential using a glass electrode. There would be a liquid junction potential when aqueous solutions are used in the two reference electrodes which would arise due to the differences in ionic mobilities in the two liquids. Liquid junction potentials would be investigated in ionic liquids in this chapter as well.

The final chapter of the thesis this knowledge of pH in ionic liquids in ILs and DESs could be used to study the electropolymerization of aniline in a variety of acidic solutions and DES mixtures. This topic has been studied within the group to produce charge storage devices for DES based batteries and capacitors. While DESs have been shown to produce more even polymer films that through aqueous or organic solvents the films are more stable in acidic solutions. The formation of polyaniline were studied in solutions of a known pH both with and without water and the properties of the films will be investigated to determine the true effect of pH and delineate it from solvent and anion effects.

### 1.12 References

- 1. W. F. Luder and S. Zuffanti, *Electronic Theory of Acids and Bases*, John Wiley And Sons, Inc. Ghapman And Hall, Ltd; London, 1946.
- R. Buck, S. Rondinini, A. Covington, F. Baucke, C. Brett, M. Camoes, M. Milton, T. Mussini, R. Naumann and K. Pratt, *Pure and Applied Chemistry*, 2002, 74, 2169-2200.
- 3. P. Spitzer and K. W. Pratt, *Journal of Solid State Electrochemistry*, 2011, **15**, 69-76.
- 4. W. J. Waddell and R. G. Bates, *Physiological Reviews*, 1969, **49**, 285-329.
- 5. L. Michaelis, Die Wasserstoffionkonzentration: Ihre Bedeutung fd Biologie ud Methoden ihrer Messung, Springer, 1914.
- 6. L. Michaelis, *Naturwissenschaften*, 1914, **2**, 829-834.
- 7. H. Galster, Ullmann's Encyclopedia of Industrial Chemistry, 2000.
- 8. P. Fisicaro, E. Ferrara, E. Prenesti and S. Berto, *Analytical and Bioanalytical Chemistry*, 2005, **383**, 341-348.
- 9. P. J. Brewer, D. Stoica and R. J. Brown, Sensors, 2011, 11, 8072-8084.
- F. G. Baucke, R. Naumann and C. Alexander-Weber, *Analytical Chemistry*, 1993, 65, 3244-3251.
- 11. J. J. Lingane, Analyst, 1966, **91**, 1-9.
- 12. C. Rius-Alonso, Y. González-Quezada and A. Q. Thorent, Proceedings of ICERI2013 Conference ISBN, 18th-20th November 2013, Seville, Spain.
- 13. F. Riddell and M. Robinson, *Tetrahedron*, 1974, **30**, 2001-2007.
- K. Ward and R. Balaban, Magnetic Resonance in Medicine: An Official Journal of the International Society for Magnetic Resonance in Medicine, 2000, 44, 799-802.
- 15. H. N. Po and N. Senozan, *Journal of Chemical Education*, 2001, **78**, 1499.
- 16. G. E. Cullen, H. Keeler and H. W. Robinson, *Journal of Biological Chemistry*, 1925, **66**, 301-322.
- 17. A. Berthod, M. Ruiz-Angel and S. Carda-Broch, *Journal of Chromatography A*, 2008, **1184**, 6-18.
- 18. H. Ohno, *Electrochemical aspects of ionic liquids*, John Wiley & Sons, 2005.
- 19. D. Skoog, D. West, F. Holler and S. Crouch, *Fundamentals of analytical chemistry*, Cengage Learning, California, USA, 2013.
- 20. I. Bertini, *Biological inorganic chemistry: structure and reactivity*, University Science Books, California, 2007.
- 21. B. Pathare, V. Tambe and V. Patil, *International Journal of Pharmacy and Pharmaceutical Sciences*, 2014, **6**, 26-34.
- 22. J. T. Stock, J. Chem. Educ, 1992, 69, 197.
- 23. M. Badr, M. El-Halafawi and E.-A. Zeid, *Glob J Environ Res*, 2012, 6, 36-43.

- 24. H. Laitinen, W. Jennings and T. Parks, *Industrial & Engineering Chemistry Analytical Edition*, 1946, **18**, 358-359.
- 25. F. Baucke, Journal of Non-Crystalline Solids, 1985, 73, 215-231.
- 26. H. T. S. Britton, *Journal of the Chemical Society, Transactions*, 1925, **127**, 2110-2120.
- 27. J. Reijenga, A. Van Hoof, A. Van Loon and B. Teunissen, *Analytical chemistry insights*, 2013, **8**, 53.
- 28. A. Avdeef, J. E. Comer and S. J. Thomson, *Analytical Chemistry*, 1993, **65**, 42-49.
- 29. M. Dole and B. Wiener, *Transactions of The Electrochemical Society*, 1937, **72**, 107-127.
- 30. K. Granholm, T. Sokalski, A. Lewenstam and A. Ivaska, *Analytica chimica acta*, 2015, **888**, 36-43.
- 31. F. Szabadváry and R. A. Chalmers, *Talanta*, 1983, **30**, 997-999.
- 32. I. Kolthoff and T. Kameda, *Industrial & Engineering Chemistry Analytical Edition*, 1931, **3**, 129-133.
- 33. E. Pungor, Oscillometry and Conductometry: International Series of Monographs on Analytical Chemistry, Elsevier, 2016.
- 34. P. W. Wigler, *Journal of Biological Chemistry*, 1963, **238**, 1767-1771.
- 35. B. Thamer and A. Voigt, *The Journal of Physical Chemistry*, 1952, **56**, 225-232.
- 36. A. Cladera, C. Tomas, J. Estela and V. Cerda, *Analytica chimica acta*, 1994, **286**, 253-263.
- 37. D. Kara and M. Alkan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2000, **56**, 2753-2761.
- 38. M. Franko and C. D. Tran, *Applied spectroscopy*, 1989, **43**, 661-668.
- 39. A. S. Meyer Jr and G. H. Ayres, *Journal of the American Chemical Society*, 1957, **79**, 49-53.
- 40. J.-H. Zhang, Q. Liu, Y.-M. Chen, Z.-Q. Liu and C.-W. XU, *Acta Physico-Chimica Sinica*, 2012, **28**, 1030-1036.
- 41. W. E. King and G. H. Campbell, *Ultramicroscopy*, 1994, **56**, 46-53.
- 42. S. G. Tajc, B. S. Tolbert, R. Basavappa and B. L. Miller, *Journal of the American Chemical Society*, 2004, **126**, 10508-10509.
- 43. E. A. Underwood, SAGE Publications, Editon edn., 1944.
- 44. D. V. Fenby, *Pure and Applied Chemistry*, 1987, **59**, 91-100.
- 45. A. Leo, C. Hansch and D. Elkins, *Chemical reviews*, 1971, **71**, 525-616.
- 46. A. Berthod and S. Carda-Broch, *Journal of Chromatography* 2004, **1037**, 3-14.
- 47. W. Vezin and A. Florence, *International Journal of Pharmaceutics*, 1979, **3**, 231-237.
- 48. R. Freeman, *Chemistry of Heterocyclic Compounds*, 1995, **31**, 1004-1005.

- 49. A. D. Gift, S. M. Stewart and P. Kwete Bokashanga, *Journal of Chemical Education*, 2012, **89**, 1458-1460.
- 50. K. Bartik, C. Redfield and C. M. Dobson, *Biophysical Journal*, 1994, **66**, 1180-1184.
- 51. A. M. Silva, X. Kong and R. C. Hider, *Biometals*, 2009, 22, 771-778.
- 52. J. Bezençon, M. B. Wittwer, B. Cutting, M. Smieško, B. Wagner, M. Kansy and B. Ernst, *Journal of pharmaceutical and biomedical analysis*, 2014, **93**, 147-155.
- 53. S. Babić, A. J. Horvat, D. M. Pavlović and M. Kaštelan-Macan, *TrAC Trends in Analytical Chemistry*, 2007, **26**, 1043-1061.
- 54. J. Kerr, *Chemical Reviews*, 1966, **66**, 465-500.
- 55. F. Bordwell, J. E. Bartmess and J. A. Hautala, *The Journal of Organic Chemistry*, 1978, **43**, 3113-3116.
- 56. J. P. Guthrie, J. Cossar and A. Klym, *Journal of the American Chemical Society*, 1982, **104**, 895-896.
- 57. E. J. Delgado, *Chemical Physics Letters*, 2009, **471**, 133-135.
- 58. P. Hazarika, R. L. Sarma, M. Karim, B. Bezbaruah, R. Kalita and C. Medhi, 2009.
- 59. J. Cleveland, M. Benko, S. Gluck and Y. Walbroehl, *Journal of Chromatography A*, 1993, **652**, 301-308.
- M. Manderscheid and T. Eichinger, *Journal of Chromatographic Science*, 2003, 41, 323-326.
- 61. F. Orosz and J. Ovádi, *Journal of Immunological Methods*, 2002, **270**, 155-162.
- 62. T. Michaowski and A. García Asuero, *Journal of Analytical Sciences, Methods* and Instrumentation (Vol. 2, p. 1-4), 2012.
- 63. J. Rudin and D. T. Wasan, *Colloids and surfaces*, 1992, **68**, 67-79.
- 64. M. Miyagi and T. Nakazawa, *Analytical chemistry*, 2008, **80**, 6481-6487.
- 65. J. J. Lagowski, *The Chemistry of Nonaqueous Solvents III*, Elsevier, United States of America, 2012.
- 66. V. Gutmann, *Coordination chemistry in non-aqueous solutions*, Springer Science & Business Media, Wien, 2012.
- 67. C. Reichardt and T. Welton, *Solvents and Solvent Effects in Organic Chemistry*, *Fourth Edition*, 2010, 65-106.
- 68. I. M. Kolthoff, Analytical Chemistry, 1974, 46, 1992-2003.
- 69. K. Izutsu, *Electrochemistry in nonaqueous solutions*, John Wiley & Sons, Weinheim, 2009.
- 70. C. Reichardt and T. Welton, *Solvents and solvent effects in organic chemistry*, John Wiley & Sons, Weinheim, Germany, 2011.
- 71. A. Maitra and S. Bagchi, *Journal of Molecular Liquids*, 2008, **137**, 131-137.
- 72. T. Welton, *Chemical reviews*, 1999, **99**, 2071-2084.

- 73. K. Sarmini and E. Kenndler, *Journal of Biochemical and Biophysical Methods*, 1999, **38**, 123-137.
- 74. A. P. Abbott, G. Frisch and K. S. Ryder, *Annual Review of Materials Research*, 2013, **43**, 335-358.
- 75. R. Hagiwara and Y. Ito, *Journal of Fluorine Chemistry*, 2000, **105**, 221-227.
- 76. R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792-793.
- 77. A. P. Abbott, G. Capper, D. L. Davies and R. K. Rasheed, *Chemistry-A European Journal*, 2004, **10**, 3769-3774.
- 78. V. V. Singh, A. K. Nigam, A. Batra, M. Boopathi, B. Singh and R. Vijayaraghavan, *International Journal of Electrochemistry*, 2012, **2012**.
- 79. A. P. Abbott, R. C. Harris and K. S. Ryder, *The Journal of Physical Chemistry B*, 2007, **111**, 4910-4913.
- 80. e.-A. S. Zein and F. Endres, *Chemphyschem: a European journal of chemical physics and physical chemistry*, 2006, **7**, 58-61.
- 81. F. H. Hurley and T. P. Wier, *Journal of the Electrochemical Society*, 1951, **98**, 203-206.
- 82. J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorganic Chemistry*, 1982, **21**, 1263-1264.
- 83. A. P. Abbott, J. C. Barron, K. S. Ryder and D. Wilson, *Chemistry-A European Journal*, 2007, **13**, 6495-6501.
- 84. H. Ohno and M. Yoshizawa, *Solid State Ionics*, 2002, **154**, 303-309.
- 85. J. S. Wilkes and M. J. Zaworotko, *Journal of the Chemical Society, Chemical Communications*, 1992, 965-967.
- 86. R. Hagiwara, T. Hirashige, T. Tsuda and Y. Ito, *Journal of Fluorine Chemistry*, 1999, **99**, 1-3.
- 87. J. Fuller, R. T. Carlin and R. A. Osteryoung, *Journal of the Electrochemical Society*, 1997, **144**, 3881-3886.
- 88. B. M. Quinn, Z. Ding, R. Moulton and A. J. Bard, *Langmuir*, 2002, **18**, 1734-1742.
- 89. F. Endres and S. Z. El Abedin, *Physical Chemistry Chemical Physics*, 2006, **8**, 2101-2116.
- 90. A. P. Abbott, G. Capper and S. Gray, *a European Journal of Chemical Physics and Physical chemistry*, 2006, **7**, 803-806.
- 91. P. Wasserscheid and T. Welton, *Ionic liquids in synthesis*, Wiley Online Library, Germany, 2008.
- 92. P. McClarty, A. O'Brien and F. Pollmann, *Physical Review B*, 2014, **89**, 195123.
- 93. C. Chiappe and D. Pieraccini, *Journal of Physical Organic Chemistry*, 2005, **18**, 275-297.
- 94. C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. Aki and J. F. Brennecke, *Journal of Chemical & Engineering Data*, 2004, **49**, 954-964.

- 95. M. E. Van Valkenburg, R. L. Vaughn, M. Williams and J. S. Wilkes, *Thermochimica Acta*, 2005, **425**, 181-188.
- 96. E. F. Smith, F. J. Rutten, I. J. Villar-Garcia, D. Briggs and P. Licence, *Langmuir*, 2006, **22**, 9386-9392.
- 97. P. Wasserscheid and W. Keim, *Angewandte Chemie International Edition*, 2000, **39**, 3772-3789.
- E. L. Smith, A. P. Abbott and K. S. Ryder, *Chemical reviews*, 2014, **114**, 11060-11082.
- 99. R. C. Harris, University of Leicester, 2009.
- 100. A. P. Abbott, P. M. Cullis, M. J. Gibson, R. C. Harris and E. Raven, *Green Chemistry*, 2007, **9**, 868-872.
- 101. A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *Journal* of the American Chemical Society, 2004, **126**, 9142-9147.
- 102. A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chemical Communications*, 2003, 70-71.
- 103. J. M. Hartly, Leicester, 2013.
- 104. Q. Zhang, K. D. O. Vigier, S. Royer and F. Jérôme, *Chemical Society Reviews*, 2012, **41**, 7108-7146.
- 105. S. Pandey, Analytica Chimica Acta, 2006, 556, 38-45.
- 106. H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt and T. Welton, *Chemical Society Reviews*, 2012, **41**, 7780-7802.
- 107. C. A. Nkuku and R. J. LeSuer, *The Journal of Physical Chemistry B*, 2007, **111**, 13271-13277.
- 108. C. Ruß and B. König, Green Chemistry, 2012, 14, 2969-2982.
- 109. T. Welton, Coordination Chemistry Reviews, 2004, 248, 2459-2477.
- 110. K. Shahbaz, F. Mjalli, M. Hashim and I. AlNashef, *Separation and Purification Technology*, 2011, **81**, 216-222.
- 111. D. A. Walsh, A. Ejigu, J. Smith and P. Licence, *Physical Chemistry Chemical Physics*, 2013, **15**, 7548-7554.
- 112. M. L. Dietz, S. Jakab, K. Yamato and R. A. Bartsch, *Green Chemistry*, 2008, **10**, 174-176.
- Z. Qureshi, K. Deshmukh and B. Bhanage, *Clean Techn Environ Policy*, 2014, 16, 1487-1513.
- 114. D. Li, F. Shi, J. Peng, S. Guo and Y. Deng, *The Journal of organic chemistry*, 2004, **69**, 3582-3585.
- 115. D. Gerhard, S. C. Alpaslan, H. J. Gores, M. Uerdingen and P. Wasserscheid, *Chemical Communications*, 2005, 5080-5082.
- 116. D. R. MacFarlane, J. M. Pringle, K. M. Johansson, S. A. Forsyth and M. Forsyth, *Chemical Communications*, 2006, 1905-1917.

- 117. M. Shen, Y. Zhang, K. Chen, S. Che, J. Yao and H. Li, *The Journal of Physical Chemistry B*, 2017, **121**, 1372-1376.
- 118. M. Campetella, M. Montagna, L. Gontrani, E. Scarpellini and E. Bodo, *Physical Chemistry Chemical Physics*, 2017.
- 119. I. A. Koppel, P. Burk, I. Koppel, I. Leito, T. Sonoda and M. Mishima, *Journal of the American Chemical Society*, 2000, **122**, 5114-5124.
- 120. D. R. MacFarlane, R. Vijayaraghavan, H. N. Ha, A. Izgorodin, K. D. Weaver and G. D. Elliott, *Chemical Communications*, 2010, **46**, 7703-7705.
- 121. M. Yoshizawa, W. Xu and C. A. Angell, *Journal of the American Chemical Society*, 2003, **125**, 15411-15419.
- 122. O. Hollóczki, F. Malberg, T. Welton and B. Kirchner, *Physical Chemistry Chemical Physics*, 2014, **16**, 16880-16890.
- 123. Z. Wang, P. Ji, X. Li and J.-P. Cheng, Organic letters, 2014, 16, 5744-5747.
- C. A. Angell, N. Byrne and J.-P. Belieres, *Accounts of Chemical Research*, 2007, 40, 1228-1236.
- 125. K. Fumino, P. Stange, V. Fossog, R. Hempelmann and R. Ludwig, *Angewandte Chemie International Edition*, 2013, **52**, 12439-12442.
- 126. T. L. Greaves and C. J. Drummond, *Chemical reviews*, 2008, **108**, 206-237.
- 127. T. Yasuda and M. Watanabe, MRS bulletin, 2013, 38, 560-566.
- M. Hasani, J. L. Yarger and C. A. Angell, *Chemistry-A European Journal*, 2016, 22, 13312-13319.
- 129. G. L. Burrell, I. M. Burgar, F. Separovic and N. F. Dunlop, *Physical Chemistry Chemical Physics*, 2010, **12**, 1571-1577.
- 130. K. Hashimoto, K. Fujii, K. Ohara and M. Shibayama, *Physical Chemistry Chemical Physics*, 2017, **19**, 8194-8200.
- 131. J. Gräsvik, J. P. Hallett, T. Q. To and T. Welton, *Chemical Communications*, 2014, **50**, 7258-7261.
- 132. H. Xing, T. Wang, Z. Zhou and Y. Dai, *Journal of Molecular Catalysis A: Chemical*, 2007, **264**, 53-59.
- 133. L. M. Mihichuk, G. W. Driver and K. E. Johnson, *ChemPhysChem*, 2011, **12**, 1622-1632.
- 134. J. D. Holbrey and K. R. Seddon, *Journal of the Chemical Society, Dalton Transactions*, 1999, 2133-2140.
- 135. C. Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts and B. Gilbert, *Journal* of the American Chemical Society, 2003, **125**, 5264-5265.
- 136. R. Barhdadi, M. Troupel, C. Comminges, M. Laurent and A. Doherty, *The Journal of Physical Chemistry B*, 2011, **116**, 277-282.
- 137. Z. Wang, H. Deng, X. Li, P. Ji and J.-P. Cheng, *The Journal of organic chemistry*, 2013, **78**, 12487-12493.
- 138. D. Himmel, S. K. Goll, F. Scholz, V. Radtke, I. Leito and I. Krossing, *ChemPhysChem*, 2015, **16**, 1428-1439.

- 139. F. Scholz, D. Himmel, L. Eisele, W. Unkrig, A. Martens, P. Schlüter and I. Krossing, *Chemistry-A European Journal*, 2015, **21**, 7489-7502.
- 140. T. M. Potewar, S. A. Siddiqui, R. J. Lahoti and K. V. Srinivasan, *Tetrahedron letters*, 2007, **48**, 1721-1724.
- 141. P.-Y. Chen and I.-W. Sun, *Electrochimica Acta*, 2001, 46, 1169-1177.
- 142. C. Adam, M. V. Bravo and P. M. Mancini, *Tetrahedron Letters*, 2014, **55**, 148-150.
- 143. A. S. Amarasekara, *Chemical Reviews*, 2016, **116**, 6133-6183.
- 144. A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu and M. Watanabe, *The Journal of Physical Chemistry B*, 2003, **107**, 4024-4033.
- 145. R. Sheldon, Chemical Communications, 2001, 2399-2407.

## Chapter 2: Expermintal

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# 2.1 Chemicals and reagents

Compound	Source	Formula	Purity %
Triflic acid	Fisher	$F \xrightarrow{F} \bigcirc 0 \\ S = 0 \\ G H$	≥99
Oxalic acid	Sigma-Aldrich	но он	98
salicylic acid	Sigma-Aldrich	ОН	99
Succinic acid	Fisher	но он	<u>≥99</u>
Citric acid	Sigma-Aldrich	о он о но от он от он	≥99
Benzoic acid	Sigma-Aldrich	ОН	>98.9
Lactic acid	Fisher	OH OH OH	<u>≥99</u>
Propanoic acid	Fluka	C <sub>2</sub> H <sub>5</sub> COOH	≥98
Butanoic acid	Fluka	C <sub>3</sub> H <sub>7</sub> COOH	≥98
Bmim BF <sub>4</sub>	Aldrich	N <sup>+</sup> ,CH <sub>3</sub> BF <sub>4</sub> <sup>−</sup> CH <sub>3</sub>	≥98
Emim OAc	Sigma-Aldrich	$ \begin{array}{c} \overset{CH_3}{\swarrow} & \overset{O}{\longrightarrow} \\ \overset{N^+}{\searrow} & \overset{O}{\longrightarrow} \\ \overset{CH_3}{\bigvee} & \overset{O}{\longleftarrow} \\ \overset{CH_3}{\longleftarrow} \\ \end{array} $	≥98
Bromophenol blue	Amresco	HO Br Br Br Br Br Br Br Br Br Br Br Br	>98.9
Acetic acid	Fluka	CH <sub>3</sub> COOH	≥99
Silver chloride	Sigma-Aldrich	AgCl	≥99
Emim HSO <sub>4</sub>	BASF	$(H_3) (H_3) (H_3$	≥99

 Table 2.1: Sources and purity of chemicals used in this study

All materials and reagents used in this work are shown in **Table 2.1** and **Table 2.2** with their purities and suppliers. All chemicals and solvents have been used as received. **Table 2.1** shows the solvents and chemical materials used in this study all were used without further purification.

#### 2.1.1 DES Preparation method

Names	Origin	Formula	Purity
Choline chloride	Sigma-Aldrich	HO N <sup>+</sup>	≥99
Ethylene glycol	Sigma-Aldrich	НООН	≥99
Oxalic acid anhydrous	Fisher	О ОН	≥99
Glycerol	Fisher	но он	98
Urea	Sigma-Aldrich		99
Citric acid	Sigma-Aldrich		≥99
Malonic acid	Sigma-Aldrich	но он	99

Table 2.2: List of chemicals used to make DESs

## 2.1.2 Synthesis of Deep Eutectic Solvents (DESs)

Five DESs were used primarily in this study; 2 ethylene glycol (EG): 1 choline chloride (ChCl), 2 glycerol: 1 ChCl, 1 oxalic acid: 1 ChCl, 1 malonic acid: 1 ChCl and 1 citric acid: 1 ChCl. They were prepared by mixing ChCl with the hydrogen bond donor (EG, glycerol, anhydrous oxalic acid, malonic acid citric acid or urea) in the given molar ratio.

The mixture was heated and stirred at 50 °C until a fully homogeneous liquid was formed. The sources of the chemicals in the preparation of DESs are shown in **Table 2.2**. The ChCl was dried by using the oven around 55 °C then the dried samples were carried out by TGa tool to measure the water content. It was found that the water content in for ChCl was approximately 0.043 wt% (TGa). All other DESs and ILs were quantified their water content by using TGa. It was found that 2 urea : 1 ChCl , 2 EG : 1 ChCl , 1 oxalic acid : 1 ChCl , 1 malonic acid : 1 ChCl , 1 citric acid : 1 ChCl , [Bmim][BF4] and [Emim][OAc] have water content % around ( $3.55 \pm 1.48$ ,  $0.98 \pm 0.023$ ,  $0.51 \pm 0.081$ ,  $1.64 \pm 0.07$ ,  $0.043 \pm 0.032$ ,  $0.039 \pm 0.012$ ) respectively.

The  $pK_a$  value of the bromophenol blue indicator were determined using a UV-vis spectrophotometric method. Solutions of bromophenol blue (6.60 x10<sup>-5</sup> mol kg<sup>-1</sup>) were made up in each of the ionic liquids (ILs), DESs and water. The solution was split into 3; one was used as was, one was made up to 0.1 mol kg<sup>-1</sup> triflic acid solution, and the third to 0.1 mol kg<sup>-1</sup> with methylamine. These were able to convert the indicator to the fully protonated and deprotonated forms respectively.

#### 2.2 Thermogravimetric analysis (TGA)

TGA is an important technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere.<sup>1, 2</sup> The measured weight loss curve gives information on changes in sample composition, thermal stability and kinetic parameters for chemical reactions in the sample.

TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. The sample environment is controlled by a purge gas, in this case N<sub>2</sub> was used. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. In this study, the water content of DESs and ILs were quantified using TGA for 2 urea : 1 ChCl , 2 EG : 1 ChCl , 1 oxalic acid : 1 ChCl , , 1 malonic acid : 1 ChCl , 1 citric acid : 1 ChCl, [Bmim][BF<sub>4</sub>] and [Emim][OAc]. A Mettler Toledo TGA/DSC 1 machine fitted with a sample robot. The TGA was able to detect a very small change in the mass c.a 0.1 µg could be detected in a 15-25 mg sample. The instrument uses the same STARe system software for data analysis.

#### 2.3 Spectroscopic techniques

Every chemical compound absorbs, transmits, or reflects light (electromagnetic radiation) over a certain range of wavelength. Spectroscopy is a very powerful tool when trying to gain information about species in solution and structural changes can be observed by measuring shifts in the absorption/transmittance spectra. The most widely used spectrophotometric technique for this purpose is Ultraviolet–visible (UV/Vis) absorbance.

### 2.3.1 UV-Vis spectrophotometry

UV-vis spectrophotometry is a common analytical technique which is used to study acidbase properties of solvents. The basic principles of UV-Visible spectrometry is associated with the absorption of visible and ultraviolet (UV) radiation that can excite electrons from a lower to a higher energy level in atoms or molecules. <sup>3</sup> The electronic energy levels of simple molecules are widely separated and usually only the absorption of a high energy photon, i.e. one of very short wavelength, that can excite an electron from one energy level to another.<sup>4</sup> **Figure 2.1** shows how electronic transitions can results in an absorbance spectrum.<sup>5</sup>



*Figure 2.1*: Schematic diagram showing electronic transitions in a molecule.<sup>5</sup>

Some molecules have conjugated systems. These molecules can be delocalised electrons due to overlapping p orbitals in the double bonds. As the amount of delocalisation in the molecule increases the energy gap between the  $\pi$  bonding orbitals and  $\pi$  anti-bonding

orbitals becomes smaller this enables light of lower energy, and longer wavelength to excite electrons. The greater the degree of conjugation the longer the wavelength of light what can cause electronic excitation. Molecules which can absorb visible light are known as chromophores.<sup>6</sup>

UV-visible spectrometers can be used to measure the absorbance of ultra violet or visible light by scanning a sample, either at a single wavelength or perform a scan over a range of wavelengths. The UV region ranges from 190 to 400 nm and the visible region from 400 to 750 nm. A schematic diagram of a UV-visible spectrometer is shown in **figure 2.2**.



*Figure 2.2*: Schematic diagram shows spectrophotometer instrument.<sup>7</sup>

The diagram shows how the combination of tungsten/halogen and deuterium of light source lamps provides the visible and near ultraviolet radiation covering the spectrum from 200 to 800 nm. The output from the light source is focused onto the diffraction grating which divides the coming light into its component colours of different wavelengths. When light passes through or is reflected from a sample, The detector converts the incoming light into a current and the amount of light absorbed is cases from the difference between the incident radiation ( $P_0$ ) and the transmitted radiation (P). The amount of light absorbed is stated as transmittance or absorbance. Transmittance mostly is given in terms of a fraction of 1 or as a percentage and is expressed as the following equation:

$$A = \log_{10} P_0 / P = \log_{10} 1 / T = \log_{10} 100 / \% T$$
(2.1)

Absorbance of the prepared solution can be determined by Beer-Lambert law

 $A = \varepsilon c l$ .

Where *A* is the absorbance *c* is the concentration *l* is the path length and  $\varepsilon$  is the extinction coefficient.<sup>7</sup>

In the UV-vis portion of the spectrum the photon energies are high enough to promote or excite an electron in a molecular orbital to a higher energy level. Where this occurs a portion of the electromagnetic spectrum will be absorbed. A variety of electronic excitations can occur in organic molecules such as the indicators used in pH measurement. These are shown in **Figure 2.3**.



*Figure 2.3*: *Electronic transitions possible in conjugated organic molecules.*<sup>8</sup>

It is only the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions which can occur in the UV-visible region of the electromagnetic spectrum. Generally the electronic transition will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

When the light is absorbed by the sample and the electron is excited to a higher energy level a spectrometer measures the wavelengths where the absorption occurs and records it as a function of the amount of light absorbed. The spectrum can provide information about the type of bonds in terms of the degree of conjugation. The more conjugation the longer the absorbance wavelength will be. The amount of light absorbed provides information about the concentration of the chromophore and the ability of the material to absorb light.<sup>9</sup>

A chromophore is a group of atoms that absorb radiation in the visible or UV region. Most indicators contain conjugated organic molecules; these molecules have one or more active functional groups working as chromophores.<sup>10</sup> For this study, the organic indicator dye, bromophenol blue was dissolved in solvents. The significant reversible colour change occurs in the pH range from 3.0 to 4.6, where a change in colour from yellow in acidic media and blue-violet in basic solutions. Bromophenol blue is closely related to the phenolphthalein indicator. The conjugation of the molecules is related to the electron transfer between the  $\pi$  and  $\pi^*$  molecular orbitals .<sup>6</sup>The chemical structure of bromophenol blue can be seen in **Figure 2.4**:



*Figure 2.4:* Effect of pH on the structure of bromophenol blue in acidic (left) and basic (right) forms.<sup>6</sup>

A Shimadzu Model UV-1601 Spectrophotometer was used to measure the UV-Vis spectra. Spectra were collected by scanning in the range of 350nm to 750 nm. The program UV PROBE was used to obtain the values for  $\lambda_{max}$  of the UV-Vis spectra.

#### 2.3.2 Dynamic light scattering

Dynamic light scattering (DLS) is a spectroscopic technique that can be used to determine the size distribution profile of small particles in a suspension or polymers in a solution. As well as DLS being able to determine the aggregation size of particles in solution it is also able to determine the size of droplets suspended in solution and identify their size distributions profile. As light scatters from the moving macromolecules, this motion imparts a randomness to the phase of the scattered light, such that when the scattered light from two or more particles is added together, there will be a changing destructive or constructive interference. This leads to time-dependent fluctuations in the intensity of the scattered light. In DLS the time-dependent fluctuations in the scattered light are measured by a fast photon counter. The fluctuations are directly related to the rate of diffusion of the molecule through the solvent, which is related in turn to the particles hydrodynamic radii. The fluctuations are quantified via a second order correlation function  $g_2(\tau)$ , given by:<sup>11</sup>

$$g_2 = [I(t)I(t+\tau)]/[I(t)]^2$$
(2.4)

Where I(t) and  $I(t+\tau)$  are the scattered intensities at some initial time *t* and some later time  $(t+\tau)$ ,  $\tau$  is the delay time, and averaging is done over the observation time, *t*. The relationship between fitting the time autocorrelation function with an exponential decay function integrated over the relaxation rate distribution,  $G(\Gamma)$ , allows the calculation of the relaxation times of the particles that can be shown in following expressing.

$$g_2(\tau) = 1 + \beta' g_1^2(\tau)$$
(2.5)

$$g_1(\tau) = \int G(\Gamma) \exp(-\Gamma_{(t)}) d\Gamma$$
(2.6)

$$\Gamma = q^2 \tag{2.7}$$

$$q^{2} = \left(4\pi \frac{n_{\circ}}{\lambda}\right) \sin(\frac{\theta}{2}) \tag{2.8}$$

where  $n_o$  is the refractive index of the solvent,  $\lambda$  is the laser wavelength in vacuum,  $\theta$  is the scattering angle, and  $\beta'$  is an instrument alignment-dependent coherence factor. In addition, at infinite dilution the hydrodynamic radii ( $R_h$ ) can be obtained from Stokes–Einstein equation.

$$D = k_B T / 6\pi \eta R_h \tag{2.9}$$

where *T* is the solution temperature,  $k_B$  is the Boltzmann constant, and  $\eta$  is the solution viscosity. <sup>12</sup> A classic diagram of DLS process is shown in **Figure 2.5**.



Figure 2.5: An example of dynamic light scattering diagram

#### 2.4 Electrochemical techniques

Electrochemical techniques are analytical techniques that use a measurement of potential, current, or charge to determine an analyte's concentration or to characterize an analyte's chemical reactivity. An electrochemical reaction is a heterogeneous reaction which involves the transfer of charge, usually electrons between an electrode (solid phase) and the ions or molecules of an electrolyte (liquid phase) in an electrochemical cell. At the anode, the oxidation occurs where the electrons are transferred from the ions or molecules in solution to the electrode (electrons lost) whilst at the cathode the electrons are transferred from electrons the ions or molecules (electrons are transferred from electrons the ions or molecules (electrons are transferred from electrons are transferred from electrons the ions or molecules (electrons are transferred from electrons the ions or molecules (electrons lost) whilst at the cathode the electrons are transferred from electrode to the ions or molecules (electron gain) and therefore the species there are reduced.

#### 2.4.1 Cyclic voltammetry (CV)

Cyclic voltammetry is an electrochemical technique used to study redox reactions. It can be used to obtain both qualitative and quantitative information about a redox process. The potential at which a redox process occurs provides information about the thermodynamics of redox reaction whereas the current provides information about the kinetics of heterogeneous electron transfer and the rate of mass transfer. The technique of cyclic voltammetry applies a ramped potential waveform to a working electrode and measures the current that flows through the circuit. The potential of the working electrode is measured against a reference electrode through which negligible current flows.

In cyclic voltammetry, a triangular waveform is linearly formed by applying an electrode potential with relevance to time, as shown in **Figure 2.6**. The plot occurs during the

switching potentials, where the working electrode potential sweeps between two limits, from  $E_1$  to  $E_2$ ; the scan direction of working electrode potential is then reversed to the starting point,  $E_1$ . Then, the currents of the oxidation and reduction peaks are quantified in the potentiostat from consequence applied potential between the working electrode and the counter electrode.

Depending upon the required results, a single, full cycle or multiple cycles can be employed. Thus the scan rate ( $V s^{-1}$ ) controls the experimental timescale. The driving force for electrochemical reactions can be supplied from the potential (equation 2.8).

$$\Delta G = -nFE \tag{2.10}$$

In the cyclic voltammetry, the redox-active species can be in both surface and solutions. The integral of the current under the peak as a function of the time is used to determine the total charge passed, which represents to the amount of electroactive species formed.



*Figure 2.6:* A typical cyclic voltammogram for potential against time in a CV experiment.

Different factors can impact on the current and the kinetics of the electrode reaction.

For instance, rate of mass transport across the electrode/solution interface ,speed of electron transfer across the electrode surface, interaction on the surface ca. electrodeposition, adsorption, or desorption and The kinetic type of the chemical reaction (heterogeneous /homogenous rate constant).

In solutions reactions, the characterisation of the electrochemical responses in a cyclic voltammogram can be identified depending on the system (i.e. reversible, irreversible and quasi-reversible).

**Figure 2.7a** illustrates a cyclic voltammogram for a redox couples. In the beginning, no current is developed due to applied potential insufficient to induce electron transfer.

At E = -0.1 V, current starts to develop, which arises from the oxidation reaction at the electrode (faradaic current). Then, the scan is rapidly increased in current until the oxidant concentration gets smaller and smaller, ultimately causing the peak maximum.

Following that, mass transfer to the electrode from the electrolyte is relatively same in comparison with the rate of consumption, and here the current response in the voltammogram is controlled by diffusion (concentration gradient). Analogous behaviour in the opposite direction occurred due to reduced species (*Red*) at the electrode surface.<sup>13, 14</sup>

For reversible solution reactions, diffusion controlled systems, the current peak increases directly with increasing concentration, and hence is proportional to the square root of the scan rate ( $i_p \propto v^{1/2}$ ). The ratio of the redox couple peak currents is unity ( $-i_p$ ,  $_c / i_{p,a} = 1$ ), as showed in **Figure 2.7**.



*Figure 2.7:* A typical cyclic voltammogram for a) reversible redox process b) the voltammogram for irreversible and quasi-reversible systems

The position of the potential voltage for the redox process,  $E^{o}$ , between the oxidation and reduction current peaks is:

$$E^{\circ} = (E_{p,} + E_{p,}) / 2 \tag{2.11}$$

While, the separation between the peak potentials,  $\Delta E_p$ , is described by the following equation:

$$\Delta E_P = E_{p,} - E_{P,} = (0.059/n) V \tag{2.12}$$

The peak potential for the reverse and forward scans is not dependent on scan rate, but the quantities of the peak currents for both scans is dependent on the sweep rate. The electrochemical reversible systems are controlled by the diffusional control mechanism in the case of the rate of electron transfer being faster than mass transport of the redox species, as well as the redox system maintaining equilibrium during the potential scan. The concentration of the reactants and the resultants at the electrode surface can be calculated using the Nernst equation:

$$E = E^{\circ} + RTnF \ln [Ox]^{\circ} / [Red]^{\circ}$$
(2.13)

Here,  $E^{\circ}$  is standard electrode potential, <sup>150</sup> and [Red]<sup>o</sup> are the formal concentrations of oxidised and reduced materials, respectively, *n* is the number of electrons for the electroactive species in redox reaction, and *F* is the Faraday Constant.

In the irreversible solutions reactions, the Nernst equation cannot be obeyed due to the rate of the electron transfer reaction being slow relative to the mass transport reaction, in this case, the peak current  $i_p$  (equation 2.13) keeps directly proportional as a function of the concentration of species in the bulk and the square root of the scan rate ( $i_p \propto v^{1/2}$ ). While, the peak potential shift grow into large with increasing scan rate (hysteresis).<sup>16, 17</sup>

$$i_p = 2.99 \times 10^5 n \,(\alpha n_a)^{1/2} \,ACD^{1/2} v^{1/2} \tag{2.14}$$

Where, ip is the peak current, n is the number of electron involved in the heterogeneous chemical reaction, C is the concentration of electrochemical active species, D is the diffusion coefficient and v is the scan rate.

Electrochemical reversibility can be decided in terms of the following cases:

$k_o \gg m_T$	reversible electrochemical	reaction
		reaction

 $k_o \ll m_T$  irreversible electrochemical reaction

Or one can determine in terms of the following values:

$$k_o \ge 0.3 \ v^{1/2}$$
 (Reversible)

  $0.3 \ v^{1/2} \ge k_o \ge 2 \times 10^{-5} \ v^{1/2} cm \ s^{-1}$ 
 (Quasireversible)

  $ko \le 2 \times 10^{-5} \ v^{1/2}$ 
 (Irreversible)

In the surface, two processes can occur at the electrode. First, the non-Faradic process which comprises no charge transferring at the solution electrode interface. This results from adsorption and desorption, or even accumulation of charge on the electrode surface. The non-Faradaic process can be seen as the capacitive current. Second, the Faradaic current is caused by charge (*i.e.* electron) transfer through solution electrode interface. This results in oxidation and reduction of species at the electrode surface.<sup>8 13, 18</sup> The integral of the current under the peak as a function of the time is used to determine the total charge passed, which represents to the amount of electroactive species formed. As the time is known, the charge Q (C) can be calculated form equation (2.15).

$$Q = \int_0^t i \, dt \tag{2.15}$$

From the charge value, the surface coverage ( $\Gamma$ ) of any deposited product for example polymer material can be measured by the application of Faraday's law with the equation (2.13):

$$\Gamma = Q / nFA \tag{2.16}$$

Q is the quantity of charge passed through the redox reaction and A is the electrode area (cm<sup>2</sup>) of the polymer deposit on the substrate and F is the Faraday Constant (96485 C mol<sup>-1</sup>) and n is the number of electrons lost per molecule of aniline as example to form the emeraldine salt.

All electrochemical experiments in this study were recorded using an Autolab Type III potentiostat with GPES software. These were carried out in three electrode mode using a (Pt working electrode (WE), a Ag wire with 0.1 M AgCl solution to made the glass reference electrode (RE) and Pt flag counter electrode (CE). The Pt disc working electrode had a surface area of  $1.963 \times 10^{-3} \text{ cm}^2$  was polished before each experiment using an alumina paste down to 0.3 µm, washed with deionised water and sonicated in deionised water for 2 min.

In chapter 5, the polymerisation of aniline were investigated to understand the proton transfer mechanism in DESs by using the cyclic voltammetry, where, PANI films were electrically polymerised from 0.2 mol dm<sup>-3</sup> aniline in DESs containing 1 M  $H_2SO_4$ . The electrode was potentiometrically cycled over the potential range from 0.0 to 1.2 V at a

scan rate of 200 mV s<sup>-1</sup> for 25 scans. The background electrolyte contained of 1 M H<sub>2</sub>SO<sub>4</sub> in 2 EG : 1 ChCl, 2 glycerol : 1 ChCl and 2 urea : 1 ChCl , except for the 1 malonic acid : 1 ChCl and 1 oxalic acid : 1 ChCl solvents without addition of H<sub>2</sub>SO<sub>4</sub>. All experiments were performed at  $(20 \pm 2)$  °C.

#### 2.4.2 Aqueous pH probe electrode

A Jenway pH electrode 3510 module number 924 005 was used as the aqueous pH electrode without modification. These experiments were run at  $25 \pm 2$  °C using the voltage setting to measure the cell potential. This electrode consists of an Ag wire, saturated AgCl with concentration around (0.013 mM) and saturated potassium chloride (4 M). The electrode has three different pH buffers solutions which are used after each measurement in aqueous tested samples to obtain more accuracy measurements. <sup>19</sup> However, in DES media, a protocol was developed to ensure that the measured cell potential was stable and reproducible. To understand the stability of the electrode and the reliability of the cell's potential measurements, three protocols were tested to treat the glass electrode between measurements. It was firstly dried on absorbent paper between measurements to physically remove the analyte solution from the previous measurement prior to re-use. Then, the electrode was used in a classical aqueous pH buffer solutions before being dried with absorbent paper. Finally, the electrode was washed in a solution of 2 EG: 1 ChCl containing 2 mol kg<sup>-1</sup> NaCl prior to reuse.

This process is essential to allow for exchange of hydrogen ions between the protons in the inner of the glass and external solution. In this case, the difference of ion exchanges in two sides of the membrane is determined by the expression which produces a potential.<sup>20, 21</sup>

$$E = K + \left(\frac{RT}{F}\right) \ln(H_{inner}^{+}) / (H_{outer}^{+})$$
(2.17)

For these protocols, 9 different concentrations different were prepared of triflic acid or methyl amine in 2 EG: 1 ChCl approximately corresponding to pHs of 1 to 9. For each solution, 5 replicate measurements were made and the average and standard deviations of the cell potential were calculated. A schematic diagram of the electrode configuration is shown in **Figure 2.8**.



Figure 2.8: An example of glass pH electrode.

#### 2.4.3 Chronopotentiometry

Chronoamperometry is an electroanalytical technique which measures the cell potential as a function of time at a given current. In Chronopotentiometry, a constant current, is caused to flow between two electrodes; the potential of one electrode is monitored as a function of time with respect to a suitable reference electrode.<sup>22, 23</sup> Chronoamperometry was used in this study to investigate the cell potential for the non-aqueous pH electrodes. The liquid junction potentials were measured by chronopotentiometry using an Autolab Type III potentiostat with GPES software. In this study the potential of the open circuit was measured when no current flowed through the system and the potential was measured for 250s and an average was take once the readings had reached equilibrium.

The cell set up involved having two reference electrode couples separated from the analyte by a porous vycor glass frit 6mm on side and an 8 mm thick frit on the other. The general cell diagram is defined by

Ag|AgCl ( $a = 0.01 \text{ mol } \text{kg}^{-1}$ ) (DES1) || Analyte ||AgCl ( $a = 0.01 \text{ mol } \text{kg}^{-1}$ ) (DES2)|Ag

The reference electrodes on either side of the liquid junction were a silver electrode in contact with 0.01 mol kg<sup>-1</sup> AgCl dissolved in one of four DESs: 2 EG : 1 ChCl, 2 glycerol : 1 ChCl,

2 urea : 1 ChCl, 2 oxalic acid : 1 ChCl. The diagram of the cell used of the two reference electrodes system can be shown in **Figure 2.9**.



*Figure 2.9:* Cell configuration for chronopotentiometry experiments to measure cell potential.

## **2.5 References**

- P. Gabbott, *Principles and applications of thermal analysis*, John Wiley & Sons, 2008.
- 2. R. Bottom, *Principles and applications of thermal analysis*, 2008, **3**, 87-118.
- 3. D. L. Pavia, G. M. Lampman, G. S. Kriz and J. A. Vyvyan, *Introduction to spectroscopy*, Cengage Learning, 2008.
- 4. H.-H. Perkampus and H.-C. Grinter, *UV-VIS Spectroscopy and its Applications*, Springer, 1992.
- 5. T. Owen, *Fundamentals of UV-visible Spectroscopy: A Primer*, Agilent Technologies, 2000.
- 6. D. Skoog, D. West, F. Holler and S. Crouch, *Fundamentals of analytical chemistry*, Cengage Learning, California, USA, 2013.
- 7. A. Primer, *Copyright Hewlett-Packard Company, Hewlett-Packard publication*, 1996.
- J. Wang, Analytical electrochemistry, John Wiley & Sons, United States of America, 2006.

- 9. D. A. Skoog, F. J. Holler and S. R. Crouch, *Principles of instrumental analysis*, Cengage learning, 2017.
- 10. R. A. Schoonheydt, *Chemical Society Reviews*, 2010, **39**, 5051-5066.
- 11. W. Goldburg, American Journal of Physics, 1999, 67, 1152-1160.
- 12. B. J. Berne and R. Pecora, *Dynamic light scattering: with applications to chemistry, biology, and physics*, Courier Corporation, 2000.
- 13. D. A. MacInnes, *Principles of electrochemistry*, Reinhold Publishing Corporation; New York, United States of America, 1939.
- 14. R. S. Nicholson, Analytical chemistry, 1965, 37, 1351-1355.
- K. Marsh, J. Boxall and R. Lichtenthaler, *Fluid Phase Equilibria*, 2004, 219, 93-98.
- K. Izutsu, *Electrochemistry in nonaqueous solutions*, John Wiley & Sons, Weinheim, 2009.
- 17. E. Gileadi and E. Gileadi, *Physical electrochemistry: fundamentals, techniques and applications*, 2011.
- 18. B. E. Conway, *Electrochemical supercapacitors: scientific fundamentals and technological applications*, Springer Science & Business Media, 2013.
- P. Gameiro, S. Reis, J. Lima and B. de Castro, *Analytica chimica acta*, 2000, 405, 167-172.
- 20. R. Chang, *Physical chemistry for the chemical and biological sciences*, University Science Books, 2000.
- J. Koryta, J. Dvořák and L. Kavan, *Principles of electrochemistry*, John Wiley & Sons Inc, New york, 1993.
- 22. R. K. Jain, H. C. Gaur and B. J. Welch, *Journal of Electroanalytical Chemistry* and Interfacial Electrochemistry, 1977, **79**, 211-236.
- 23. J. J. Lingane, Analyst, 1966, **91**, 1-9.

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## Chapter 3: Spectroscopic determination of pH / pKa

#### Chapter three: Spectroscopic determination of pH / pKa

#### 3.1 Methodology for spectroscopic determination of pH / pKa

The dependence of proton donating and ionization properties of liquids is related to the structure of molecules and the nucleophilicity of the component ions in the media.<sup>1</sup> The fundamental aspect of Brønsted acidity in ionic liquids systems is dominated by electron and proton transfer but the activity of protons, in a liquid which is essentially a buffer, is poorly understood.

The ability to tailor the acidity or basicity of an ionic liquid has been demonstrated with whole classes of liquids such as acidic ionic liquids, protonic ionic liquids, basic ionic liquids and zwitterionic liquids, however, comparatively little is understood about how their acidity compares with aqueous solutions.<sup>2, 3</sup>

Within this class of solvents, Deep Eutectic Solvents (DES) were first reported in 2003<sup>4</sup> and are interesting as they can be tailored by the functionality of either the quaternary ammonium salt or the hydrogen bond donor.<sup>5</sup> For example the quaternary ammonium salt can have an acidic functionality e.g. betaine hydrochloride HOOCCH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>HCl or the hydrogen bond donor can be a carboxylic acid e.g. oxalic or citric acid. These liquids are not only more air and moisture stable compared to conventional ionic liquids e.g. chloroaluminate salts, but they can also be prepared at low cost and with high purity.<sup>6</sup>

Research has focused on the use of DESs in many application such as synthesis and metal oxide dissolution<sup>7</sup> where proton activity is extremely important. For metal oxides the solubility has been found to be higher in the acid-based DESs but the solubility is less in most cases compared to 1 M HCl. It is therefore important to get an understanding of the relative acidity of DESs compared with aqueous solutions. <sup>8,9</sup>

Recently, Germani *et al.* prepared halogen-free Brønsted acidic deep eutectic solvents by mixing new quaternary ammonium methanesulfonate salts with p-toluenesulfonic acid (PTSA). They used them as dual solvent-catalysts for esterification of several carboxylic acids with different alcohols with a reagent molar ratio of 1:1.<sup>7, 10-12</sup> Some studies have found that proton activity, and hydrogen bond interactions of DESs played significant roles in modulating species reactivity and mass transport properties governing the genesis of nanostructure when using DESs as designer solvents to produce well-defined nanomaterials.<sup>12</sup> DES has also been used as reaction media for a variety of reactions.<sup>13</sup>

For some of these, the choice of DES can simplify product separation at the end of the reaction.<sup>14, 15</sup>

#### 3.1.2 General description of indicator method

The activity of protons in ionic liquids has received some attention in recent years, and some qualitative methods for estimating acidity have been suggested. Most of methods have used colourimetric indicators and determined qualitative colour changes as an indication of pH.<sup>16</sup>

For this methodology, the organic indicator dye, bromophenol blue was dissolved in water. A significant, reversible colour change occurs in the pH range from 3.0 to 4.6;<sup>17</sup> solutions are yellow when acidic and blue-violet when basic. Bromophenol blue is closely related to the phenolphthalein indicator. The conjugation of the molecules is related to the electron transfer between the  $\pi$  molecular orbitals.<sup>18</sup> **Figure 3.1** shows the protonated and deprotonated forms of bromophenol blue. The different degrees of conjugation in the two forms results in the absorbance of visible light in different parts of the spectrum resulting in the two peaks shown in **Figure 3.2**. In acidic solutions, the sp<sup>3</sup> hybridised carbon between the three aromatic rings isolates the conjugation whereas in less acidic solutions (pH > 5) the central carbon is *sp*<sup>2</sup> hybridised and extends conjugation across the whole molecule. Extending the degree of conjugation should move the absorbance maximum to longer wavelengths as confirmed in Figure 3.4.



*Figure 3.1*: *The molecular modes for bromophenol blue a) acidic form b) basic form.*<sup>10</sup>

The proportion of indicator molecules in the protonated and deprotonated forms can be used to quantify the relative acidity of the solutions. The aim behind this section is to develop a method to *quantify* the pH of a solution and the pKa of an acid using these pH

indicator solutes. These indicators are commonly used to determine end points through titration but the ubiquitous use of pH electrodes mean that the old method of quantifying pH is seldom used today. This section will firstly compare the method of quantifying pH using absorbance values for aqueous solutions and compare the data obtained with that from a pH electrode. The same method will then be used to obtain the values in deep eutectic solvents and ionic liquids. This section will deal primarily with determining the pKa of simple organic acids and seeing how they compare with values in aqueous solutions. The hypothesis is that the anion of the IL or DES will generally control the pKa of the acid and the study will attempt to construct a relative acidity scale for different ILs and DESs.

#### 3.1.3 Validation of indicator method in pure water

Initial studies of the extent of protonation indicator molecule have been carried out to validate a UV spectrometric method in water media. Since most of the acids studied in this section are relatively weak carboxylic acids it was decided to choose an indictor which was active in the pH range 3 to 4. For this reason, bromophenol blue was chosen initially as an indicator.

This method uses indicator molecules which have different proton affinities which can be quantified through their acid dissociation constants  $pK_{in}$ . Where, it is important to develop a method which accurately determines  $pK_{In}$  as all subsequent measurements depend on its value.

A Bromophenol blue indicator solution was split into 3 equal parts; one sample was used in a potassium hydrogen phthalate/ hydrochloric acid buffer solution at pH= 4, one was made up to (0.1 mol kg<sup>-1</sup> HCl) hydrochloric acid solution, and the third to (0.1 mol kg<sup>-1</sup> NaOH) sodium hydroxide. These latter two converted the indicator to the fully protonated and deprotonated forms respectively. The  $pK_{in}$  of solution has been calculated based on the relative peak ratios. In each solvent the concentration of bromophenol blue was 6.60 x10<sup>-5</sup> mol kg<sup>-1</sup>. The UV-vis spectra of the solutions were measured and are shown in **Figure 3.2.** 



*Figure 3.2:* The absorption spectra of bromophenol blue with (0.1 M HCl, 0.1M NaOH, Water).

It can be seen that the absorbance maximum of the deprotonated BPB occurred at approximately 592 nm whereas the protonated formed had an absorbance maximum at 438 nm. Different concentrations of BPB were used to determine the extinction coefficient of both the protonated and deprotonated forms and these were used to calculate the concentration of the different forms of protonated and deprotonated forms. In all cases the Beer Lambert law was found to be valid across the concentration ranges studied.

From **Figure 3.2** the *pK*<sub>*In*</sub> has been calculated by measuring the ratio of absorbances for the protonated and deprotonated forms of the indicator.<sup>19</sup> Using this method the *pK*<sub>*In*</sub> for BPB was found to be 3.99 with relative standard error (S.D  $\pm$  0.05). This compared well with the literature value of 4.00.<sup>17</sup>

**Figure 3.3** shows the effect of adding triflic acid to an aqueous solution of BPB. Triflic acid was chosen as it has a large negative pKa (-14.7) which means it is fully dissociated in most media. The fact that it is a liquid and available without a significant water content meant that it could be used in ILs and DESs without worrying about solubility or contamination of water.



Figure 3.3: Shows different concentrations of triflic acid in water with B.P.B.

The data showed that as the concentration of triflic acid is increased there is an increase in the absorbance of the peak at 438 nm and an associated decrease in the intensity of the peak at 592 nm which causes the solution to change colour from purple to yellow after the addition of higher concentrations of the acid. Triflic acid is a super acid and fully protonates the indicator and there is no isotropic point observed in the solution. The same prepared solutions were tested with pH electrode to test the reliability of the measurements with the above method. The values obtained from both the spectroscopic and electrochemical cell are listed in **Table 3.1** below.

Concentration of HOTf/ mM	pH <sub>Theoretical</sub> .	pH <sub>prob.</sub>	pH <sub>UV-Vis</sub>
0.200	3.69	$3.67\pm0.024$	$3.65\pm0.023$
0.250	3.60	$3.61\pm0.021$	$3.57\pm0.011$
0.320	3.49	$3.48\pm0.013$	$3.47\pm0.043$
0.401	3.39	$3.37\pm0.023$	$3.36\pm0.038$
0.501	3.30	$3.31\pm0.019$	$3.30\pm0.034$

*Table 3.1*: comparison of pH values for aqueous triflic acid in obtained using the bromophenol blue indicator and an electrochemical pH probe.

The pH values for all of the triflic acid solutions were relatively similar using both methods (indicator and pH electrode). The values were also compared with the theoretical
values calculated from  $pH = -log_{10} [H^+]$  assuming that the acid was fully dissociated. The error bars for the two methods taken as the standard deviation of 5 measurements are comparable between the two methods. Both measured sets of data are also very close to the theoretical value which falls within the error bar of the measurement.

The spectroscopic method is also slightly complicated because the extinction coefficient of the protonated and deprotonated forms need to be considered. The molar extinction coefficient has been calculated for the mixture BPB with HOTf at both peaks 438 and 592 nm. The molar absorptivity increases as the concentration of indicators increases. The extinction coefficient and relative standard errors were found (115618 M<sup>-1</sup> cm<sup>-1</sup>  $\pm$  9.65%), (114270 M<sup>-1</sup> cm<sup>-1</sup>  $\pm$  10.21%) at 438 and 592 nm respectively. The experimental results are in the appendix section.

To determine the accuracy of the method with a weak acid, oxalic acid ( $pKa_1 = 1.23$ ) was chosen as an example as it is commonly used as a HBD in making the DES Oxaline, a 1:1 molar mixture of oxalic acid and choline chloride. **Figure 3.4** shows how the addition of oxalic acid changes the absorbance spectrum of BPB in water.



*Figure 3.4:* absorbance of aqueous BPB solutions with different concentrations of oxalic acid.

This method provides a good route to measure hydrogen ion activities in the solutions. The pH values in aqueous systems are also examined for same solutions in the above **Figure 3.4** by using a pH electrode; the purpose of these measurements is to attain the pH values of the mixtures with UV-Vis spectrophotometry method. The comparison can be seen in **Table 3.2** below.

Concentration Oxalic acid/ mM	pH <sub>Theoretical</sub> .	pH <sub>prob.</sub>	$pH_{\rm UV-Vis}$
2.95 x 10 <sup>-4</sup>	3.85	$3.80\pm0.013$	$3.80\pm0.23$
2.46 x 10 <sup>-4</sup>	3.91	$3.88\pm0.032$	$3.89\pm0.13$
1.95 x 10 <sup>-4</sup>	3.96	$3.98\pm0.018$	$3.97\pm0.20$
1.47 x 10 <sup>-4</sup>	4.02	$4.02\pm0.021$	$4.04\pm0.20$

 Table 3.2: Comparison of pH values for aqueous oxalic acid solutions using the indicator method and the pH electrode.

**Table 3.2** shows that both methods provide both an accurate and reproducible method by which to compare the pH of a weak acid and in all cases the values determined were within experimental error of the theoretical value.

# 3.1.4 Validation of the indicator method in DESs

The acidity and coordination properties of a non-protonic ionic liquid are mainly determined by the nature of its anion. Many chemical reactions of acidic ionic liquids indicate that an increase of the anion's Brønsted acidity improves its catalytic activity.<sup>10, 20, 21</sup> Some PILs are considered as good catalysis with many reports professing advantages over aqueous systems. One of these advantages is that some reactions require no organic solvent e.g. in the production in high yields of esters, the product can simply be separated by decantation. The PILs can then be reused after the removal of water.<sup>22</sup> As the majority of those acidic reactions are dependent on the *pKa* of a molecule, this parameter is important to predict reaction products and responses to understand the reaction mechanism.<sup>19</sup> Therefore, the knowledge of the *pKa* are useful to compare basicity or acid strength in ILs by means of the value of their equilibrium constant. The *pKa* values some times are enough to understand the acid/ base properties of liquids.

In this section of work, the *pH* was determined by measuring the ratio of absorbances for the protonated and deprotonated forms of the indicator.<sup>19</sup> Equation (3.2) has been applied but the issue with this approach is the unknown value of  $pK_{In}$  in an ionic medium. The  $pK_{In}$  can be determined by titrating a solution of the indicator with an acid and measuring the relative absorbances of the protonated and deprotonated indicator. At the mid-point where the absorbances are the same,  $pK_{In} = pH$ . The initial study to quantify the  $pK_{In}$  was carried out in a mixture of 2 ethylene glycol: 1 choline chloride (2 EG: 1 ChCl). This deep eutectic solvent was chosen because of previous studies on electrode potentials of simple redox couples. The cell potential of a standard hydrogen electrode (Pt|  $H_2$  | $H^+_{DES}$ ) was measured as a function of acid molality.<sup>23</sup> Triflic acid was chosen as the acid as it was thought as the most likely to fully dissociate in an ionic medium ( $pK_a$  -14.7 in aqueous solution).<sup>24</sup> It was found that over 6 orders of magnitude concentration the  $H_2/H^+$  redox couple exhibited Nernstian behaviour up to a molality of 1 mol kg<sup>-1</sup>. It was assumed from this that the acid was effectively totally dissociated over this concentration range and behaved as an ideal solution.

Another factor that needs to be considered in the indicator method is the extinction coefficient of the protonated and deprotonated forms of the indicator molecule. This complicates the process slightly because it changes in each ionic liquid and DES, although in practice the differences are not large. For all of the data presented in this chapter the change in extinction coefficient was taken into account. In this study for each ILs and DESs was measured for the protonated and deprotonated forms using 4 different concentrations of bromophenol blue. Extinction coefficients data are given in the appendix section.

Figure 3.5 shows solutions of bromophenol blue in 2 EG: 1 ChCl containing different concentrations of triflic acid at 20 °C. The molalities of triflic acid ranged from  $10^{-2}$  to  $10^{-8}$  mol kg<sup>-1</sup> and it can be seen that the indicator is largely protonated at the higher concentration and partially dissociated at the lower concentration.



*Figure 3.5:* solutions of bromophenol blue in 2 EG: 1 ChCl containing different molalities of triflic acid ranged from (l to r)  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$  and  $10^{-8}$  mol kg<sup>-1</sup>

**Figure 3.6.a** shows the absorbance spectra of 9 solutions of different triflic acid molalities and **Figure 3.6.b** shows the absorbance of the deprotonated signal at 602 nm as a function of log concentration. It is not possible to find an absolute pH in any liquid other than water and so a comparative scale will be made using the assumption that the triflic acid is fully dissociated and the molality can be converted to a relative pH using the same method and assumption that would be used in water *i.e.*  $pH = -\log_{10} a_{H^+}$ .

Using the assumption of MacFarlane in equation (3.2) this appears to be a reasonable approximation.<sup>2</sup>

$$H_{-} = pK(HI) + \log_{10} ([I]/[HI])$$
(3.2)

**Figure 3.6.b** shows a plot of absorbance *vs* effective pH on a molality scale assuming complete dissociation of the acid. This is effectively a titration curve for the indicator and the  $pK_{In}$  is the mid-point of the absorbance – concentration curve. This same approach of using a strong acid and assuming full dissociation has been used by Kanzaki *et al.* for the protic ionic liquid ethylammonium nitrate.<sup>6</sup> The  $pK_{In}$  of the BPB is  $3.74 \pm 0.012$  in 2 EG: 1 ChCl which is slightly lower than that in water  $(4.0)^{25}$  which would be logical as the liquid will be a slightly weaker base than water.



Figure 3.6: (a) The absorbance of spectra of different BPB with different concentrations of triflic acid in 2 EG: 1 ChCl (b) absorbance of the peak at 602 nm as a function of relative pH.

In the same context, a study by Matthews *et al.* measured *pKa* values of acids in DMSO using the same indicator method. The study compared the values obtained for different acids both potentiometrically and with the indicator method. It established the method of determining relative equilibrium acidities of carboxylic acids in DMSO.<sup>26</sup> They highlighted that the measurements found using the indicator method in DMSO were in good agreement with those found potentiometrically.

## **3.2 Acidity in DESs**

## **3.2.1 Effect of the anion**

In DESs the anion content can be varied independently of the HBD. This will in effect change the acidity of the liquid since in the case of ChCl this is effectively acting as the Lewis or Brønsted base in the system. The effect of the anion of the DES can be determined by working with mixtures of HBDs and QASs in different molar ratios. It would be expected that increasing the amount of QAS would make the liquid more basic as the chloride will act as the main base in the liquid. It may also be expected that the HBD may effect the pH of the liquid to some extent as it will affect the activity of the chloride ions in solution through the strength of the interaction between the quaternary ammonium salt and the hydrogen bond donor.

To determine the strengths of acids in DESs the  $pK_{In}$  values of BPB need to be determined in each of the DESs. This was done by the same method described above. As an example, Figure 3.9 shows the proton dependent UV-vis spectra of BPB with 2 glycerol: 1 choline chloride. While triflic acid can be used to protonate the indicator KOH cannot be used as the base but it was found that methylamine acts as a suitably strong base to deprotonate the indicator.<sup>27</sup> By this method the  $pK_{In}$  was found to be 3.89 ± 0.28 in 2 glycerol: 1 choline chloride. This is a smaller value than in water which would seem logical as the chloride is not as good a base as water.

**Table 3.3** shows the  $pK_{In}$  values for BPB in different ethylene glycol (EG): choline chloride molar mixtures. It can be seen that the more chloride that is added the less acidic the liquid becomes. These were chosen to exemplify how the different structural in particular the hydrogen bond donor in different DESs.

<b>Table 3.3</b> : pK <sub>In</sub> for bromophenol blue in some DESs					
Solvent	Water	2 EG: 1 ChCl	3 EG: 1ChCl	4 EG: 1ChCl	ethylene glycol
pK <sub>In</sub>	$3.99\pm0.05$	$3.61 \pm 0.02$	$3.55 \pm 0.04$	3.39 ±0.13	$3.23\pm0.09$

The data in **Table 3.3** is logical because the chloride anions are relatively basic compared to the ethylene glycol molecules. **Figure 3.7** shows the correlation between  $pK_{In}$  and the mole fraction of ChCl in the mixture. A good correlation is obtained between the two parameters as might be expected.



Figure 3.7: Correlation between pK<sub>In</sub> and mole fraction of ChCl

While the effect of the salt content is relatively logical, it is interesting to compare the effect of the HBD. The DES 2 glycerol: 1ChCl has a  $pK_{In}$  value of  $3.89 \pm 0.28$  compared to  $3.61 \pm 0.02$  for 2 EG: 1 ChCl. Even though both contains the same chloride

concentration there is a difference of almost 0.3 in the  $pK_{In}$  value. It can be seen that the HBD does have an effect on the acidity of the DES.

Abbott et al. investigated the effect of ChCl concentration on liquid density and viscosity. It was shown that increasing the ChCl content in the mixture decreases the viscosity of glycerol whereas in EG ChCl increases the viscosity with increasing content. From this it was concluded that the interaction between the chloride and glycerol is stronger than between the chloride and EG.<sup>28</sup> Abbott et al. also previously showed that the protons in 2 EG: 1 ChCl are more labile than in 2 glycerol: 1ChCl despite the similarities in their *pKa* values in water (ethylene glycol (14.22) and glycerol (14.15)).<sup>29</sup> Clearly the HBDs do not behave in the same way in DESs as they do in water.

#### 3.2.2 pH measurements in DESs and ILs

To determine the pH value in neat DESs and ILs suitable indicators should be selected to measure the acidity. To find the suitable indicator approximate values of pH are necessary and these were determined using universal indicator paper. **Figure 3.8** shows 9 ILs and DESs with indicator paper. The liquids are arranged in order of increasing pH. As expected Oxaline is the most acidic while Reline is the most basic liquid.

**Figure 3.8** shows that Oxaline, Maline, Ciline and EmimSO<sub>4</sub> are all in the range 1 - 2. Bmim BF<sub>4</sub>, Ethaline, Glyceline and Emim OAc are in the range 6-7 whereas Reline is slightly more basic at approximately 8.



Figure 3.8: The range of pH in different ILs and DESs by using universal indicator.

To determine the pH of the neutral and basic ILs and DESs bromothymol blue was chosen as an indicator. It has a pK<sub>In</sub> of 7.1. The absorbance method as described above was used and the value of bromothymol blue in water was found  $6.99 \pm 0.011$  confirming the validity of the method. The *pK<sub>In</sub>* of bromothymol blue was used to measure the acidity of basic liquids the *pK<sub>In</sub>* was found around  $6.36 \pm 0.056$  in Ethaline while in Emim OAc was found around  $7.03 \pm 0.01$ . The same above indicator was also used in Reline which found around  $7.32 \pm 0.036$ .

**Figure 3.9.b** shows a plot of absorbance *vs* effective pH on a molality scale assuming complete dissociation of the acid and base used. This is effectively a titration curve for the indicator and the  $pK_{In}$  is the mid-point of the absorbance – concentration curve also used as shown in **Figure 3.9.a**. **Figure 3.9** also shows the structures of the protonated and deprotonated forms of bromothymol blue.



Figure 3.9: (a) The absorbance of spectra of different Bromothymol blue with different concentrations of triflic acid in 2 EG: 1 ChCl (b) absorbance of the peak at 619 nm as a function of relative pH.

The same approach was used for the acidic DESs and ILs. In this case methyl violet 2B was used to measure the pH of Oxaline, Maline, Ciline and Emim HSO<sub>4</sub>. In water it changes from yellow at pH < 1 to violet at pH > 3.2. Data for the standardisation of this indicator are shown in the appendix. In **figure 3.9** it would be expected an observation of isosbestic between the protonated and deprotonated species in all different pHs prepared.

However, it was found a difference of the absorbance of the reaction mixture for Bromothymol blue at pH over 5 this happen due to the error weight indicator during the preparation which leads to cause a slightly deviation of isosbestic point between the protonated and deprotonated in Bromothymol blue indicator as shown in **figure 3.9**.

**Table 3.4** shows the pH values determined using the spectroscopic method. The values tie in well with those observed from the indicator papers. The values are also in an approximate accord with what would be expected from the behaviour of the pure HBD.

Given that Oxaline contains approximately 4.34 mol kg<sup>-1</sup> oxalic acid and in water Oxalic acid has a  $pK_a$  of 1.27 ( $K_a = 5.9 \times 10^{-2}$ ) since

$$K_a = [H^+][A^-]/[HA]$$
 (3.3)

then assuming that  $[H^+] = [A^-]$  the pH of an aqueous solution of that molality would be approximately 0.59. As shown in the next section, the *pK<sub>a</sub>* of organic acids in water is about 0.5 *pK<sub>a</sub>* units lower than that in DESs so this would yield an approximate pH of 1.1 which is what is observed in **Table 3.4**.

For Oxaline if it is assumed that the chloride acts as a buffer then there is an equal molality of chloride to acid so the [A<sup>-</sup>] and [HA] will cancel and  $Ka = [H^+]$  or  $pK_a = pH$  i.e. the pH of acidic DESs can be approximated from the  $pK_a$  values of the HBD and the chloride is just acting as a buffer. The  $pK_a$  values for malonic acid and citric acid are 2.83 and 3.13.

<b>Table 3.4</b> : measurements of pH for various ILs and DESs using different indicatorsbromophenol blue, methyl violet 2B and bromothymol blue				
Liquid	$pK_a$	Type of indicator		
Oxaline	$1.10 \pm 0.012$	Methyl violet 2B		
Maline	$2.49 \pm 0.032$	Methyl violet 2B		
Ciline	$2.33\pm0.16$	Methyl violet 2B		
Emim HSO <sub>4</sub>	$2.74 \pm 0.074$	Methyl violet 2B		
Bmim BF <sub>4</sub>	$3.88 \pm 0.23$	Bromophenol blue		
Ethaline	$5.93 \pm 0.018$	Bromophenol blue		
Glyceline	$6.97\pm0.06$	Bromophenol blue		
Emim OAc	$7.38 \pm 0.14$	Bromothymol blue		
Reline	$8.31\pm0.05$	Bromothymol blue		

#### 3.2.3 *pKa* of weak organic acids in Ethaline *vs*. H<sub>2</sub>O

Once the  $pK_{In}$  values are known in the DESs then the pH of weak acids can be determined using the same method described above. For a given DES, the relative pKa values of organic acids should be related to their values in aqueous solutions since it is just a comparison of the two bases; 55 mol kg<sup>-1</sup> of H<sub>2</sub>O in water and 3.8 mol kg<sup>-1</sup> of chloride in Ethaline. Knowledge of  $pK_{In}$  for BPB in Ethaline allows the calculation of  $pK_a$  for a variety of carboxylic acids in 2 EG: 1 ChCl. The  $pK_a$  values for 10 carboxylic acids are shown in **Figure 3.10**. These acids were chosen to have  $pK_a$  values which should be in the active region for BPB. The molecules are all of a similar size and are a mixture of monoprotic and diprotic acids. It can be seen that a good linear correlation is obtained between the  $pK_a$  values in 2 EG: 1 ChCl and that obtained in water.



*Figure 3.10:* Comparison the average  $pK_a$  values of 9 carboxylic acids in 2 EG: 1 ChCl and water.

The  $pK_a$  values of the carboxylic acids are all approximately 0.5 units higher in Ethaline than in water. The chloride anion is a good Brønsted base although not as good as water.<sup>1</sup> Since the base in Ethaline (Cl<sup>-</sup>) is constant and at a roughly constant concentration, it is not surprising that there is a linear relation between the  $pK_a$  in Ethaline and in water. As discussed above the chloride ions act as a buffer and the concentrations equate to a change of approximately 0.5 pH units. An alternative explanation for differences between  $pK_a$  in Ethaline and water could be due to the activity coefficients in the two liquids.

$$K_{a} = \frac{a_{H+} a_{A-}}{a_{HA}} = \frac{m_{H+} m_{A-}}{m_{HA}} \cdot \frac{y_{H+} y_{A-}}{y_{HA}}$$
(3.5)

A difference of 0.5  $pK_a$  units equals to a 3 fold difference in the activity coefficient term in equation 3.5. Given that Hartley <sup>30</sup> found the activity coefficient for H+ in DES  $\approx$  1 it is less likely that this will be the cause of the disparity in  $K_a$  particularly given the observation that the buffering effect (equation 3.4) correlate almost exactly with observed difference.

The data in **Table 3.3** shows that the difference between the  $pK_{ln}$  values for BPB in water and Ethaline (0.39) is very similar to the offset in the **Figure 3.10**. This is an important observation as it gives a simple method by which to approximate the  $pK_a$  for an acid in an ionic liquid which is to measure the difference in  $pK_{ln}$  values in water and the ionic liquid and add the difference to the aqueous literature value of the  $pK_a$  for an acid.

A recent study by Kanzaki et al. studied the  $pK_a$  of 14 acids in the protonic ionic liquid ethylammonium nitrate (EAN) and found that the  $pK_a$  values were approximately 1 smaller than in water. These results are consistent with what would be expected given the relative basicity of the chloride anion compared to water. It should also be noted that the concentration of base is considerably lower in the DES than in water (chloride concentration in DES is 3.8 mol kg<sup>-1</sup> *c.f.* water concentration which is 55.6 mol kg<sup>-1</sup>).

In **Table 3.5** a comparison of results has been made for the acidity with electrochemical method in aqueous media and literature values.<sup>26</sup> The anion in 2 EG: 1 ChCl is less basic than the OH<sup>-</sup> anion in water. As a consequence it is less effective at deprotonating the carboxylic acids.

The error bars in the  $K_a$  and  $pK_a$  data are mostly of a similar magnitude to those observed using aqueous solutions showing that there is nothing fundamental about the method that is inducing error in the measurements. The only slightly larger errors are associated with citric, malonic and oxalic acids. This could be because these are the diprotic acids and the properties of the second carboxylic acid group could play a factor. This can be seen from the spectra of BPB in the appendix of Chapter 6 where some of the diprotic acids show a shoulder on the absorbance for the protonated form of the indicator.

Carboxylic acids	<i>pKa</i> literature	<i>pKa</i> (water) pH probe	<i>Ka</i> Ethaline Indicator method	<i>pKa</i> Ethaline Indicator
Oxalic acid	1.25	$1.30 \pm 0.013$	$5.0 \times 10^{-3} \pm 3.7 \times 10^{-3}$	$2.29 \pm 0.154$
Malonic acid	2.82	$2.87\pm0.057$	$3.2 \times 10^{-5} \pm 6.8 \times 10^{-6}$	$4.49\pm0.091$
Succinic acid	4.16	$4.19 \pm 0.014$	$4.4 \times 10^{-5} \pm 6.8 \times 10^{-6}$	$4.36\pm0.072$
Citric acid	3.14	$3.11 \pm 0.057$	$2.3 \times 10^{-4} \pm 7.3 \times 10^{-5}$	$3.63 \pm 0.121$
Benzoic acid	4.20	$4.19 \pm 0.011$	$3.2 \times 10^{-5} \pm 1.1 \times 10^{-5}$	$4.50 \pm 0.073$
Lactic acid	3.86	$3.85 \pm 0.025$	$1.2 \times 10^{-4} \pm 1.0 \times 10^{-5}$	$3.93\pm0.030$
Salicylic acid	2.97	$2.96\pm0.002$	$9.1 \times 10^{-4} \pm 2.1 \times 10^{-6}$	$3.03 \pm 0.016$
Acetic acid	4.75	$4.78 \pm 0.032$	$1.3 \times 10^{-5} \pm 1.1 \times 10^{-6}$	$4.90\pm0.036$
Propanoic acid	4.88	$4.85 \pm 0.017$	$6.0 \times 10^{-6} \pm 7.1 \times 10^{-7}$	$5.22 \pm 0.052$
Butanoic acid	4.82	$4.81 \pm 0.007$	$6.5 \times 10^{-6} \pm 2.8 \times 10^{-7}$	$5.18 \pm 0.014$

Table 3.5: Comparison of acidity in 2 EG: 1 ChCl and water solutions

# **3.2.1.** Comparison of $pK_a$ of acids in ILs and DESs

The above method was applied to different types of ILs and DESs to calculate  $pK_{In}$  and the results are shown in **table 3.6**. It can be seen that the  $pK_{In}$  values for BPB are all lower in the ionic liquids than in water which is consistent with the data found for 2 EG: 1 ChCl of the three anions tested acetate was the most basic and triflate the least basic. The  $pK_{In}$  data correlate with the  $pK_a$  values for the corresponding acids of the ionic liquid anions.<sup>2</sup>

	C <sub>4</sub> mimOTf	C4mimBF4	C <sub>2</sub> mimOAc	Water
рК <sub>In (ВРВ)</sub>	3.38 + 0.15	3.84 + 0.10	3.92 + 0.09	4.0
	HOTf	HBF <sub>4</sub>	HOAc	H <sub>2</sub> O
$pK_a^{\text{ref3}}$	<i>c.a.</i> -2.8	-0.44	4.75	14

**Table 3.6**:  $pK_{In}$  for bromophenol blue in some ionic liquids and a comparison of the pKa of the corresponding acid of the ILs anion.

Using the  $pK_{in}$  data in **table 3.3**, the  $pK_a$  values of 4 carboxylic acids; acetic, succinic, lactic and salicylic acid were determined for Emim OAc and Bmim BF<sub>4</sub> and a related DES, 2 glycerol: 1ChCl. MacFarlane used OAc<sup>-</sup> and BF<sub>4</sub><sup>-</sup> salts as examples of weakly basic and basic anions respectively and estimated the  $pK_a$  of the ionic liquids.<sup>2</sup> The BF<sub>4</sub><sup>-</sup> salts are also thought to be acidic due to hydrolysis of the anion by traces of water<sup>31</sup> so it

was thought to be a useful system to quantify and see how the practical  $pK_a$  compares with the predicted value.<sup>2</sup> Figure 3.11 shows the  $pK_a$  of 4 acids; acetic, succinic, lactic and salicylic acid in 4 ionic liquids and DESs compared to the values in water.



*Figure 3.11:* Correlation of  $pK_a$  values of acetic, succinic, lactic and salicylic acid in 4 ionic liquids and DESs compared to the values in water.

It can be seen that the  $pK_a$  values of all the acids are largest in Emim OAc and smallest for Bmim BF<sub>4</sub>. MacFarlane *et al.* predicted that the acids should be less dissociated in Bmim BF<sub>4</sub> than in aqueous solutions due to its moderately weak basicity.<sup>2</sup> The  $pK_a$  values for the acids in Bmim BF<sub>4</sub> are, however, lower than might be expected due to the presence of water which is known to hydrolyses the anion to HF and BF<sub>3</sub> making the solutions more acidic, so this observation should not be surprising. The corresponding  $pK_a$  values in both 2 glycerol: 1ChCl and 2 EG: 1 ChCl are similar which would be expected from the  $pK_{ln}$  values in **Table 3.3**.

It is difficult to remove the presence of all water from the samples so hydrolysis of Bmim  $BF_4$  is not surprising. To show the effect of water on Bmim  $BF_4$  the  $pK_{In}$  was measured with extra water added to the liquid. The initial content in the as supplied material was approximately 0.043 wt% (TG). To this liquid, 1 and 5 wt% water were added and the

 $pK_{In}$  of BPB in the liquids were determined. Without additional water being added the  $pK_{In}$  was  $3.74 \pm 0.012$ . The addition of 1 wt % water caused the  $pK_{In}$  to decrease to  $3.66 \pm 0.034$  and with 5 wt % water this fell further to  $pK_{In}$  3. 59  $\pm$  0.029 showing that the liquid was becoming significantly more acidic which confirmed the formation of HF. The role of water in ionic liquids has been discussed by several groups.<sup>32-34</sup> Recently, it has been suggested that nano-domains of water exist rather than the water being homogeneously mixed with the ionic liquid and DES.<sup>35,36</sup>

Abbott *et al.*<sup>37</sup> used dynamic light scattering to investigate ionic liquids and DESs containing 5 wt% water. Two of the samples studied were Bmim BF<sub>4</sub>, Emim OAc, and it was found that the average droplet sizes for these two liquids were  $96 \pm 4.0$  and  $72 \pm 8.0$  nm respectively. Clearly, far from creating homogeneous solutions the water forms Nano domains. These were found to be even larger in DESs e.g. in 2 EG: 1 ChCl they had an average diameter of 311 nm. This is effectively a microemulsion with a droplet containing approximately 4 x  $10^8$  molecules. It is unlikely that this will be a pure water droplet and there will be an equilibrium between water monomers in the DES and the constituent parts of the DES in the water phase.

In recent work, the self diffusion coefficients of the constituent species in 2 EG: 1 ChCl - water mixtures were measured.<sup>16</sup> At low water content (<2.5 wt %) the OH protons on Ch<sup>+</sup> and EG were found to diffuse at the rate controlled by the bulk viscosity of the liquid. At higher water content the OH diffused at a rate more characteristic of bulk water showing that a biphasic system existed.

It was noted the observation that microemulsion form must mean that ionisation occurs at the interface between the two phases such that a zeta potential is set up stabilising these large droplets. It is interesting to note that the droplet size distribution is relatively narrow. The 2 glycerol: 1ChCl liquid has a slightly smaller droplet with an average diameter of 105 nm. [Bmim][BF<sub>4</sub>] and [Emim][OAc] are slightly smaller but still show that the domains are significant in size. There are two consequences of this observation; firstly, the acid is more likely to partition into the aqueous phase which could lead to regions of different micro pH, and secondly these nano-domains may explain several unusual phenomena such as the stability of proteins in aqueous-ionic liquid mixtures.<sup>37-40</sup>

#### **3.3 Proton Activity of ADESs and PILs**

While ADESs and PILs have been applied to a variety of proton transfer applications little is known about their relative acidities. The proton-transfer applications can be tuned by using stronger bases or stronger acids. While intuitive estimations may be made about the strength of DESs from the pKa of the HBD e.g. it may be expected that ChCl: oxalic acid is more acidic than ChCl: citric acid, it requires quantification to be able to determine the extent of dissociation. The same is true for PILs where salts prepared from stronger amines may be expected to be weaker acids.

#### 3.3.1 Relative acidity of ADESs and PILs

In this section the relative activity of protons in a variety of ADESs and PILs were determined by the same method as that described above. The experiments performed in **Figure 3.6** were carried out in low concentrations of weak acids (approximately  $10^{-3}$  mol kg<sup>-1</sup>) however in ADESs the acids are present at a molality of approximately 3 mol kg<sup>-1</sup>. It is therefore not surprising that the liquids are more acidic and BPB cannot be used as an indicator as it is totally protonated in all the ADESs. To circumvent this issue, a different indicator, methyl violet 2B was used as the indicator. **Table 3.7** shows photographs of samples 4 ADESs and 1 PIL containing methyl violet 2B. The colour change with this indicator is from green (protonated) to blue (deprotonated). **Table 3.7** shows the calculated values of  $pK_{In}$  for methyl violet 2B together with the literature value of the  $pK_a$  for the acid in water. It can be seen that the  $pK_{In}$  values show some correlation with the acid dissociation constant in water but there are also some significant anomalies. Although all 4 DESs have the same ionic species (Ch<sup>+</sup> and Cl<sup>-</sup>) the proton will have a higher mobility than Ch<sup>+</sup>.

It can also be seen that the lowest  $pK_{In}$  value is for the ChCl: oxalic acid. 2H<sub>2</sub>O eutectic which is lower than the anhydrous analogue by 0.1 units. Given that the difference in pKa between oxalic acid in water and oxalic acid in Ethaline is approximately 1 unit in **Table 3.4** it is logical that the addition of 2 mol equivalent of water is the equivalent of a water concentration of 7.4 mol kg<sup>-1</sup> of water. This is approximately 13% of the water content of bulk water which would mean that the change in pH is in proportion with the water content if the DES.

<b>Table 3.7</b> : $pK_{In}$ for methyl violet 2B in some DESs and ILs					
liquid	1Oxalic acid.2H <sub>2</sub> O: 1 ChCl	1Oxalic acid: 1 ChCl	1Citric acid: 1ChCl	1 Malonic acid: 1ChCl	Emim HSO <sub>4</sub>
$pK_{In}$	$0.86\pm0.038$	$0.96\pm0.09$	$1.32\pm0.073$	$1.59 \pm 0.13$	$1.73\pm0.021$
рКа	1.25	1.25	3.14	2.82	1.92 (KHSO <sub>4</sub> )

The  $pK_{In}$  value of critic acid is lower than that of malonic (1.32 vs 1.59) despite the pKa values for the acids in water being the other way around 1Citric acid: 1ChCl is 3.14 whereas 1 Malonic acid: 1ChCl is 2.82. This appears anomalous but similar to the case with oxalic acid, citric acid although classified as anhydrous is very difficult to extract water from. TGa of the samples showed that malonic acid contained  $0.51 \pm 0.081$  % water content, while, in citric acids was found around  $7.81 \pm 0.31$  %. This is obviously explained why the citric acid appears to be a stronger acid than malonic acid based DES.

In [Emim] [HSO<sub>4</sub>] ionic liquid appears to be a significantly weaker proton donor than any of the acidic DESs. This is due to the effect of the anion in [Emim] [HSO<sub>4</sub>] which is weaker compared to other DESs. It is previously been shown that Brønsted acidic AILs with the HSO<sub>4</sub><sup>-</sup> anion all had similar selectivity for catalyst reactions, which indicated at

least qualitatively that they only possessed fairly moderate acidity.<sup>2, 41, 42</sup> In terms of comparison of the acidity values in **Table 3.6**. It is true to order the acidity of those liquids according to the degrees of dissociation of the indicator depending on the type of the anion as a most basic anion in pure water is HSO<sub>4</sub> due to their second *pKa* which is around (1.92).<sup>18</sup>

## 3.4 Effect of water in ionic liquid system

The pH of an IL or DES will change if another acid or base is introduced either deliberately or as an impurity.<sup>29, 43, 44</sup> Probably the most important of these is the presence of water since almost no ILs or DESs are totally water free. In order to elucidate the influence of water on proton behaviour in DESs, *pKa* of weak carboxylic have been measured for oxalic acid and salicylic acid in 2EG:1ChCl in the presence of water at 5, 10, 20, 50 and 80 wt%. Some physical properties of DESs are relatively insensitive to the addition of water, but others change significantly with only small additions of water. As described above the Abbott group has recently demonstrated that the water- 2EG: 1ChCl is heterogeneous and so it might be expected that the addition of water would have a complex effect on acid-base equilibria.<sup>29</sup>

**Figure 3.12** shows the  $pK_a$  for two carboxylic acids (salicylic (left) and oxalic acid (right)) in 2EG:1ChCl as a function of water content. It can be seen that the addition of water in DESs decreases the  $pK_a$  value from that in the pure DES to that in pure water. The change in pKa is not linear. Both systems show a small decrease until there is an equimolar composition of water and ChCl. This occurs at about 3-7 wt% water (depending on the DES). Thereafter, there is a significant decrease in the  $pK_a$  value. This is logical because under these conditions the water is under molar excess. One issue which does need to be discussed is the partitioning of species in different regions if the mixtures are not totally homogeneous. It may be expected that the indicator will be more hydrophobic than the acids and may partition initially in the non-aqueous regions of the liquid. If the acid partitions initially in to the water this may cause the initial gradual change in  $pK_a$  which is observed. However, it may just be an artefact of the way in which the data are presented.



*Figure 3.12: pKa of salicylic (top) and oxalic acids (bottom) in 2EG:1ChCl as a function of water content.* 

Comparable studies for binary IL-water mixtures have been reported by different groups in the literature. <sup>45 46</sup> Some presented two phases by mixing water, weak acids, and ionic liquids.<sup>47, 48</sup> Another studies showed that the addition of water is a major factor affecting the dissociation of acids in catalyst systems.<sup>49, 50 51</sup> Jacquemin and co-workers used NMR spectroscopy to understand the effect of water and acetic acid in [C<sub>n</sub>mim][NTf<sub>2</sub>] ionic liquids. Han *et al.* investigated the degree of dissociation of ILs, namely [Bmim][BF<sub>4</sub>], [Bmim][CF<sub>3</sub>CO<sub>2</sub>] and [PF<sub>6</sub>], in solutions. They noticed that the organic solvents promote the ionic association of [Bmim][CF<sub>3</sub>CO<sub>2</sub>] and [PF<sub>6</sub>], the effect of ionisation depending on the solvent dielectric constant. They noticed that the ability to form strong hydrogen bonds became stronger with trace amounts presences of water in ILs.<sup>52</sup>

### 3.5 pH Scales of ILs and DESs

Using the data presented above a scale of relative pH for ILs and DESs can be constructed. This is presented in **Figure 3.15** as a linear scale without specific values. The ordering of the liquids looks logical from a knowledge of the constituent components. For the ADESs, the acidic HBDs with the lowest aqueous  $pK_a$ . are the ones which exhibit the strongest acidity as might be expected. Waters of hydration increase the acidity in proportion to the amount of water but the overall effect is not more than 1 pH unit. ILs with relatively acidic anions e.g.  $HSO_4^-$  are relatively weak acids in comparison the ADESs.



Figure 3.13: Acidity scales in some ILs and DESs

The same appears to be true for the basic ionic liquids although again the relatively weak basic nature of most HBDs and anions means that most DES and ILs are relatively weak bases. In general it can be seen that most liquids have acidities and basicities that would be comparable to an aqueous pH scale running from roughly 1 to 10. It appears that the liquids do not show extreme acidities or basicities and it could be concluded that these are buffered by the high ionic concentration in the liquids.

### 3.6 Conclusions

An analytical procedure has been developed to determine the acidity in DESs and ILs and its validity was tested by on aqueous solutions comparing the values obtained with results from an aqueous pH electrode. Good correlation was obtained for both strong and weak acids in water showing the validity of the method.  $pK_{In}$  data for three indicators were determined in DESs and ionic liquids and it was found that the values were lower when the amount of salt was decreased. The  $pK_{In}$  values were also lower in DESs than in water which would be expected given that the chloride anion is a weaker base than water and that chloride is acting as a buffer. Surprisingly the  $pK_{In}$  values were found to depend slightly on the HBD in the mixture. This could have two reasons; the activity of the chloride could change and the ability of the HBD to partially dissociate must also be considered.

The comparison of the acid dissociation equilibrium constants of nine carboxylic acids in a deep eutectic solvents was measured and these values were compared with the corresponding values in water. It was found that the  $pK_a$  values were higher in DESs than in water showing that water acted as a better base than Ethaline. A good linear correlation between the  $pK_a$  values in the two liquids was observed. This would be expected given the differences in concentration and strength of the base in the two liquids.

The process was repeated to determine the acidity of different ionic liquids as a function of the basicity of the anion. The data shows the effect of different hydrogen bond donors on the acidity of DESs. These values were compared with ionic liquids with different anions to determine the effect of the anion on the pH of a liquid. The acidity of ionic liquids was found to depend on the basicity of the anion. The unusually low  $pK_a$  value for [Bmim][BF<sub>4</sub>] was rationalised by hydrolysis of the anion to form HF. The  $pK_a$  values for 4 carboxylic acids were determined in two ILs and two DESs. The values were lowest in the BF<sub>4</sub><sup>-</sup> based IL and highest in the acetate-based liquid.

The pKa of acidic DESs and protonic ionic liquids were measured for the first time. It was found that eutectic mixtures of oxalic acid and ChCl were more acidic than those based on citric or malonic acid. The  $pK_{In}$  values were quite high considering that they are weak acids but can be understood when the high concentration of acid is taken into account comparison of the acidity of the acids in water at the same concentration gave comparable results.

The effect of water on the pH of ionic liquids and DESs was also tested and it was found that the  $pK_a$  value of carboxylic acids decreased as the water content increased. It required a molar excess of water to ChCl before the  $pK_a$  changed significantly.

The most notable conclusion from this study was that the acidity of weak acids in DESs and ILs was not overly dissimilar to their behaviour in aqueous solutions. The  $pK_{In}$  results for the pure ILs also gave results which correspond to values that could be predicted from the properties of the pure components so it must be concluded that the acidity in ILs and DESs is in fact exactly what would be expected given the composition and properties of the constituents. The DESs and ILs act as buffers decreasing the pH by approximately 0.5

pH units which can be predicted from the anion molality in solution. This gives a clear basis from which approximate pH values can be predicted without the need for measurement.

## **3.7 References**

- 1. J. Stoimenovski, E. I. Izgorodina and D. R. MacFarlane, *Physical Chemistry Chemical Physics*, 2010, **12**, 10341-10347.
- 2. A. S. Amarasekara, *Chemical reviews*, 2016, **116**, 6133-6183.
- 3. D. R. MacFarlane, J. M. Pringle, K. M. Johansson, S. A. Forsyth and M. Forsyth, *Chemical Communications*, 2006, 1905-1917.
- 4. A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chemical Communications*, 2003, 70-71.
- 5. A. P. Abbott, R. C. Harris and K. S. Ryder, *The Journal of Physical Chemistry B*, 2007, **111**, 4910-4913.
- E. L. Smith, A. P. Abbott and K. S. Ryder, *Chemical reviews*, 2014, **114**, 11060-11082.
- E. Durand, J. Lecomte and P. Villeneuve, *European journal of lipid science and* technology, 2013, 115, 379-385.
- M. Hayyan, M. A. Hashim, A. Hayyan, M. A. Al-Saadi, I. M. AlNashef, M. E. Mirghani and O. K. Saheed, *Chemosphere*, 2013, 90, 2193-2195.
- A. P. Abbott, G. Capper, D. L. Davies, K. J. McKenzie and S. U. Obi, *Journal of Chemical & Engineering Data*, 2006, **51**, 1280-1282.
- 10. Y. Leng, P. Jiang and J. Wang, *Catalysis Communications*, 2012, 25, 41-44.
- J. Lu, X. T. Li, E. Q. Ma, L. P. Mo and Z. H. Zhang, *ChemCatChem*, 2014, 6, 2854-2859.
- 12. A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *Journal* of the American Chemical Society, 2004, **126**, 9142-9147.
- 13. S. B. Phadtare and G. S. Shankarling, *Green Chemistry*, 2010, **12**, 458-462.
- A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Green Chemistry*, 2002, 4, 24-26.
- A. P. Abbott, T. J. Bell, S. Handa and B. Stoddart, *Green Chemistry*, 2005, 7, 705-707.
- 16. Z. Wang, P. Ji, X. Li and J.-P. Cheng, *Organic letters*, 2014, **16**, 5744-5747.
- 17. J. Wang, Analytical electrochemistry, John Wiley & Sons, 2006.
- 18. D. Skoog, D. West, F. Holler and S. Crouch, *Fundamentals of analytical chemistry*, Cengage Learning, California, USA, 2013.

- J. Reijenga, A. Van Hoof, A. Van Loon and B. Teunissen, *Analytical chemistry* insights, 2013, 8, 53.
- X. Jiang, W. Ye, X. Song, W. Ma, X. Lao and R. Shen, *International journal of molecular sciences*, 2011, 12, 7438-7444.
- M. Hasani, J. L. Yarger and C. A. Angell, *Chemistry-A European Journal*, 2016, 22, 13312-13319.
- 22. T. Welton, *Chemical reviews*, 1999, **99**, 2071-2084.
- 23. A. P. Abbott, G. Frisch, H. Garrett and J. Hartley, *Chemical Communications*, 2011, **47**, 11876-11878.
- 24. A. Trummal, L. Lipping, I. Kaljurand, I. A. Koppel and I. Leito, *The Journal of Physical Chemistry A*, 2016, **120**, 3663-3669.
- 25. M. Windholz, S. Budavari, L. Y. Stroumtsos and M. N. Fertig, *The Merck index*. *An encyclopedia of chemicals and drugs*, Merck & Co., 1976.
- W. S. Matthews, J. E. Bares, J. E. Bartmess, F. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum and N. R. Vanier, *Journal of the American Chemical Society*, 1975, 97, 7006-7014.
- 27. W. N. Olmstead, Z. Margolin and F. G. Bordwell, *The Journal of Organic Chemistry*, 1980, **45**, 3295-3299.
- A. P. Abbott, R. C. Harris, K. S. Ryder, C. D'Agostino, L. F. Gladden and M. D. Mantle, *Green Chemistry*, 2011, 13, 82-90.
- C. D'Agostino, L. F. Gladden, M. D. Mantle, A. P. Abbott, I. A. Essa, A. Y. Al-Murshedi and R. C. Harris, *Physical Chemistry Chemical Physics*, 2015, 17, 15297-15304.
- 30. A. Abbott, G. Frisch, S. Gurman, A. Hillman, J. Hartley, F. Holyoak and K. Ryder, *Chemical Communications*, 2011, **47**, 10031-10033.
- 31. M. G. Freire, C. M. Neves, I. M. Marrucho, J. A. Coutinho and A. M. Fernandes, *The Journal of Physical Chemistry A*, 2009, **114**, 3744-3749.
- H. Rodríguez and J. F. Brennecke, *Journal of Chemical & Engineering Data*, 2006, **51**, 2145-2155.
- H. Katayanagi, K. Nishikawa, H. Shimozaki, K. Miki, P. Westh and Y. Koga, *The Journal of Physical Chemistry B*, 2004, **108**, 19451-19457.
- M. G. Freire, C. M. Neves, P. J. Carvalho, R. L. Gardas, A. M. Fernandes, I. M. Marrucho, L. M. Santos and J. A. Coutinho, *The Journal of Physical Chemistry B*, 2007, **111**, 13082-13089.

- 35. K. Saihara, Y. Yoshimura, S. Ohta and A. Shimizu, *Scientific reports*, 2015, 5.
- E. A. Cade, J. Petenuci and M. M. Hoffmann, *ChemPhysChem*, 2016, **17**, 520-529.
- 37. A. P. Abbott, S. S. Alabdullah, A. Y. Al-Murshedi and K. S. Ryder, *Faraday Discussions*, 2017.
- 38. R. Sheldon, *Chemical Communications*, 2001, 2399-2407.
- 39. Z. Yang and W. Pan, *Enzyme and Microbial Technology*, 2005, **37**, 19-28.
- 40. Y. Kohno and H. Ohno, *Chemical Communications*, 2012, **48**, 7119-7130.
- 41. R. Gillespie, T. Peel and E. Robinson, *Journal of the American Chemical Society*, 1971, **93**, 5083-5087.
- 42. S. Koenig, R. Brown and G. Jacob, in *Biophysics and Physiology of Carbon Dioxide*, Springer, Editon edn., 1980, pp. 238-253.
- K. E. Gutowski, G. A. Broker, H. D. Willauer, J. G. Huddleston, R. P. Swatloski,
  J. D. Holbrey and R. D. Rogers, *Journal of the American Chemical Society*, 2003,
  125, 6632-6633.
- 44. O. S. Hammond, D. T. Bowron and K. J. Edler, *Angewandte Chemie*, 2017, **129**, 9914-9917.
- 45. S. K. Shukla and A. Kumar, *The Journal of Physical Chemistry B*, 2013, **117**, 2456-2465.
- 46. J. E. Reid, R. J. Gammons, J. M. Slattery, A. J. Walker and S. Shimizu, *The Journal of Physical Chemistry B*, 2017, **121**, 599-609.
- 47. W. Jiang, Y. Wang and G. A. Voth, *The Journal of Physical Chemistry B*, 2007, 111, 4812-4818.
- 48. C. Adam, M. V. Bravo and P. M. Mancini, *Tetrahedron Letters*, 2014, **55**, 148-150.
- 49. E. Santos and W. Schmickler, *Catalysis in electrochemistry: from fundamental aspects to strategies for fuel cell development*, John Wiley & Sons, 2011.
- 50. E. Durand, J. Lecomte, B. Baréa, G. Piombo, E. Dubreucq and P. Villeneuve, *Process biochemistry*, 2012, **47**, 2081-2089.
- 51. H. Zhao and G. A. Baker, *Journal of Chemical Technology and Biotechnology*, 2013, **88**, 3-12.
- 52. W. Li, Z. Zhang, B. Han, S. Hu, Y. Xie and G. Yang, *The Journal of Physical Chemistry B*, 2007, **111**, 6452-6456.

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#### Chapter four: Electrochemical determination of pH

## Introduction

In the previous chapter, an analytical method was developed to quantify the pH of ILs and DESs. This was achieved by using classical spectroscopic indicator solutes to determine proton activity. The comparison of the acid dissociation equilibrium constants of carboxylic acids in deep eutectic solvents with the values obtained in aqueous solvents found the higher values in DESs than in water. The acidic DESs containing carboxylic acids as hydrogen bond donors were found to be quite strongly acidic despite the carboxylic acids being relatively weak. This was accounted for by the high concentration of HBD in the DES. Oxaline for example contains 4.3 mol kg<sup>-1</sup> of acid.

The aim in this chapter is to develop an electrochemical pH sensor which can be used in ionic systems. Firstly, this will be attempted using a standard aqueous pH probe with a glass membrane. The conditions required to obtain reliable, reproducible readings will be investigated with a protocol for treating the electrode between readings. In addition, a new electrode using all ionic liquids will be constructed and compared with an aqueous cell. The standard redox couple  $Ag^{+/0}$  was used to compare the liquid junction potential arising between ionic liquids. Finally, a comparison will be carried out of the pH values obtained in different DESs and ILs using different analytical methods (spectroscopic and potentiometry) to see whether there are any consistent deviations in the values.

#### 4.1 Electrochemical sensors

Electrochemical sensors are amongst the most commonly used analytical techniques to provide accurate and precise data on the concentrations of specific chemical species. Generally, there are three classical types of the electrochemical sensors: amperometric, conductimetric and potentiometric.<sup>1</sup> Amperometric sensors apply a given potential between a working and a reference electrodes, to produce the oxidation or reduction of an electroactive species; the resulting current is directly correlated to the bulk concentration of the electroactive species. Conductimetric sensors are involved with the measurement of conductivity at a series of frequencies. While, potentiometric sensors set up an equilibrium between the analyte and an electrode at the sensor interface and measure the cell potential. For many of these sensors a membrane can be used to make it specific to a given analyte.<sup>2</sup>

## 4.2 Potentiometric sensors

Potentiometric sensors can be classified in three main types ion- selective electrodes (ISE), coated wire electrodes (CWE) and field effect transistors (FET). The ion selective electrode is a sensor or electrode capable of selectively converting the activity of specific ion dissolved in a solution into an electrical potential. The voltage is theoretically based on the logarithm of the ionic activity according to redox potential measurements. The potential difference appears as a result of different ion activities at the interface. The electrode potential between the interface and solution can be expressed according to the Nernst equation:<sup>3</sup>

$$E_{cell} = E^0 + RT/F \ln a (H) / a' (H)$$
 (4.1)

where *E* is the potential difference between the working electrode and reference electrode,  $E^0$  is the standard reduction potential, *R* is the gas constant, *T* is the temperature, *F* is Faraday's constant, *a* (H) and *a'* (H) are the activities of the hydrogen ion outside and inside the membrane respectively.<sup>4</sup>

## 4.2 Types of reference electrodes

Reference electrodes can be classified in different ways.<sup>4</sup> Koryta *et al.* classified reference electrodes into three types.<sup>5</sup> The first type is based on an equilibrium between an electrode and their corresponding anions or cations in solution such in a  $Ag/Ag^+$  electrode. <sup>5, 6</sup>

The second type is based on a three-phase system, where a metal wire is coated in a layer of a sparingly soluble salt of that metal and then immersed in a solution containing a known concentration of the corresponding anion of the salt. An example of this type is the  $Hg/Hg_2Cl_2/Cl^-$  (Saturated Calomel Electrode).<sup>7</sup>

The final type can be setup using soluble redox couples. An inert metal, such as gold or platinum, is immersed in a solution containing both the reduced and oxidised species of a redox couple and the potential of that redox couple is then determined. some examples of reference couples are cobaltocene/cobaltocenium and ferrocene/ferricenium.<sup>8</sup>

Standard Hydrogen Electrode (SHE) is another type of reference electrode which has been used for pH measurements. It consists of a platinum wire inserted in an acidic solution through which hydrogen is bubbled. The  $H^+/H_2$  redox couple can be used to

define the standard electrode potential and is supposed to have a voltage of 0.00V in aqueous media with 1 mol kg<sup>-1</sup> activity of HCl and 1 bar hydrogen pressure.

One of the requirements of electrochemical processes used for a sensor is that it should reach equilibrium quickly. In the case of the SHE the platinum electrode is platinised with platinum black to provide a suitably large surface area for the hydrogen to adsorb.<sup>9</sup> A number of inaccuracies remain in determination of the hydrogen electrode compared to the theoretical estimation. The difficulty arises in the preparation of the platinized surface and in controlling the concentration of the reactants. For this reason the SHE is referred to as a hypothetical reference electrode with the potential of other reference electrodes being referred back to this value.<sup>9</sup>

The most extensively used reference electrode for pH measurement as a potentiometric sensor is the glass pH electrode, which has long been used in aqueous system. Its success is attributed to its simplicity, low cost and ease of construction. It is also sensitive over a wide pH range and extremely selective for hydrogen ions.<sup>10, 11</sup> The glass electrode functions by having a conducting glass membrane which can exchange hydrogen ions. The glass membrane is a silicate matrix based on molecular network of silicon dioxide (SiO<sub>2</sub>) with addition of other metal oxides, such as Na, K, Li, Al, B, Ca.<sup>12</sup> When immersed in an aqueous solution some of the metal ions are exchanged with the protons in solution setting up a liquid junction potential across the glass membrane. An important factor which is often forgotten with the use of analytical pH electrodes is that the potential is set up due to an equilibrium and so the electrode has a memory of the environment in which it was last immersed. It is therefore important to equilibrate the electrode before its next measurement. This is usually achieved by immersing the electrode in a standard buffer solution which contains sodium ions to re-equilibrate the ions in the glass membrane. It does, however also mean that the glass can be sensitive to measuring pH in solutions of high ionic strength of metal ions.

**Figure 4.1** shows a broadly accepted mechanism of potentials at the glass surface. Application of glass electrodes for other monovalent cations, including sodium, lithium,<sup>13, 14</sup> amonium and potassium sensors based on new glass compositions, have also been reported.<sup>15, 16</sup>



Figure 4.1: Different types of potentials set up at a glass-solution interface <sup>11, 17</sup>

# 4.3 Issues of reference electrodes in non-aqueous solvents

A specific method of measuring pH by using electrode potentials in non-aqueous solvents has not been well established. The most important issue is obtaining a stable reference potential. There is no specific reference redox couple like the SHE or Ag/AgCl to which other redox potentials can be compared. The problem is due to a lack of thermodynamic data in non-aqueous solutions and the lack of information about liquid junction potentials,

 $E_{LJP}$ , which arise between the aqueous reference electrode and the non-aqueous solutions.<sup>18</sup>

Abbott *et al.* studied the cell potential of the  $H^+/H_2$  couple as a function of acid concentration over 6 orders of magnitude in Ethaline and found a Nernstian behaviour. This showed not only that triflic acid was fully dissociated but also gave the basis upon which a standard electrode potential could be based. The study also showed that the  $Ag^{+/0}$  and the  $Cu^{2+/+}$  couples also behaved in a Nernstian manner showing that the solutions were ideal.<sup>19</sup>

Kanzaki *et al.* studied the pH of ionic liquids using a similar electrochemical cell. They created a hydrogen electrode to measure the pH of organic acids in ethylammonium nitrate. While the  $H^+/H_2$  couple appeared to be Nernstian in these solutions, the performance of the glass membrane and the meaning of a liquid junction potential in an ionic liquid needed to be reviewed.<sup>20</sup>

# 4.4 Results and Discussion

### 4.4.1 Characterisation of an aqueous glass electrode in DESs

Although the aqueous pH electrode was developed solely for use in aqueous solutions it is proposed in this study that it may be possible use it in non-aqueous solutions. To address the developed method for measuring the activity of the proton in DESs glass electrode were used in this section of work. As the glass membrane is exposed to different proton activities on either side of the membrane. Most aqueous pH electrodes (or more accurately the proton ion selective electrode) are based on the cell:<sup>21</sup>

$$Ag|AgCl|HCl|_{1}H^{+} (analyte)|_{2} Ref_{2}$$
(Cell 1)

Where  $\|_1$  is the conducting glass membrane and Ref<sub>2</sub> is a second reference electrode separated by a salt bridge  $\|_2$  from the analyte. This is usually another silver-silver chloride electrode or a mercury-calomel couple.

The pH meter measures a cell potential which can be approximated as;

$$E_{cell} = \text{constant} + \frac{RT}{F} \log_{10} a_{H^+}$$
(4.2)

So in most cases it is assumed that the change in cell potential with proton activity should be approximately -59 mV. The issue with the application of glass membranes to this type of study is the assumptions inherent in the sensing mechanism. It is clearly inappropriate to measure pH directly using a classical meter but it may be appropriate to test equation 4.3 by measuring the cell potential as a function of HOTf molality.<sup>22</sup>

The purpose behind this section of work is to outline a reliable way to use an aqueous pH electrode for measuring pH in ILs media. The process for ion exchange on the surface of the glass membrane in an aqueous system is shown schematically in **Figure 4.2** When the glass is immersed into in the solution of acid/base, the protons diffuse into the hydrated glass layer of the pH probe and jump between Si-O<sup>-</sup> sites, to generate a balance of electrons through the glass with protons (H<sup>+</sup>) present in the solution.<sup>18</sup> An increase of the protons in the external solution, consistent with a pH decrease, shifts the equilibrium to favour the silanol over the siloxy group concentrations.



*Figure 4.2*: Schematic diagram showing the migration of charge through a glass electrode

The reduction of the negative charge density at the external glass surface is related to an increase of the electrical potential of the glass relative to that of the internal solution side (which is always fixed). This results in an electric potential differences across the glass membrane.

This process is clear in aqueous systems, however, in DESs the issue is with the hydrogen ions H  $^+$  which are not surrounded by H<sub>2</sub>O molecules. This may preclude the formation of the silicic acid later which may preclude ion exchange of the glass.

As described above, the difficulties with using a glass electrode is the need to reequilibrate the electrode after each measurement. The standard method of doing this in aqueous solutions is to dip the tip of the glass membrane into an aqueous buffer solution containing sodium ions. The same can be done with non-aqueous solutions of the salt bridge usually saturated NaCl.<sup>23</sup> This must be taken into account during the measurements to make the recorded potential accurate and reliable.<sup>22</sup> This will allow the rest potential of the glass cell to always return to its original value and will preclude potential drift through a series of experiments. This deprotonation is essential for the proper functioning of the sensor and is a regular source of error in aqueous pH measurement. The ionic exchange of metal ions (Na<sup>+</sup>) with H<sup>+</sup> ions is essential to obtain the linear pH vs potential response. It is also the reason why pH electrodes do not give an accurate response in media of high Na<sup>+</sup> or K<sup>+</sup> ionic strength.<sup>24</sup>

It is known that the buffer solution is defined as an ionic material that resists changes in pH; including a solution containing either a weak acid and its salt or a weak base and its salts. However, Mussini *et al* recommended that aqueous buffers may not accurately calibrate non-aqueous or mixed solutions.<sup>21</sup> The above method was used previously by Avdeef *et al*. who calibrated the glass electrode in methanol/water media and applied to pKa determination of water-insoluble substances with a high degree of precision and reproducibility.<sup>25</sup>

A detailed standard protocol was investigated for measuring pH in DESs and ILs. The response to the Nernst equation with respect to the potential-defining species in the solution is also considered.<sup>26</sup> In the current study, a series of triflic acid solutions in Ethaline were prepared containing  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$  and  $10^{-7}$  mol kg<sup>-1</sup> by subsequent dilution. Basic solutions were also prepared using methylamine in 2 EG: 1 ChCl. All measurements were carried out at  $27 \pm 2$  °C as some of the liquids were too viscous to use at room temperature.

In case of the current method, the electrode was activated before each measurements by soaking in 2 M NaCl in Ethaline as a buffer solution. The usual manner of calibrating the pH cell is using buffer solutions of known pH and cell potentials are standardised to read

the pH values directly on the meter by adjusting the slope and intercept parameters of equation 4.3 to calibrate the *constant* and *T* values. The lack of standardised buffer solutions meant that a calibration curve had to be constructed. For this it was assumed that triflic acid was fully dissociated in DESs, the justification of which was previously shown by Abbott *et al*<sup>19</sup> and which is further shown below.

# 4.4.2 Effect of washing

Another question that needs to be addressed is whether the glass needs to be hydrated to function and whether washing is necessary between measurements. Several groups have studied the influences of hydration of the glass on the equilibrium of ion exchange processes. Mathias *et al* showed that there is a substantial effect on the measured potentials if the electrode is washed or not between measurements.<sup>27</sup> The charge transport inside the membrane occurs on account of the acidic and alkali ions inside the glass which was firstly studied by Nicolsky.<sup>4</sup>

Goldman and co-workers found that the potential measurement against pH with different buffer types is affected by reprotonation of the membrane surface<sup>28</sup> and concluded that there was a significant effect of washing the electrode with different types of buffer solutions. They concluded that this was in important part of the standardisation of the pH measurement development.

To understand the effect of the pre-treatment of the electrode on the reliability of the cell potential measurements three protocols were tested to treat the glass electrode between measurements.

- The electrode was simply dried on absorbent paper between measurements to physically remove the analyte solution from the previous measurement prior to re-use.
- The electrode was washed in classical aqueous buffer solutions (pH 7) before being dried with absorbent paper.
- The electrode was washed in a solution of Ethaline containing 2 mol kg<sup>-1</sup> NaCl prior to reuse.

These protocols were used in 9 solutions of triflic acid or methyl amine in Ethaline approximately corresponding to pHs of 1 to 9. For each solution 5 replicate measurements

were made and the average and standard deviations of the cell potential were calculated. These are displayed in **Figure 4.3**.

The least sensitive protocol and the one with the largest deviation in cell potential was the physical removal of the excess DES with absorbent paper between measurements. This shows that the electrode retains a memory of the previous measurement. The measurements show random deviation in sequential measurement but the error bars are nevertheless relatively small. In each case the measurements were made from the highest pH to the lowest pH. It also shows that with time the re-equilibration of the glass with sodium ions is not occurring. This resulted from the deficiency of the glass membrane as the surface dehydrated with subsequent measurements.<sup>29, 30</sup>

Washing the electrode in aqueous buffer solutions between measurements should result in the rehydration of the glass and the deprotonation of the silanol groups. **Figure 4.3** shows values which are more similar to expected Nernstian behaviour but there is clearly some memory effect of water as the response deviates from the expected Nernstian response. The error bars are generally smaller than with the physical drying process but they still deviate significantly from the expected linear response for *Ecell* vs pH.<sup>28</sup>



*Figure 4.3*: Cell potential of an aqueous glass electrode in Ethaline using different treatments between measurements
The third method used 2 M sodium chloride in Ethaline as a buffer solution as the washing solution between measurements. A relatively linear response was obtained between *Ecell* and *pH* and while not perfectly Nernstian it should provide a basis for a useful calibration curve. The cell potential data shows a good stability and reproducibility with an acceptable error bar (SD  $\pm$  0.78). This suggests that either the hydration of the glass is not overly important or more likely there is sufficient water in the Ethaline to suitably hydrate the glass. The process also shows that the protocol for use is extremely important.

It is important to mention that in all of the above measurements the glass probe was not left in the analyte for more than 2 minutes. Leaving it for longer resulted in spurious results which could be due to leaching of the aqueous solution from the fritted compartment which could result in liquid junction potential issues. This will be discussed in more details as in **section 4.4.8** 

Previously, it has also been shown that the concentration of other ions in the analyte solution can lead to spurious results using a glass electrode. The study showed that the adsorption of ions at the glass electrode /water interface could change the measured pH.<sup>14,27, 31</sup> This should not be an issue with choline ions as they are too large and the charge density is too low to compete with other cations or protons.

Glass electrode efficiency was also studied by Maura *et al.* who addressed the effect of electrolytes on pH measurements via glass electrodes with changing of buffered in protein media. They noticed significant phenomena of changes in measured pH show up most strongly with anions in the glass surface.<sup>27, 28, 31</sup>

#### 4.4.3 Effect of Time

An important factor in the use of ISE is the response time. This is usually dependent upon the time taken for the system to reach equilibrium. The cell potential for the aqueous glass electrode was measured as a function of time for the 3 pre-treatment protocols listed in the previous section. In all three measurements the cell was immersed in 10<sup>-1</sup> mol kg<sup>-1</sup> of triflic acid in 2 EG: 1 ChCl. The electrode was washed; firstly in aqueous buffer solutions at pH 4 prior to use, secondly in 2 mol kg<sup>-1</sup> of sodium chloride buffer in Ethaline and thirdly wiped in dry tissue.

**Figure 4.4** shows the *Ecell* vs time response for all three pre-treatment protocols. It is clear that the response of the electrode is much faster when the electrode is washed in 2

mol kg<sup>-1</sup> of sodium chloride buffer in 2 EG: 1 ChCl. A much slower response is obtained for the other two pre-treatment protocols. This could be because fully hydrating the glass could make the electrode slow to exchange water with DES. It has recently been shown that water and DESs are not completely miscible and this could be the reason for a slow exchange at the glass interface.<sup>32</sup>

The slow response of the electrode could be some of the reason for the non-linearity and large error bars associated with the data in **Figure 4.3**. **Figure 4.4** also shows that the potential at equilibrium is more stable when washed in the NaCl buffer solutions than by the other two protocols.

As a result of the chemical equilibrium between a glass response and a solution of its ions discussed, it is clear that the reference electrolyte solution functions best when there is a relatively immersed with buffer high concentration of NaCl in Ethaline with error bar around ( $\pm$  0.45). Fortuitously this corresponds to the typical calibration of glass found in acetonitrile (AN).<sup>33</sup> Kolthoff estimated the dissociation constant in acetonitrile from measurements in unbuffered solutions of picric acid. The data showed that no reliable values of the constant *pKa* can be expected from measurements in unbuffered solutions with an uncertainty in the location of the midpoint for the potentiometric titration of the order of (e.m.f = 5 mV).<sup>34</sup>



*Figure 4.4*: *Time dependence the glass electrode immersed in 10<sup>-1</sup> mol kg<sup>-1</sup> of triflic acid in Ethaline to reach equilibrium* 

#### 4.4.4 Measurements in DESs

With a standardised protocol for use the aqueous pH probe it is possible to determine the effect of water on the *Ecell* values. Clearly the electrode should give a Nernstian response in water and this was tested and checked against a nominally dry DES and a 50: 50 wt mixture. **Figure 4.5** shows the change in cell potential for a glass electrode in an aqueous solution of triflic acid as a function of proton activity assuming complete dissociation of the acid. The response shows the expected linear correlation with a slope of  $-56 \pm 2.4$  mV. The experiment was repeated with the same molalities of triflic acid, this time in a mixture containing 50 wt% water and 50 wt% Ethaline. The response of cell voltage as a function of nominal pH is still very similar although the slope of the graph has decreased to  $-55 \pm 2.4$  mV. Repeating the experiment using pure Ethaline results in a linear correlation but the slope of the line was  $-52 \pm 2.8$  mV. It is clear, that this glass membrane provides a roughly linear response between cell potential and acid molality in all cases although the slope is not the same in the three liquids. A glass electrode could, however give an analytical signal which gives a measure of relative pH if calibrated against solutions of a strong acid of known molality in an ionic liquid or DES.



*Figure 4.5*: Correlation of cell potential with relative pH for triflic acid in (a) water (b) Ethaline and (c) a 50:50 wt mixture of a and b.

The applying of triflic acids in terms of concentration rather than activity the reason behind that is assumed triflic acid a fully dissociation in Ethaline. Abbott *et al.* previously determined the activity of silver ions in different imidazolium liquids by measuring the reduction potential of silver ions over a range of concentrations, in imidazolium-based ILs with different anions and in Ethaline. The activity coefficients of Cu<sub>2</sub><sup>+</sup> and H<sup>+</sup> were also measured in Ethaline. They showed that the change in redox potential as a function of molality for the imidazolium IL solutions, along with the Nernstian line which assumes that both the working and reference couples are ideal solutions ( $\gamma \pm = 1$ , a = m), for the cell.<sup>19</sup>

The discrepancies in the slopes of **Figure 4.5** probably originates from the way in which the glass electrode functions. The glass used is an amorphous silicon dioxide with alkali metal oxides and the glass becomes protonated in acidic aqueous solutions

 $Si-O- + H_3O^+ \rightarrow Si-OH^+ + H_2O \tag{4.3}$ 

The ability of the silica to become protonated depends on its degree of hydration. Dehydration of pH electrodes can significantly affect their response and reversibility.

The response of the glass electrode in relatively anhydrous DES is worse than in water and even in a 50:50 mixture which shows that the use of glass membranes can cause difficulties in anhydrous conditions. Even though the E vs pH response is not strictly Nernstian it does form a linear calibration plot.

Previously, it has been shown that in certain non-aqueous solvents the glass electrode also responds to proton activity, if occasionally sluggishly in its response times.<sup>35</sup> Kolthoff *et al* found that the glass electrode could be used in DMSO to determine the *pKa* of a number of weak acids. Ritchie *et al* used a similar apparatus to titrate some weak acids in DMSO using a glass electrode and a silver reference electrode.<sup>36</sup> They found that the Nernst equation was obeyed, however, large errors were observed in the absolute values of pH<sub>DMSO</sub> and *pKa* of weak acids which resulted from neglecting activity effects and liquid junction potential effects. Theoretically the e.m.f. should decrease by 59 mV upon a tenfold concentration change but the observed values were greater than theoretical value. However, the liquid junction potential between the reference electrode and test solution were considerable for their study. The study also recommended that water content can be

influenced of the changing of the e.m.f. response with glass membrane in the DMSO used in such measurements.<sup>33, 35</sup>

Quantitative potentiometric studies of the relative proton acceptor of series of amines have been carried out by Hall and co-workers.<sup>37</sup> In those studies the values of the potential with a glass electrode at the midpoints in the titration of a series of amines with perchloric acid were taken as an index of the relative strengths of the amine. Results obtained from such titrations can be quite valuable for exploratory purposes but are not suitable for precise correlations. This study also neglected the net liquid junction potential changes during the titration and the titrant introduces a competing proton acceptor (dioxane or water). However, it was demonstrated that the glass electrode responds reversibly to hydrogen ion activity in an anhydrous solvent.<sup>37</sup>

So in most cases it is assumed that the change in cell potential with proton activity should be approximately -59 mV. The issue with the application of glass membranes to this type of study is the assumptions inherent in the sensing mechanism. It is clearly inappropriate to measure pH directly using a classical meter but it may be appropriate to test equation (4.2) by measuring the cell potential as a function of HOTf molality.

Using the data shown in **Figure 4.5** for pure Ethaline as a calibration plot the cell potential for an aqueous glass electrode was measured with a variety DESs and ILs and an approximate value for the liquid pH was determined. These data are shown in **Table 4.1**. The data are logical given the acidity of the HBDs and the anions. They are also in good agreement with the values obtained in Chapter 3. This shows good agreement between the two techniques and lends confidence to the validity of both approaches to pH determination.

Table 4.1: Cell potential and pH for various ILs and DESs determined using				
liquid	E <sub>cell</sub> / V	рН	Indicator	
Oxaline	255	$1.32 \pm 0.022$	$1.10 \pm 0.012$	
Maline	143	$2.39\pm0.014$	$2.49\pm0.032$	
Ciline	109	$2.84\pm0.15$	$2.33\pm0.16$	
[Emim][HSO <sub>4</sub> ]	98	$3.01 \pm 0.31$	$2.74\pm0.074$	
[Bmim][BF4]	62	$4.25\pm0.59$	$3.88 \pm 0.23$	
Ethaline	-96	$6.89\pm0.91$	$5.93 \pm 0.018$	
Glyceline	-124	$7.48\pm0.32$	$6.97\pm0.06$	
[Emim][OAc]	-130	$7.73\pm0.12$	$7.38\pm0.14$	
Reline	-183	8.91 ± 0.33	$8.31\pm0.05$	

**Table 4.1** shows differences in pH values of neat DESs and ILs. While the trends are the same there are some significant discrepancies between the two values. The biggest discrepancies seemed to occur where there was the largest error bar in the electrochemical data, most notably with Ethaline. In general, the error bars on the glass electrode data are larger than those of the indicator. In some, but not all, cases the two sets of data lie within the error bars of the two methods. In general, the larger discrepancies were measured for the liquids which were more hydroscopic.

The order of acidity is affected by the electronegativity of the anion, by the following order  $HSO_4 > BF_4^- > CI^- > Ac$ , suggesting some correlation with hydrogen bond strength. For a number of applications measuring proton behaviour of liquids is important for properties such as wettability, capability of mass transfer for liquid-liquid extraction, or in multi-phasic heterogeneous catalysis.<sup>32, 38-40</sup>

## 4.4.5 Determination of acid dissociation constant

It is relatively well known that the *pKa* values of carboxylic acids are influenced by the type of the solvets.<sup>41, 42</sup> The coulombic force, *F*, between two charges, Z is given by

$$F = \left| Z_+ Z_- \right| / 4 \pi \varepsilon_0 \varepsilon r^2 \tag{4.4}$$

Where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon$  is the relative permittivity and *r* is the distance between the ions. Thus as the medium becomes less polar, the relative permittivity decreases so the force of attraction increases and the value of *Ka* decreases.

In chapter three, an analytical method was found to predict the *Ka* of variety of carboxylic acids in DESs and ILs. This process was repeated using the aqueous pH probe to determine the pH of the same carboxylic acids (oxalic, citric, malonic, lactic, succinic, acetic and butanoic acids) in Ethaline and the results are shown in **Figure 4.6**.

All pH measurements were taken from the triflic acid calibration curve shown in **Figure 4.5. Figure 4.6** shows a plot of *pKa* values obtained using a glass electrode and compared them with the values obtained in Chapter 3. A good linear correlation between the both electrochemical and spectroscopic *pKa* values was obtained. However, it was found that in all cases the *pKa* values obtained in Ethaline with the glass electrode showed a  $\Delta pKa$  of 0.2 to 0.4 differ values between the indicator and the pH probe. In Chapter **3** in **section 3.1.3**, it was found that in aqueous solutions two methods differed only by a round 0.011 units. This shows that the DESs produce a larger disparity.



**Figure 4.6**: Comparison the average  $pK_a$  values of 7 carboxylic acids in Ethaline by two different methods

From **Table 4.2** a *pKa* of  $3.21 \pm 0.05$  was determined for citric acid compared to  $3.63 \pm 0.12$  and a *pKa* of  $4.79 \pm 0.14$  was determined for acetic acid compared to  $4.90 \pm 0.04$ . This shows that both methods give comparable values of *pKa* although the glass electrode produces slightly lower values than that using the indicator dye. This is probably because the indicator is measuring the average interaction of the dye with the liquid whereas the

pH electrode is an interfacial measurement and can be affected by wetting of the interface by water.

Carboxylic	рКа	рКа	$\Delta p K a$
acids	indicator dye	(pH probe)	
Oxalic acid	$2.29 \pm 0.154$	$1.99 \pm 0.15$	0.30
Citric acid	$3.63 \pm 0.12$	$3.21 \pm 0.05$	0.42
Lactic acid	$3.93\pm0.030$	$3.84\pm0.032$	0.09
Acetic acid	$4.90 \pm 0.04$	$4.79 \pm 0.14$	0.07
Succinic acid	$4.36\pm0.072$	$4.16 \pm 0.21$	0.2
Butanoic acid	$5.18\pm0.014$	$4.97 \pm 0.17$	0.21
Malonic acid	$4.49 \pm 0.091$	4.16± 0.042	0.33

**Table 4.2:** Summary of equilibrium acidities in Ethaline obtained by indicator and potentiometric methods

It indicates that, *pKa* values found in DESs follow the same trend, for a weak acids with a relatively small  $\Delta pKa$  value, spectroscopic methods could be applied to determine the ionic character of those acids in DESs. Millan and co-workers used two different methods; the first one was an interpolation of data from the linear plot of *pKa* in ionic liquids and pKa in water and the second one was the Hammet –Taft approach to predict *pKa* values of N-based amines in ionic liquids. They reported that both methods provided good responses with some disparity between the two methods as seen here.<sup>43</sup>

Disparity in the *pKa* values depending on the method by which they were obtained was also observed in other in non-aqueous systems.<sup>44</sup> For example a study to determine the *pKa* of triflic acid in DMSO obtained a value of 1 by the potentiometric titration, -1 by a spectrophotometric method and a value of -2.7 by the NMR chemical shifts of the protons, showing significant variation in the extent of the association between a proton with a DMSO molecule and water. In general, chemical shift measurements show the closest correlation between data in water and DMSO whereas electrochemical methods show the largest variances.<sup>44, 45</sup> This shows that the differences in **Table 4.2** are not specific to this study and are relatively small compared to other investigations.

Doherty and co-workers used electrochemical methods, to determine the pKa of carboxylic acids in ILs. The potentiometric method was unsuccessful since no available acetate salt was sufficiently soluble in the ILs used.<sup>46</sup> While in the current method the pKa of acetic acid was successfully measured in Ethaline with a pKa of 4.83 which was higher compared to water.

#### 4.4.6 pH measurements of DESs -water mixtures

In the last few years several studies have investigated the properties of water/ DESs mixtures. Edler and co-workers found that the relative hydration of DESs can significantly influence the physical characterisation of DESs in water.<sup>39, 47</sup> The physical properties have been characterised as a function of water content.<sup>32, 46, 48, 49</sup> The influence of water on the proton activity and pH scales have not really been studied.

The inclusion of water in ionic liquid systems leads to a significant change in the physical properties including that of the proton activity. It is also a major factor affecting the dissociation of acids in catalyst systems applications since it should in principle be a more polar liquid and water acts as a better base than most anions of most ionic liquids. In the following section the pH of DES-water mixtures is characterized by measuring the emf of the glass electrode.

A recent study by Al-Murshedi has shown that water is not totally miscible with DESs. It was shown using NMR and electrochemical diffusional techniques that species diffuse faster in DES-water mixtures that would be expected from their bulk viscosity indicating that there were regimes of water. It was later proven using dynamic light scattering that the water phases were relatively large c.a. 100 nm. If this model is correct then acids will probably partition preferentially into the water phase which should significantly increase the dissociation of the acid. This process is shown schematically in **Figure 4.6**.



Figure 4.6: Schematic diagram showing potential behaviour of water in DESs

**Figure 4.7** shows the plot of pH versus the *Ecell* for Oxaline, Ethaline, Reline, Maline, Ciline, Glyceline and Emim HSO<sub>4</sub> as a function of water content. It can be seen that regular trend are found when the experimental pH values are changing related to the type of the anion used in ILs.

**Figure 4.7** shows that the trends in *Ecell* and the associated changes in pH do not all show the same trend with increasing water content. Water will have two effects on the *pH*; firstly it will make the liquid more polar and induce ionic dissociation, secondly it will dilute the acid and decrease the overall proton activity. For Oxaline the *Ecell* values decrease with water dilution showing that it becomes less acidic. By contract Maline increase *Ecell* when diluted with water. While this may seem counterintuitive it can be understood in terms of the heterogeneity of the liquids. If water is more miscible with the DES then it likely that the addition of water will have a smaller effect on the *pH*. Using Oxaline and Maline as examples; a decrease in *Ecell* with increasing water content could arise because the Oxaline is strongly hydrogen bonded to itself and less likely to partition into the water phase. The small amount that does is diluted by subsequent addition of water. By contrast, Maline is less strongly H-bonded to the chloride allowing it to mix more homogeneously with the water so the more water that is added the more it causes the acid to dissociate.



*Figure 4.7*: The Ecell for a glass electrode immersed in different DESs as a function of water content

Ethaline and Glyceline are relatively unaffected by water content. Although they form more homogeneous mixtures with water the proton activity is relatively low in both liquids. For Reline an increase in *Ecell* is observed with increasing water content. Reline is known to be slightly basic due to the release of ammonia from the decomposition of traces of urea during the synthesis. Reline forms the most heterogeneous mixtures with water so the addition of water just dilutes the ammonia in the water phase.<sup>50</sup> Mjalli *et al* studied the pH of Reline, they suggested that this DES is weakly basic. They also noted that when the system contains 1-3 wt% of water, the pH values decrease slightly (from 10.77 to 10.65) due to a partial solvation of basic sites.<sup>51</sup> It is not surprising because Abbott *et al* have been reported that Reline has significantly and unusual solvent properties when compared to most molecular solvents and are more typical of the properties observed for ionic liquids.<sup>52</sup>

In a comparable studies for binary IL-water mixtures, Han *et al.* investigated the degree of dissociation of ILs, namely [PF<sub>6</sub>],[Bmim][BF<sub>4</sub>], and [Bmim][CF<sub>3</sub>CO<sub>2</sub>] in solutions. They deduced that the organic solvents enhance the ionic association of ILs, the effect of

ionisation depending on the solvent dielectric constant, while water promotes dissociation significantly due to its high dielectric constant and its ability to form strong hydrogen bonds became stronger with trace amounts presences of water in ILs. <sup>53</sup> They found that the addition of water increased the pH of [Emim][HSO4] by more than 0.4 pH unit. The values are comparable to those for most imidazolium based ionic liquids. The pH are strongly affected by the water and hence the activity of the protons changing could be tailored for tailored application .<sup>49</sup> Rollet *et al.* used NMR spectroscopy to understand the water diffusion of hydrophobic ionic liquids as in 1-n-butyl-3- methylimidazolium bis(triflimide) [C4mim].<sup>32</sup>

The pH and the ability of water in these mixtures to form separate micro-phases could be responsible for some of the observations in biochemical and mineral processing applications e.g. the stability of enzymes in water DES mixtures.

#### 4.4.7 Non-aqueous pH electrode

It should be possible to construct a cell analogous to that shown above for an aqueous glass electrode using ionic liquids in the two reference cells. The first issue to be addressed is which redox couples to use as reference electrodes. While electrochemistry has been carried out in ionic liquids for more than 40 years most of the initial investigations used pseudo reference electrodes so as to decree the resistance of the cell. A silver wire pseudo reference electrode was commonly used as a reference electrode for pure ionic liquids systems,<sup>54, 55</sup> using a silver wire immersed straight into the solution. However, this reference potential cannot be considered as stable as the silver can be oxidised by more electronegative species in solution. A number of efforts have been dedicated to obtain ILs reference electrodes<sup>56, 57</sup> and miniature liquid-junction reference electrodes. <sup>58-60</sup> However, these attempts do not seem to be successful with regard to the stability and reliability in comparison with traditional reference electrodes having an internal solution, such as Hg/Hg<sub>2</sub>Cl<sub>2</sub>/aq. KCl.

Abbott *et al* have proposed the use of a Ag| AgCl(IL) ||Analyte reference electrode which is easy to prepare and very stable and reversible.<sup>61</sup> A cell was constructed made of two Ag| AgCl cells. A vycor glass membrane 8 mm thick was used as the glass membrane. The cell was constructed in the following way:

Ag| AgCl (a=0.1 mol kg<sup>-1</sup>) (Ethaline) || analyte ||<sub>2</sub> HOTf (a=0.1 mol kg<sup>-1</sup>) +0.1Ag OTf (Ethaline) | Ag (Cell 2)

This is the same as the aqueous glass electrode described above except that the redox couples are

$$Ag^+ + e^- \leftrightarrow Ag$$
 (4.5)

Rather than

$$\operatorname{AgCl}_{(s)} + e^{-} \leftrightarrow \operatorname{Ag} + \operatorname{Cl}^{-}$$

$$(4.6)$$

(Cell 2) was constructed with an inside solution containing 0.1 mol kg<sup>-1</sup> AgOTf and 0.1 mol kg<sup>-1</sup> AgCl both dissolved in 2 EG: 1 ChCl. The vycor frit was glued at the end of a glass tube to allow electrical and ionic conductivity between the bulk solution and the internal filling solution, while preventing chemical mixing of the solutions. Samples of trifluoromethanesulfonic acid (F<sub>3</sub>CSO<sub>2</sub>H) were prepared from (10<sup>-1</sup>, 10<sup>-2</sup>, 10<sup>-3</sup>, 10<sup>-4</sup>, 10<sup>-5</sup> and 10<sup>-6</sup>, 10<sup>-7</sup>) mol kg<sup>-1</sup> concentrations in Ethaline to measure those samples by chronopoteiometry. Triflic acid was chosen because of its ability to fully dissociate and to provide a proton activity of exactly 1 (*i.e.*unity) in the DES.

The *Ecell* values of the triflic acid solutions were measured as a function of concentration and the results are shown in **Figure 4.8** The *Ecell* values of two weak carboxylic acids, citric and succinic acid were also made up in the pH (3.0 to 3.6) and the results are also shown in **Figure 4.8**.

**Figure 4.8** shows the  $E_{cell}$  measurements of the electrode as a function of pHs. There is a linear trend in  $E_{cell}$  with acid activity for triflic but the slope of the line is much less than that observed in **Figure 4.5**. The slope of the calibration curve is only 14 mV decade<sup>-1</sup> which is considerably lower than that seen above and that of the theoretical Nernstian slope of 59 mV decade<sup>-1</sup>. Also, the values obtained for succinic and citric acid are considerably higher than those expected from the above study showing that there is an issue with the non-aqueous cell.



Figure 4.8: The open circuit potentials  $E_{ocp}$  of Ag/AgCl electrodes as a function of pH value of different acids in Ethaline

To test that it was not just a case of the reference couple the I<sub>2</sub>/I reference couple was substituted with one of the Ag| AgCl cells. The cell can be described as

Ag| AgCl (a=0.1 mol kg<sup>-1</sup>) (Ethaline)  $\|_2$  HOTf (a=0.1 mol kg<sup>-1</sup> +0.1Ag OTf (Ethaline) | I<sub>2</sub>/I<sup>-</sup> (a=0.1 mol kg<sup>-1</sup>) |Pt (Cell 3)

**Figure 4.9** shows the *Ecell* values for (Cell 3) with succinic and citric acids as analytes. The sensitivity of this cell is very low with only -1.4 mV decade<sup>-1</sup>. This clearly shows that the vycor frit is not enabling the cell to act as a sensitive potentiometric sensor. The most probable cause of this low sensitivity is the thickness of the glass membrane which is typically an order of magnitude thinner in practical sensors.<sup>62</sup> Buhlmann and co-workers confirmed that the large potential variations result from electrostatic screening of ion transfer through the frit due to the negatively charged surfaces of the glass. They also emphasised that the increasing of the pore size of the glass frit substantially decreases the sample dependence of the potential and improves the performance of an electrode. However, a disadvantage of larger pores is a more rapid intermixing of the reference and sample solutions due to higher flow rates through the frit, which can result in the contamination of test solutions.<sup>63</sup>



*Figure 4.9:* The open circuit potentials  $E_{ocp}$  of Pt electrode in  $I_2/I$  as a function of *pH* value of different concentrations of carboxylic acids in Ethaline

Since no suitable membranes were commercially available, an alternative cell was constructed by dismantling a commercial aqueous pH electrode and filling the two cells with suitable DES solutions and electrode couples. To demonstrate that a new glass electrode was made from the traditional aqueous Ag/AgCl glass electrode but with modification the electrode for using in DESs systems. The cell was prepared by filling the glass cell in the following way:

Ag| AgCl (a=0.1 mol kg<sup>-1</sup>) (Ethaline) || analyte ||<sub>2</sub> HOTf (a=0.1 mol kg<sup>-1</sup>) + Ag OTf 0. 1 mol kg<sup>-1</sup> (Ethaline) | Ag (Cell 4)

**Figure 4.10** shows the potentiometric response of the new non-aqueous glass electrode (Cell 4) for different DESs. The pH values for the DESs are those assigned using the aqueous glass electrode. This shows that the response of the all DES filled cell is similar to the aqueous glass electrode. Interestingly, the new pH electrode response is roughly of the Nernstian response slope of 59 mV. The offset in the potentials between the two cells is a combination of different liquid junction potentials. While the  $E^0$  values for equations 4.5 and 4.6 are different, because the two halves of the cell are the same reference cells they should not contribute significantly to the offset potential. The differences between both cells is illustrated in **Figure 4.11**.



Figure 4.10: Ecell for DESs as a function of pH for both the aqueous glass electrode and the non-aqueous (DES) glass electrode



*Figure 4.11:* The difference between the aqueous electrode and non-aqueous electrode

The fact that the all DES based pH electrode has a Nernstian response shows that the role of water is not overly important in controlling the performance of the cell. These potentiometric responses by the glass electrode in neat DESs show that it performs well in high ionic concentration liquids around 4 to 5 mol kg<sup>-1</sup> with near Nernstian responses to several DESs. This suggestion that ion exchange of the glass surface charge is possible

using a buffer solution of 2 M NaCl in Ethaline to equilibrate sodium ions in the glass. It also proves that water is not essential for the operation of the glass membrane.

## 4.4.8 Liquid junction potential

With ionic liquids in the pH electrode it is important to get an idea of the magnitude of the liquid junction potential arising when different ionic liquids/DESs are placed in contact with each other. An exact comparison of electrode potentials in various solvents will be impossible because of the unknown liquid junction potential.<sup>64, 65</sup>Liquid junction potentials arise when the two liquids at an interface have ions with different mobilities. This is particularly important when the ions are of significantly different size or mobility and so it is particularly the case where the pH is different on opposite sides of the liquid junction.

A number of efforts have been made in electrochemical studies to find a system electrode potential of which is the same in various solvents but a ubiquitous issue is still the definition of the electrode with the same activities of the constituents of the system.<sup>66, 67</sup> Although the use of the glass electrode as a reference electrode in potentiometric studies in water gives reproducible results, it nevertheless the glass electrode was found in DESs introducing an unknown liquid junction potential ( $E_{LJP}$ ) into the measurements.<sup>61</sup> A lack of reliable information about ionic mobilities in ionic liquids makes it difficult to calculate liquid junction potentials.<sup>9, 17, 26</sup>

To determine the LJP a dynamic and equilibrium method were used to measure the redox potential of a standard  $Ag^{+/0}$  couple in 0.01 mol kg<sup>-1</sup> AgCl in different DESs with reference to a reference electrode made from [Ag/ 0.1 M AgCl (Ethaline)]. Clearly when Ethaline is on both sides of the liquid junction the LJP will be 0 V.

Firstly, the potential was measured using cyclic voltammetry as shown in **Figure 4.12**. To be able to compare the voltammograms in different DESs the peak currents for silver stripping on the anodic cycle were normalised. Usually the peak currents would be different due to the differences in viscosity between these liquids. **Figure 4.12** shows a classical reversible deposition and stripping process for silver. The  $E_{cell}$  for the process is taken as the midway between the onset potential for the anodic and cathodic processes. The reduction potential for Reline is the most cathodic and that for Ethaline is the most anodic. This is understandable from the results shown in **Figure 4.10**. If two neutral ionic liquids were in contact, then the LJP would be dominated by the mobility of the two types

of ions in the respective liquids. This would be in part controlled by the sizes of the ions and in part by the viscosity of the liquids.<sup>32</sup>In an acidic liquid, the mobility of the proton would be much higher than that of a quaternary ammonium cation.

The LJP for Reline in contact with Ethaline is the largest due in part to the pH difference between them (c.a. 2) but also because there is an order of magnitude difference between their viscosities. Thus, the LJP also acts as an indicator of pH difference.



**Figure 4.12**: Normalised Cyclic voltammograms of 0.01AgCl in DESs at a 1mm Pt disk working electrode using Ag/AgCl (in Ethaline) reference electrode and at scan rate 5 mV.s<sup>-1</sup>in 20 °C.

It was noticed that the mobility of  $H^+$  has some issues experienced with the glass membrane it is possible that there could be artefacts associated with the the liquid junction potential (LJP) at salt bridge,  $\|_2$ . To demonstrate this, cells were constructed with different DESs in them. These were;

Ag| AgCl (a=0.01 mol kg<sup>-1</sup>) (DES1) 
$$\parallel_2$$
 AgCl (a=0.01 mol kg<sup>-1</sup>) (DES2) | Ag (Cell 5)

The chronopotentiometry measurements  $E_{ocp}$  of Ag/AgCl in Ethaline, Reline, Glyceline and Oxaline were measured against Ag/AgCl reference electrode in Ethaline and these were used to quantify the E<sub>LJP</sub> between the different DESs and the results are shown in **Figure 4.13**. **Table 4.3** also shows the liquid junction potentials,  $E_{LJP}$ , for those 4 DESs in contact with each other.



*Figure 4.13:* Chronopotentiometry measurements  $E_{ocp}$  of different DESs with Ag/AgCl reference electrode in Ethaline in 20 °C.

It can be seen that the  $E_{LJP}$  values increase with increasing acidity. Although all 4 DESs have the same ionic species (Ch<sup>+</sup> and Cl<sup>-</sup>) the proton will have a higher mobility than Ch<sup>+</sup> and this will set up an LJP as the migration of the proton will be easier than that of Ch<sup>+</sup>. In the oxalic acid-based DES proton activity will clearly be the largest and this has the most positive  $E_{LJP}$ . The urea-based DES is relatively basic due to traces of ammonia formed duing synthesis of the DES.

The chronoamperometric response also shows that the more viscous liquids take a longer time to reach an equilibrium potential whih is also not particularly surprising.

 Table 4.3: Cell potential of cell (5) where DES1 is Ethaline and DES is a n HBD:1

 ChCl

n HBD	1 Oxalic acid	2 EG	2 Glycerol	2 Urea
$E_{LJP}$ / mV	15.9 <u>+</u> 1.8	0.5 <u>+</u> 0.09	-9.8 <u>+</u> 0.41	-13.9 <u>+</u> 0.21

This is therfore an issue that needs to be addressed when using ionic liquids of different relative proton activities in contact with eachother e.g. with electrochemical reference

electrodes. It should however be noted that this is potentially another method of quantifying pH albeit less sensitive than cell 4.1.

# 4.5 pH scales of DESs and ILs

According to the electrochemical methods in this chapter, it is possible now to estimate and classify the acidity of different DESs and ILs. The quantitative information about the proton activity in DESs can be illustrated in **Figure 4.14**. The relative pH scale shows that the more acidic HBDs produce the more acidic DESs. Oxaline was the most acid while Reline was the most basic. However, the alcoholic HBDs Ethaline and Glyceline were relatively neutral with pH around 6.9 and 7.5 respectively. This is a significant result as the OH on the Ch<sup>+</sup> weaker associated than DESs formed form carboxylic acid and it seems true for Maline and Ciline as shown the **Figure 4.14**.



## Figure 4.14: pH values of variety DESs and ILs by electrochemical process

By comparing between the data in **figure 4.14** for pH values that obtained from glass electrode method with the pH values obtained from indicator method as shown in figure **3.13**. It was found that indicator method has less error bar than glass electrode method. However, both methods give comparable values of pH scales although the glass electrode produces slightly higher values than that using the indicator dye. This is probably because the indicator is measuring the average interaction of the dye with the liquid whereas the pH electrode is an interfacial measurement and can be influenced by wetting of the interface by water.

## 4.6 Conclusion

This chapter has shown that the pH of DESs and ILs can be determined using a glass membrane electrode. Surprisingly, it was shown that the response of a glass electrode was almost Nernstian in a DES with minimal water incorporated. The Nernstian slope increased as more water was added to the DES. It was proposed that the deviation from Nernstian response was possibly due to dehydration of the silica layer close to the solution interface. While the response was non-Nernstian it was nevertheless linear and gave pH values for an organic acid in a DES which corresponded to those observed in solution using the bromophenol blue indicator. A protocol was developed to ensure that the glass membrane was equilibrated with sodium ions between measurements. This ensured that cell potentials were reproducible with only small error bars on each reading. This equilibration also ensured that the electrode had a relatively short response time, reaching equilibrioum in approximaely 20 s. This was, however, considerably slower than an aquoeus glass electrode. It was also shown that the liquid junction potential in an electrochemical cell is pH dependent due to the preferential transport of protons compared to large organic cations.

A new, non-aqueous glass electrode was constructed by dismantling an aqueous glass electrode and filling the two cells with Ag/AgCl in Ethaline reference electrode. It was shown that this did have a Nernstian response showing that the glass membrane could function with only the traces of water naturally incorporated in the DESs.

The liquid junction potentials between different DESs were measured and it was found that these depended on the proton activity in the different DESs. The largest difference was between Reline and Oxaline. In the former the mobile cation is  $Ch^+$  where as in Oxaline the  $H^+$  ion has much greater mobility. Finally, the electrochemical method was developed to measure variety of DESs and ILs. It was shown that the major effect of the proton activity induced by the type of anion for ionic liquids act as a conjugated base in the liquid. The order of acidity is affected by the electronegativity of the anion, by the following order  $F^-$  > HSO<sub>4</sub> > Cl<sup>-</sup>> Ac suggesting some correlation with hydrogen bond strength.

The important discovery of this chapter is that the pH scale developed in this chapter is consistent with that shown in the previous chapter. The disparity between the two methods is also observed in aqueous solutions showing that it arises because one is a bulk analysis whereas the other is interfacial.

## 4.7 References

- 1. Z. Wang, H. Deng, X. Li, P. Ji and J.-P. Cheng, *The Journal of Organic Chemistry*, 2013, **78**, 12487-12493.
- 2. E. Bakker and M. Telting-Diaz, *Analytical chemistry*, 2002, **74**, 2781-2800.
- 3. A. K. Covington, *Ion-selective electrode methodology*, CRC press, 1979.
- D. J. Ives, G. J. Janz and C. King, *Journal of The Electrochemical Society*, 1961, 108, 246C-247C.
- J. Koryta, J. Dvořák and L. Kavan, *Principles of electrochemistry*, John Wiley & Sons Inc, 1993.
- 6. J. Wang, *Analytical electrochemistry*, John Wiley & Sons, 2006.
- 7. E. Gileadi and E. Gileadi, *Physical electrochemistry: fundamentals, techniques and applications*, 2011.
- 8. G. Gritzner and J. Kuta, *Pure and applied chemistry*, 1984, **56**, 461-466.
- 9. A. A. Isse and A. Gennaro, *The Journal of Physical Chemistry B*, 2010, **114**, 7894-7899.
- J. D. Neuss and W. Rieman III, *Journal of the American Chemical Society*, 1934, 56, 2238-2243.
- 11. M. Dole, J. Chem. Educ, 1980, 57, 134.
- 12. F. G. Baucke, in *Electrochemistry of Glasses and Glass Melts, Including Glass Electrodes*, Springer, Editon edn., 2001, pp. 35-268.
- 13. P. K. Glasoe and F. Long, *The Journal of Physical Chemistry*, 1960, **64**, 188-190.
- 14. T. Nakamura, Bulletin of the Chemical Society of Japan, 1975, 48, 1447-1451.
- 15. L. A. Pioda, V. Stankova and W. Simon, *Analytical Letters*, 1969, 2, 665-674.
- 16. H. Bach, F. K. Baucke and D. Krause, *Electrochemistry of glasses and glass melts, including glass electrodes*, Springer Science & Business Media, 2013.
- 17. H. Galster, *pH measurement: fundamentals, methods, applications, instrumentation*, VCH, 1991.
- D. J. Graham, B. Jaselskis and C. E. Moore, *Journal of Chemical Education*, 2013, 90, 345-351.
- 19. A. Abbott, G. Frisch, S. Gurman, A. Hillman, J. Hartley, F. Holyoak and K. Ryder, *Chemical Communications*, 2011, **47**, 10031-10033.
- 20. R. Kanzaki, H. Kodamatani, T. Tomiyasu, H. Watanabe and Y. Umebayashi, *Angewandte Chemie*, 2016, **128**, 6374-6377.

- 21. K. Cheng and D.-M. Zhu, *Sensors*, 2005, **5**, 209-219.
- 22. K. Izutsu, *Electrochemistry in nonaqueous solutions*, John Wiley & Sons, Weinheim, 2009.
- P. Spitzer and K. W. Pratt, *Journal of Solid State Electrochemistry*, 2010, 15, 69-76.
- J. I. Partanen and P. O. Minkkinen, *Journal of Solution Chemistry*, 1997, 26, 709-727.
- A. Avdeef, J. E. Comer and S. J. Thomson, *Analytical Chemistry*, 1993, 65, 42-49.
- 26. S. Rondinini, Analytical and bioanalytical chemistry, 2002, 374, 813-816.
- 27. M. Boström, V. S. Craig, R. Albion, D. R. Williams and B. W. Ninham, *The Journal of Physical Chemistry B*, 2003, **107**, 2875-2878.
- 28. D. Hubbard and R. G. Goldman, J Res Nat Bureau Standards, 1952, 48, 428-437.
- 29. N. Lakshminarayanaiah, *Membrane electrodes*, Elsevier, 2012.
- 30. H. Kahler and F. DeEds, *Journal of the American Chemical Society*, 1931, **53**, 2998-3012.
- A. Salis, M. Cristina Pinna, D. Bilanic<sup>\*</sup>ova, M. Monduzzi, P. L. Nostro and B. W. Ninham, *The Journal of Physical Chemistry B*, 2006, **110**, 2949-2956.
- C. D'Agostino, L. F. Gladden, M. D. Mantle, A. P. Abbott, I. A. Essa, A. Y. Al-Murshedi and R. C. Harris, *Physical Chemistry Chemical Physics*, 2015, 17, 15297-15304.
- I. M. Kolthoff, M. K. Chantooni Jr and S. Bhowmik, *Journal of the American Chemical Society*, 1968, 90, 23-28.
- I. Kolthoff and M. Chantooni Jr, *Journal of the American Chemical Society*, 1965, 87, 4428-4436.
- 35. I. Kolthoff and T. Reddy, *Inorganic Chemistry*, 1962, **1**, 189-194.
- 36. J. R. Jones, *ionisation of carbon acids [by] JR Jones*, 1973.
- 37. H. Hall Jr, *The Journal of Physical Chemistry*, 1956, **60**, 63-70.
- 38. T. Welton, *Chemical reviews*, 1999, **99**, 2071-2084.
- S. Khandelwal, Y. K. Tailor and M. Kumar, *Journal of Molecular Liquids*, 2016, 215, 345-386.
- 40. P. Wasserscheid and W. Keim, *Angewandte Chemie International Edition*, 2000, 39, 3772-3789.

- 41. K. Sarmini and E. Kenndler, *Journal of Biochemical and Biophysical Methods*, 1999, **38**, 123-137.
- 42. J. Reijenga, A. Van Hoof, A. Van Loon and B. Teunissen, *Analytical Chemistry Insights*, 2013, **8**, ACI. S12304.
- 43. D. Millán, M. Rojas, J. G. Santos, J. Morales, M. Isaacs, C. Diaz and P. Pavez, *Journal of Physical Chemistry B*, 2014, **118**, 4412-4418.
- 44. A. Trummal, L. Lipping, I. Kaljurand, I. A. Koppel and I. Leito, *The Journal of Physical Chemistry A*, 2016, **120**, 3663-3669.
- 45. C. D. Ritchie and R. E. Uschold, *Journal of the American Chemical Society*, 1967, 89, 1721-1725.
- S. Wang, J. Liu, R. Hembre, S. Barnicki, P. Goodrich, T.-L. Hughes, D. W. Rooney, C. Sink, J. Jacquemin and C. Hardacre, *Journal of Chemical & Engineering Data*, 2017, 62, 653-664.
- 47. O. S. Hammond, D. T. Bowron and K. J. Edler, *Angewandte Chemie*, 2017, **129**, 9914-9917.
- 48. C. R. Ashworth, R. P. Matthews, T. Welton and P. A. Hunt, *Physical Chemistry Chemical Physics*, 2016, **18**, 18145-18160.
- 49. J. E. Reid, R. J. Gammons, J. M. Slattery, A. J. Walker and S. Shimizu, *The Journal of Physical Chemistry B*, 2017, **121**, 599-609.
- 50. E. Durand, J. Lecomte, B. Baréa, G. Piombo, E. Dubreucq and P. Villeneuve, *Process Biochemistry*, 2012, **47**, 2081-2089.
- 51. M. A. Kareem, F. S. Mjalli, M. A. Hashim and I. M. AlNashef, *Journal of Chemical & Engineering Data*, 2010, **55**, 4632-4637.
- 52. A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chemical Communications*, 2003, 70-71.
- 53. W. Li, Z. Zhang, B. Han, S. Hu, Y. Xie and G. Yang, *The Journal of Physical Chemistry B*, 2007, **111**, 6452-6456.
- 54. C. Bonnaud, I. Billard, N. Papaiconomou, E. Chainet and J. Leprêtre, *Physical Chemistry Chemical Physics*, 2016, **18**, 8148-8157.
- G. Inzelt, in *Handbook of Reference Electrodes*, Springer, Editon edn., 2013, pp. 331-332.
- 56. A. Van Den Berg, A. Grisel, H. Van Den Vlekkert and N. De Rooij, *Sensors and Actuators B: Chemical*, 1990, **1**, 425-432.

- 57. G. Snook, A. Best, A. Pandolfo and A. Hollenkamp, *Electrochemistry Communications*, 2006, **8**, 1405-1411.
- H. Suzuki, T. Hirakawa, S. Sasaki and I. Karube, *Analytica chimica acta*, 1999, 387, 103-112.
- M. A. Nolan, S. H. Tan and S. P. Kounaves, *Analytical Chemistry*, 1997, 69, 1244-1247.
- 60. D. Diamond, E. McEnroe, M. McCarrick and A. Lewenstam, *Electroanalysis*, 1994, **6**, 962-971.
- 61. A. P. Abbott, G. Frisch, H. Garrett and J. Hartley, *Chemical Communications*, 2011, **47**, 11876-11878.
- 62. F. Helfferich and J. Dranoff, Pergamon, Editon edn., 1963.
- 63. M. P. Mousavi, S. A. Saba, E. L. Anderson, M. A. Hillmyer and P. Bühlmann, *Analytical Chemistry*, 2016, **88**, 8706-8713.
- 64. R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorganic Chemistry*, 1980, **19**, 2854-2855.
- 65. E. Bakker, *Electroanalysis*, 1999, **11**, 788-792.
- 66. I. Kolthoff and F. Thomas, *The Journal of Physical Chemistry*, 1965, **69**, 3049-3058.
- 67. I. Nelson and R. Iwamoto, *Analytical Chemistry*, 1963, **35**, 867-871.

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#### Chapter 5: Effect of pH on process thermodynamics and kinetics

#### 5.1 Introduction

In the previous chapters two methods have been used to establish a measure of proton activity in ionic liquids and DESs. While both methods give values which are similar, there is a difference in the absolute values of 0.2 to 0.5 pH units. Numerous processes have been investigated in DESs where the extent of an equilibrium process or the kinetics of the reaction are dependent on the pH. These include; the dissolution of metal oxides,<sup>1</sup> esterification reactions,<sup>2</sup> biochemical processes,<sup>3</sup> for the synthesis of zeolites<sup>4</sup> and polymerisation reactions.<sup>5-10</sup> In this section the methods developed in the previous chapters are used to determine whether the pH values can be used to interpret solution phase data about processes in DESs.

Most chemical processes involve the transfer of a proton and so pH plays an important role in controlling process thermodynamics and kinetics.<sup>11</sup> pH can affect the equilibrium of a process and hence the thermodynamics. Protons may also be involved in the rate determining steps of reactions and so they may change the overall rate of a reaction. In this chapter two processes will be investigated to see if the data in different DESs fit the pH data collected in the previous two chapters.

In the first of these two processes the effect of pH on the solubility of metal oxides in DESs will be determined. This is clearly an equilibrium process and will depend on the protonation of the oxide forming a charged species which can be solvated. The second process will involve the polymerisation of aniline to create the conducting polymer polyaniline. This has been studied previously in the group and has been found to only proceed in acidic solutions although this was a qualitative analysis and the aim in this study is to correlate polymer growth kinetics with solution pH.

## 5.2 Metal oxide solubility in DESs

Hydrometallurgy is essential to many industrial processes and produces large volumes of aqueous waste. These are usually acidic and basic and involve large amounts of energy and chemicals to treat them. They are one of the largest sources of metal-based emissions into the environment. Many groups have used ionic liquids and DESs as alternative media for metal dissolution, extraction and recovery.

Metal oxides have different degrees of ionic and covalent character but to dissolve in polar media they need to form charged species so that the solvation enthalpy will be larger than the lattice energy. Many metal processes use molten salts at high temperatures e.g. for recovery of metals like Li, Na, Ti and Al.<sup>12-14</sup> While high temperature molten salts have high conductivities, wide potential windows, low viscosities and high solubilities for metal salts they do have the difficulties of being difficult to process and have a high energy input requirement.

The initial interest in digestion of metal oxides in ionic liquids was associated with the digestion of uranium oxide in imidazolium chloride: AlCl<sub>3</sub> eutectic mixtures.<sup>15</sup> The solubility was about 10 mM in Lewis basic melts and the oxide was converted into  $[UO_2Cl_4]^{2-}$  in solution. Imidazolium PF<sub>6</sub> was used to extract zinc from phosphors extracted from discarded light fixtures.<sup>16</sup> Fundamentally, ionic liquids on their own are not particularly successful for the digestion of metal oxides as the anion is poor at forming an ionic complex with many metal oxides. The liquids used to date have also been either very expensive or water sensitive. Notwithstanding, ionic liquids have been studied extensively in the area of solvent extraction of metal ions from aqueous solutions. The general area of metal processing has been covered in several reviews.<sup>17</sup>

While ionic liquids with discrete anions are not particularly good at dissolving metal oxides, DESs have significantly better solubility. Abbott *et al.* studied the solubility of 17 metal oxides in three deep eutectic solvents. They are more practical of metal oxide dissolution than ionic liquids with discrete anions as they are easier to produce on a large scale. The acidity can be tuned by changing the hydrogen bond donor as shown in Chapters 3 and 4. Metals can be recovered from mixed metal oxides using electrochemistry and cementation.<sup>18, 19</sup> **Figure 5.1** shows the solubility of 10 metal oxides in 3 DESs and compares the results to those obtained in HCl.



*Figure 5.1*: Solubility of metal oxides in three DESs and HCl.<sup>1</sup>

In **Figure 5.1** it can be seen that in most cases the metal oxide solubility is in the order  $HCl > Maline > Ethaline \approx Reline$ . This matches roughly the pH of the solutions but clearly correlation is difficult with only 4 liquids and without a measure of pH. Classical models for solubility rely on a knowledge of the solution species and until recently little was known about the speciation of the metals dissolved in DESs. Speciation depends on main factors including the Lewis and Brønsted acidity/Basicity of the DES anion, the metal oxide and the hydrogen bond donor. Speciation has recently been studied using EXAFS, Raman, FAB-MS and UV-Vis spectroscopy and the results in ionic liquids and DESs are discussed in two reviews.<sup>18, 19</sup>

The way in which metals are solvated is poorly understood but Kobrac used information about liquid structure to explain dynamics, and solvation in ionic liquids.<sup>17</sup> Other groups have attempted to model solubility using polarity parameters,<sup>20, 21</sup> and these have been satisfactory for strongly hydrogen bonding ionic liquids.<sup>22</sup> Polarity parameters are better at predicting the properties of Brønsted acidity rather than Lewis acidity.

## 5.2.1 Solubility of metal oxides in DESs

A recent study by Pateli at the University of Leicester has studied the solubility of various metal oxides in a range of DESs. The data were collected on 5 DESs at 60 °C using ICP-MS to measure the saturation concentration of metal in DESs. These data are shown in **Table 5.1**.

Compound	Reline	Ethaline	Lactiline	Maline	Oxaline	HCl
pH	(8.91)	(6.89)	(3.1)	(2.39)	(1.32)	(0.74)
Fe <sub>2</sub> O <sub>3</sub>	7.7	7	465	858	1116.9	10523
Fe <sub>3</sub> O <sub>4</sub>	1	5	541	596	1675.3	22403
ZnO	604	233	822	713	645	63896
PbO	541	10	194	779	1262	
PbO <sub>2</sub>	366	15	168	497	1249	
CuO	23.7	69.8	556.7	-	637	52047
Cu <sub>2</sub> O	209.7	382.8	-	-	630	53942

**Table 5.1**: Solubility of metal oxides in ppm for five DESs of differing pH measuredafter 2 days digestion at 60 °C

**Table 5.1** shows that the solubility is in good agreement with the data previously reported using ICP-OES.<sup>1</sup> The previous study had investigated the solubility in Reline, Ethaline and Maline and had shown that the solubility of the oxides in Maline showed some correlation with the solubility in 0.18 M aqueous HCl.<sup>1</sup>It also showed that the solubility of different metal oxides was related to the charge density on the metal. In **Table 5.1** data show that solubility are higher in more acidic DESs which is understandable for some of the metal systems. For metal oxides such as copper oxide UV-vis spectroscopy coupled with EXAFS shows that the dissolution of CuO leads to the tetrachloro cuprate ion<sup>1, 23</sup> i.e.

$$CuO + 4H^{+} + 4Cl^{-} \leftrightarrow CuCl_{4}^{2-} + 2H_{2}O$$
(6.1)

The speciation of other metals is less obvious and EXAFS shows that many of the metals, particularly the more oxophillic metals contain oxygen donating ligands making the equilibria less easy to define.

**Figure 5.2** shows the solubility of the metals as a function of pH. Metal solubility as a function of pH is an important topic, not only for the recovery of metals from ores, but also for the mobility of metals from waste sites. The leaching of heavy metals such as lead and cadmium in soils have been studied in depth but is not directly comparable to this study due to the presence of numerous complexing agents in organic matter. <sup>24, 25</sup> Higher temperature studies of metal oxide solubility in water (subcritical) have been reviewed by Ziemniak and these also show a strong pH dependency. <sup>26</sup>The only directly comparable results were those carried out by Abbott et al.<sup>1</sup>



*Figure 5.2*: log solubility vs  $pH(-log_{10}[H^+))$  for the data in table 5.1

**Figure 5.2** shows log solubility vs pH ( $-\log_{10}$  [H<sup>+</sup>]) for the data in **Table 5.1**. There is some correlation for most metal oxides as would be expected but there are also some deviations which explains specific interactions between the metal and HBD. In the acidic liquids there is a relatively good correlation between hydrogen ion concentration and solubility for most metal oxides. This shows the importance of the proton in formation of a charged species for dissolution. For ZnO the solubility decreases in the order lactic acid > malonic acid > oxalic acid. This is probably because Zn is very oxophillic and oxalic acid forms a strong complex with Zn which precipitates zinc oxalate. The anomalous behaviour of PbO<sub>2</sub> in Ethaline has also been observed previously for V<sub>2</sub>O<sub>5</sub> and CrO<sub>3</sub>.<sup>1</sup> These metal oxides are strongly oxidising and react with Ethaline to form a Pb<sup>II</sup> species which shows a higher solubility than expected.

This study shows that the pH data obtained in the previous chapters are in agreement with metal oxide solubilities obtained in previous work in the group. They also highlight anomalies which can be explained through specific metal-ligand interactions. This is very important to work within the group on ionometallurgy which is looking for specific metal – HBD interactions to separate metals from mixtures.

In Ethaline and Reline there is a 3 order of magnitude diffrence in the solubilities of the metal oxides compared to Oxaline where the solubilities are all roughly the same order

of magnitude. In Oxaline the proton dominates the speciation of the soluble species whereas in Ethaline and Reline the solubility is controlled by the HBD.

## 5.3 Conducting polymers

The second topic investigated in this chapter is the kinetics of conducting polymer formation in DESs. This has recently been studied by Ismail and it was shown that qualitatively the rate at which polyaniline formed could be changed by adding different acids to DESs. This section will quantify the pH of these and related systems and attempt to confirm the role of solution pH in the mechanism of polymer formation.

Polymers are produced by the reaction of bi- or poly-functional molecules to form chains or networks.<sup>27, 28</sup> Most polymers are good electrical insulators due to the saturation of the polymer backbone. However, in 1977 Heeger *et al.* <sup>29</sup> reported the first synthesis of a polymer which was electrically conducting.<sup>30</sup> The first material was a polymer consisting of alternating single and double bonds i.e. *polyacetylene*, which was prepared chemically from acetylene **Figure 5.3**.



Figure 5.3: Structure of polyacetylene

However, conjugation in itself was not sufficient to enable charge transfer. To allow the motion of charges, the material needs charge carriers which are introduced through either oxidation or reduction of the material which is a process known as *doping*.

For a current to flow along the polymer chain one or more electrons need to be removed or inserted. For polyacetylene this was initially done using chemical doping as shown below;

Oxidation with a halogen (*p*-doping):  $[CH]_n + 3x/2 I_2 \rightarrow [CH]_n^{x+} + x I_3^{-1}$ 

Reduction with an alkali metal (*n*-doping):  $[CH]_n + x \text{ Na} \rightarrow [CH]_n^{x-} + x \text{ Na}^+$ 

The electrons in the  $\pi$ -bonds can move rapidly along the molecule chain when an electrical field is then applied across the material. The doped polymer is a salt but it is not an ion conductor, but rather it is an electron conductor. Polyacetylene is, however, not particularly stable and it readily degrades in air. An alternative way of making conducting polymers is by polymerising heterocyclic compounds and the three most common families of conducting polymers are polypyrroles, polythiophenes and polyanilines the structures of which are shown in **Figure 5.4**. These are easily made, usually by electrochemical oxidation or reduction and the monomers are easily chemically modified and substitutes to make a variety of materials with useful properties and applications.



*Figure 5.4: Structures of a) polyaniline b) polypyrrole and c) polythiophene* 

The conductivity of a conducting polymer (CP) depends on the doping density and so it can be varied to be intermediate between those of a conductor and an insulator as shown in **Figure 5.5**.<sup>31</sup>



*Figure 5.5:* Showing the comparison between the conductivity of CPs with other materials

One of the most widely studied conducting polymers is polyaniline (PANI).<sup>32</sup> PANI is conjugated compound, i.e. it contains of  $\pi$  electron delocalisation along the polymer backbone giving them the optical and electrical properties of semiconductors.<sup>33</sup>

PANI is generally formed by the electrochemical polymerisation of aniline in acidic aqueous solutions by the mechanism shown in **Figure 5.6**.



Figure 5.6: Mechanism of polyaniline formation

The polymerization of a cyclic monomer depends on both thermodynamic, and kinetic factors, one of which is the pH of the solution.<sup>34</sup> The pH plays an important role in the modification of the redox properties of PANI and the changes in the electrical and optical properties. At a high pH (less acidic solution), the conductivity of PANI is decreased and the polymerisation of aniline is inhibited.<sup>35-37</sup> A sufficiently low pH is required to help solubilize the aniline monomer in water and to avoid excessive branching of the growing chain.<sup>38</sup>

## 5.3.1 Mechanisms of proton transport

The mechanism of proton transfer and charge transfer across the film/solution interface of conducting polymers is also an important aspect in electrochemical systems.<sup>39-41</sup> A considerable amount of work has been carried out on the effect of charge transfer in the PANI redox switching mechanism depending on the pH value of the solution.<sup>33, 42, 43</sup> It has also been reported that an acidic medium is an essential condition for PANI synthesis.<sup>37</sup> The influence of pH on the electrochemical synthesis of PANI film in aqueous acid solutions has been reported by Pei *et al.* They found that aniline is electro polymerized mainly at the polyurethane-platinum interface, which is strongly acidic even in a basic electrolyte solution due to the strong limitation of the polyurethane layer of the PU/Pt electrode on the diffusion of H<sup>+</sup> released during the reaction and OH<sup>-</sup> in the bulk electrolyte solution through the polyurethane layer. The rate of polymerization increased with an increase in pH from 1 to 13.7. <sup>42</sup>



*Figure 5.7:* Mechanism of protonation and redox reactions between the various forms of polyaniline in different pHs.

The nature of the anions has an important effect on the rate of the aniline oxidation reaction and consequently on the rate of growth of the PANT film. The aniline oxidation reaction is pH dependent in solutions of pH < 2 in which protonated aniline species react. The oxidation is accompanied by the loss of protons. While at higher pH values non-protonated aniline species participate in the oxidation reaction, which is not pH dependent. PANI can be synthesized over the whole pH region provided that a suitable anion is present. The growth of the PANI film is facilitated by a medium of higher conductivity, which at pH < 3 is a protonated polyaniline, and in a solution of high pH is the solution of the supporting electrolyte. There is a different mechanism of PANT film growth involved depending on the pH of the solution. At pH > 4 there is evidence of a progressive nucleation process which protonated aniline species react. The oxidation is accompanied by the loss of protons.

In aqueous solutions the unprotonated and partially protonated forms of PANI have different redox behaviour at different potentials and this in turn affects the optical properties of the materials. **Figure 5.7** shows the summarised of the speciation mechanism for PANI in different acidic solutions.

The electrical properties of PANI prepared in aqueous media of different acidities have been reported quantitatively in the literature. It was found that the conductivity of PANI is strongly affected by the oxidation state as well as the degree of protonation, while other conductive polymers are affected by their oxidation state alone.

The conductive of PANI films have been prepared in solutions of different acidities .it was found that the quality of films and their doping levels are much better controlled when they are prepared under acidic conditions pHs less than 4, it showed a high average conductivity of  $(4.9 (1.3) \times 101 \text{ S/cm})$ . While, when PANI films prepared at higher pHs having a compact structure with large grains show lightly doped semiconducting properties, and the average conductivity of the doped PANI films prepared at pH 5.0 was found around  $(1.54 (0.09) \times 10-4 \text{ S/cm})$ . the degree of protonation of the monomers and the polymerization properties are affecting the chemical structure of the PANI as well as their conductivities and morphologies.<sup>37</sup>

**Figure 5.8** shows an example of a cyclic voltammogram for the formation of PANI in HCl. It shows three redox processes which correspond to three redox states. The intensity of each of these peaks depends on the pH of the solution.



*Figure 5.8*: An example of the change in the potential of the second redox reaction with pH polyaniline film on a platinum electrode in 1 M HCl at a scan rate 0.1 V s<sup>-1</sup> by cyclic voltammogram.<sup>5</sup>

The formation and cycling of a conducting polymer in a non-aqueous systems is more difficult to understand as the meaning of pH in these types of media is not well
established.<sup>35</sup> A number of studies have shown that the type of the liquid influences the growth mechanism of the polymer.<sup>41, 42, 45-48</sup>

The delocalized, positively charged free radicals were found to be the main source of conduction in polyaniline. It was previously found that the maximum conductivity was obtained when the number of radical cations in the polymer chains is maximized. This is illustrated by the fact that leucoemeraldine and pernigraniline (neither of which contains free radicals) are completely insulating.<sup>48</sup> It is possible to produce a conducting polymer in non-aqueous solvents when nucleophilic attack of OH<sup>-</sup> on the radical cation is inhibited. Valle *et al* found that the acidity of non-aqueous solvents can effect on the polymer films formed and ion pairing between the anion of the electrolyte and the anilinum species can be directly impact on the stability of the monomer.<sup>47, 49, 50</sup>

The behaviour of PANI in DESs is of interest due to its ability to act as an electrode material in a rechargeable battery. Although lithium batteries are widely used in a wide variety of applications due to their high energy density, alternatives are sough which have lower cost and increased safety (Lithium batteries can combust if they get wet). Ryder *et al.* have created batteries of the form

Zn| ZnCl<sub>2</sub> in DES, H<sup>+</sup> | PANI

Which show good cyclability and relatively high energy densities.

Ismail studied the polymerisation of polyaniline in DESs in detail and compared the results with those obtained in aqueous solutions. **Table 5.2** shows the polymer coverage of PANI grown in aqueous solutions of different pH and it can be seen that films grown under identical conditions grow faster in more acidic solutions.

Polymer		Coverage $\Gamma$	Thickness	pH of Anodic current		Anodic		
growth		mol cm <sup>-2</sup>	of polymer	solution with	(i /µA)		potentials (V)	
from 1 M			nm	0.2 M aniline	Ι	II	Ι	II
a	$H_2SO_4$	1.167×10 <sup>-6</sup>	905	0.27	320	324	0.26	0.87
b	HC1	4.00×10 <sup>-7</sup>	310	0.5	122	125	0.26	0.85
c	HNO <sub>3</sub>	1.383×10 <sup>-7</sup>	107	0.6	54	55	0.25	0.84
d	$HClO_4$	5.77×10 <sup>-8</sup>	45	0.7	11	13	0.23	0.84

*Table 5.2:* PANI growth as a function of aqueous electrolyte type.<sup>5</sup>

The study by Ismail showed that not only was the thickness deposited affected by pH but there was also a significant change in the PANI morphology; sulfuric acid has a porous structure whereas perchloric acid was a more dense structure.

Taking a PANI film grown in sulfuric acid and cycling it in a DES (Ethaline) cause the charge to decrease significantly. The charge could, however, be restored by cycling in sulfuric acid again as shown in **Figure 5.9**.



**Figure 5.9:** a) Cyclic voltammogram for the preparation of PANI film ( $\Gamma = 1.58 \times 10^{-4}$  mol cm<sup>-2</sup>) deposited potentiodynamically from 0.8 M aniline /1 M H<sub>2</sub>SO<sub>4</sub> (-0.2 V to 1.0 V; 100 mV s<sup>-1</sup>); b) PANI film exposed to the electrolytes (monomer free) 0.5 M H<sub>2</sub>SO<sub>4</sub>, Ethaline, and 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively, at a scan rate of 100 mV s<sup>-1</sup>; cycles 1 and 20 are shown.<sup>5</sup>

Ismail used EQCM to determine the mobile species going into an out of the film on cycling in the aqueous and DES electrolytes. It was found that in the DES the large sizes of the ions precluded the movement of charges between the polymer and the electrolyte and this resulted in the reduced charge on cycling. The mechanism was proposed to be that shown in **Figure 5.10**.



*Figure 5.10:* Schematic representation of PANI oxidation in a) H<sub>2</sub>SO<sub>4</sub> and b) *Ethaline* 

Ismail also studied the growth of PANI in different DESs. It was shown that PANI could not be grown in Ethaline unless aqueous sulfuric acid was added. At lower aniline concentrations a weakly adherent film was formed and thick adherent deposits (similar to those obtained using sulfuric acid) were only obtained when the aniline concentration was increased to 0.8 mol dm<sup>-3</sup>. It was, however possible to grow PANI in Oxaline and in Ethaline to which 3 mol dm<sup>-3</sup> of anhydrous oxalic acid had been added. From this it was concluded that the pH of the solution was important in controlling the growth of PANI.

Valle *et al* studied the effect of adding water on the polymerisation of PANI in DESs.<sup>51, 52</sup> The conductivity and growth of the polymer was significantly improved by addition of 10% water in DESs.

Ionic liquids with discrete anions have been used for the electropolymerisation of conducting polymers. These liquids have high chemical and thermal stabilities, suitable ionic conductivities, and low volatilities which makes them promising candidates for development of polymeric materials.<sup>53, 54</sup> 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [EmimCF<sub>3</sub>SO<sub>3</sub>]<sup>55</sup> and 1-ethylimidazilium trifluoroacetate [Emim Tfa]<sup>56</sup> have been used for the electropolymerization of PANI and have produced films with good stability.<sup>57-59</sup> It should be noted that all of these studies added aqueous acid (typically HCl) to the solution to an approximate concentration of 1 M.

In this chapter some of the work of Ismail is repeated using exactly comparable conditions in DESs and aqueous solutions. The pHs of the DESs are determined with and without aniline which is clearly important as it will act as a base in the DES. The effect of pH on polymerisation kinetics was determined by measuring the charge after a given number of cycles. The main goal of this work will address the developed method for measuring a pH of solutions and will address the effect of additive water to understand the charge and mass transport for successfully employed polymerisation process. This clearly will provide better idea of the factors affecting the polymer process in aqueous and non-aqueous solutions.

## 5.4 Results and Discussion

#### 5.4.1 Effect of pH on PANI growth from aqueous media

The first part of the study was to categorise the effect of pH on PANI growth in aqueous sulfuric acid solutions. Ismail had shown recently that irrespective of whether it is grown in aqueous solutions or DESs, the charge on the anodic or cathodic scan is a good indicator or the thickness or amount of the PANI film which has been deposited. <sup>60, 61</sup> This was achieved by preparing a range of sulfuric acidic solutions of (1, 0.1, 0.01 and 0.001 mol. dm<sup>-3</sup>) with 0.2 mol dm<sup>-3</sup> of aniline in aqueous solution. The cyclic voltammograms of the sample tested is shown in **Figure 5.11**.

**Figure 5.11** shows that the overall shape of the cyclic voltammograms and the charged passed for both oxidation and reduction are different in different pH solutions. At the low pH values, The charge for oxidation is larger than at higher pH which is in agreement with previous studies.<sup>62,63</sup> **Figure 5.12**, shows a plot of pH  $vs Q^+$  after 15 scans over the same potential range at the same sweep rate. As expected there is a roughly linear increase in charge passed with pH. It also suggests that the conducting polymer will not grow when the pH is higher than 3.5 which corresponds to practical observation. This then explains the observations of Ismail that PANI did not grow in Ethaline pH = 6.89 without any added aqueous acid but it was observed to grow in Oxaline pH = 1.32.



**Figure 5.11:** Cyclic voltammograms of 0.2M aniline recorded at 0.5mm Pt electrode in aqueous  $H_2SO_4$  at different concentrations a) 1 M b) 0.1 M c) 0.01 M d) 0.001 M at 20 mV/s and 20 °C.

The shape of the voltammograms also explains the role of the counter-ion in controlling the polymerisation. In the more concentrated acid there is a high concentration of  $HSO_4^-$  which favours the production of the more oxidised species so the chain can carry a higher charge. In the pH 3 solution the concentration of anions is relatively low and so it is difficult for the chain to carry significant charge. The correlation between the Q+ charges of the PANI formed after 15 scan rate and the pH values is roughly an exponential relation although, there is no physical basis for this observation as shown in **figure 5.12**.



Figure 5.12 : The correlation between the pH scale cycles of the aniline mixture in NaCl with Q+ charge of the PANI formed after 15 scan rate at 20 mV/s.

**Figure 5.12** also ties in with the results found by Ismail and shown in table 5.3 and with other studies carried out in aqueous systems.<sup>30, 48, 64</sup> Unfortunately, aqueous solution have limited electrochemical potential windows<sup>58</sup> and this affects the lifetime and performance of the film when repeatedly cycled, particularly under high charging currents. For instance, PANI can electrochemically degrade after only a few cycles in some aqueous electrolytes because of nucleophilic attack on the polymer.<sup>45</sup>

In non-aqueous solutions, PANI has been found to be more stable and has been used for devices such as capacitors, batteries, ion switching devices and electrochromic devices.<sup>56, 65</sup> For example, propylene carbonate has been used with lithium salts to enhance the performance of polyaniline in electrochemical actuators. Propylene carbonate has a relatively high boiling point 241.7°C, with a relatively wide electrochemical window (– 1.9 to +1.7 V) *vs.* SCE, high dielectric constant 64.4 and high ionic conductivity with dissolved lithium salts (0.1 to 1.0 mS/cm).<sup>66</sup> This study shows that the pH affects polymer growth, but changing the acid concentration also affects the anion concentration. It would therefore be useful to measure the effect of pH when the anionic and cationic strength were kept constant in a way they would be kept in an IL or DES. To test this, the above experiments were repeated with a constant 1.0 mol dm<sup>-3</sup> of NaCl in the aqueous solution.

**Figure 5.13** shows the cyclic voltammograms of 0.2 mol dm<sup>-3</sup> of aniline obtained using aqueous sulfuric acidic solutions of different concentrations (0.1, 0.01 and 0.001 mol. dm<sup>-3</sup>) each with and 1 mol.dm<sup>-3</sup> NaCl in solution.



*Figure 5.13:* Cyclic voltammograms of 0.2M aniline recorded at 0.5mm Pt electrode in aqueous H<sub>2</sub>SO<sub>4</sub> + 1 mol.dm<sup>-3</sup> NaCl at different concentrations a) 0.1 M b) 0.01 M c) 0.001 M. Comparison of scan 5 for the different solutions at 20 mV/s and 20 °C d)No NaCl, e) 1M NaCl.

At low pH values the CV for polyaniline growth looks similar whether there is NaCl present or not, however at 0.01 and 0.001 mol.  $dm^{-3}$  H<sub>2</sub>SO<sub>4</sub> the shape of the voltammogram changes considerably when NaCl is added compared to when it is absent. The addition of NaCl means that the shape of the voltammogram remains constant and only the total charge decreases slightly when the pH increases. In the absence of NaCl the total charge decreases more significantly with pH but the signal for the pernigraniline formation decreases slightly. This is logical as it requires the PANI film to be more highly oxidised which in turn requires anions to balance the charge on the polymer backbone. Adding NaCl ensures that there are sufficient anions to balance the charge formed through oxidation.

This suggested that it is not only the pH that is important to growth of polyaniline, but the anion concentration is also a vital to aid growth of the polyaniline film. In a DES, the anion concentration should be roughly constant and so it is important to compare the trend in PANI charging in a DES with that in aqueous solutions with a high electrolyte concentration.

In the same context, Nyholm *et al* used with different sodium chloride and aniline in different pHs range (1-9) to investigate the influence of the buffer capacity of the electrolyte on the electroactivity of PANI.<sup>67</sup> It is commonly assumed that the oxidation of leucoemeraldine is associated with an expulsion of protons at low pH values and incorporation of anions at higher pH values while the oxidation of emeraldine is associated with an expulsion st form pernigraniline. This is also in agreement with the findings of Odin *et al.*<sup>68</sup>

Figure 5.12 shows the correlation of the oxidative charge  $Q_+$  with pH in aqueous solutions with and without NaCl. In all cases the addition of NaCl increases the oxidative charge (in this case after 15 scans) by two to three times. This shows that the pH dependency of PANI film growth is quite complex and has a significant anion contribution.<sup>69</sup>

#### 5.4.2 Effect of pH on PANI growth from non-aqueous media

In this section the electropolymerization of aniline was studied in Oxaline, Ethaline, Glyceline and Reline with the addition of sulfuric acid and with the addition of 10 wt %

water. The aim is to determine the pH of these liquids and to use these data to measure the effect of pH on the growth of the polymers.

The rate of electropolymerization of aniline is clearly affected by the concentration of the monomer and the concentration of acid as shown in the previous section, but more specifically it will be dependent on the concentration of the species at the electrode-solution interface. This means that the mobility of species in the liquid will be important and this is affected by the viscosity of the liquids. Ismail showed that the addition of sulfuric acid to DESs did not significantly affect the viscosity of the mixture as it was made up from 18 M sulfuric acid which is in itself quite viscous. (25 cP at 25 °C).

**Table 5.3:** *pH* values of variety mixtures of DESs, 1M H<sub>2</sub>SO<sub>4</sub> and 0.2 M aniline (\*without H<sub>2</sub>SO<sub>4</sub>).

DESs	рН	pH with 1 M H <sub>2</sub> SO <sub>4</sub> without aniline	pH with 1 M H <sub>2</sub> SO <sub>4</sub> with 0.2M aniline	Viscosity /cP
Ethaline	6.89	$0.86\pm0.091$	$0.98\pm0.048$	48
Glyceline	7.48	$0.89\pm0.075$	$1.01\pm0.026$	446
Reline	8.91	$1.93 \pm 0.013$	$2.05 \pm 0.135$	617
Oxaline	1.32	$1.32 \pm 0.05*$	$1.39 \pm 0.08*$	212

**Table 5.3** shows the pH values determined for the different DESs with and without aniline. As expected the sulfuric acid acts as a strong acid although not quite as strong as triflic acid in the previous chapter. It is interesting to note that the pH of the DES-H<sub>2</sub>SO<sub>4</sub> mixture depends on the pH of the DES i.e. it acts as a buffer. The pH measurements in this section of work used the same method as shown in **Chapter 4 section 4.4.4** with the aqueous pH electrode. The reason for using this method was because the indicator method did not work as the solutions appeared slightly cloudy and the light was scattered by the sample. The turbidity of the solutions is clearly shown in **Figure 5.14**. This highlights that there may be some issues with the homogeneity of the solutions. This was not raised in the published literature although discussions with Ismail showed that this was a common observation with many of these systems. This fact will be seen to be very important later in the discussion.



*Figure 5.14:* samples of A)1M  $H_2SO_4$  +aniline in ethaline, B) aniline in Oxaline and C) 1M  $H_2SO_4$  + aniline in Reline with a pH indicator.

While Ethaline and Glyceline have similar pH values when sulfuric acid was added to the liquid, the value for Reline was significantly higher (less acidic). This could be due to the fact that the urea always contains some trapped ammonia which could neutralise a small proportion of the sulfuric acid.

**Figure 5.15** shows the cyclic voltammograms of 0.2 M aniline recorded at a 0.5mm Pt electrode in Ethaline, Reline, Oxaline and Glyceline. The results are similar to those obtained by Ismail and these show that only in Oxaline was it possible to grow appreciable amounts of PANI on the electrode surface under these conditions.

The addition of sulfuric acid to the DESs protonates the aniline to a roughly equal extent and even though the pH is comparable to the values in aqueous solutions, polyaniline does not really grow on the electrode surface. This again shows that the pH is not necessarily the over-riding factor affecting polymer growth. Comparing Ethaline with sulfuric acid to Oxaline without sulfuric acid it can be seen that the former has a lower pH and a lower viscosity but PANI does not grow significantly in the former but it does in the latter. The same is also the case for Reline and Glyceline but Oxaline is different. **Figure 5.6** suggests that the mechanism involves only aniline and protons but this does not correlate with the data shown in **Figure 5.16** and **Table 5.3**.



Figure 5.15: Cyclic voltammograms of 0.2 M aniline recorded at 0.5 mmPt electrode in a) Ethaline, b) Reline, c) Glyceline and d) Oxaline (a-c) contained 1 M  $H_2SO_4$  at 20 mV/s and 20 °C.

Ismail<sup>5</sup> showed that increasing the aniline concentration to 0.5 M did not significantly improve the growth of PANI but when the aniline concentration was further increased to 0.8 M a response similar in shape to that in aqueous solutions was obtained **Figure 5.16** however the charge is very much lower than in aqueous solutions. Ismail<sup>5</sup> did, however show that this change only occurs when an additional 10 wt% water is added to the mixture. The presence of water in the polymerisation of aniline in ILs and DESs is a topic which is not covered in significant detail in the literature.



Figure 5.16: 20 Cyclic voltammogram scans of aniline polymerisation in Ethaline. a) 0.5 M aniline + 1M  $H_2SO_4$  and b) 0.8 M aniline + 1M  $H_2SO_4$ .<sup>5</sup>

It is quite clear in the current study that the charge for PANI growth in DESs is considerably lower than that in aqueous solutions. This shows that mass transport is an important factors governing the growth of PANI. This is emphasised more clearly when analysing the data for PANI in the DESs. The viscosity of the aqueous sulfuric acid solutions are about 1-2 cP whereas the values for the DESs with sulfuric acid range from 40 cP for Ethaline to 600 cP for Reline at 25°C.<sup>5</sup> This shows that the growth rate depends on both mass transport and pH.

## 5.4.3 Effect of adding water to DESs on PANI growth

All DESs contain water to some extent, the most thorough drying results in liquids with at least 50 ppm of water and at atmospheric conditions in an open laboratory many DESs can absorb up to 5 wt % water quite rapidly. Recent studies have investigated the properties and structure of DES/water mixtures as a function of water content.<sup>70, 71</sup> Most of physical and chemical properties change quite significantly with relatively small additions of water.<sup>51, 72-74</sup> The effect of water on the proton activity is clearly important and all acids will introduce water into the DES; 18 M H<sub>2</sub>SO<sub>4</sub> for example contains 2 wt % water. This water could affect the pH of the solution and accordingly the polymerisation of the monomer.

Abbott *et al.* showed that DESs significantly change their properties when between 5 and 10 wt% water has been added.<sup>75</sup> This equates in most cases to 2-5 mole equivalents of water to ChCl.<sup>76</sup> A recent study by Al-Murshedi has shown that water is not totally miscible with DESs.<sup>51</sup> It was shown using NMR and electrochemical diffusional techniques that species diffuse faster in DES-water mixtures that would be expected from their bulk viscosity indicating that there were regimes of water. It was later proven using

dynamic light scattering that the water phases were fairly large *c.a.* 100 nm.<sup>77</sup> If this idea is correct then acids will probably partition preferentially into the water phase which should significantly increase the dissociation of the acid. In this section PANI was grown in the DES- sulfuric acid- aniline systems studied as above but in this case 10 wt% of water was added to the mixtures.

Ismail showed that water was a crucial element in the polymerisation of aniline in DESs and at least 10 wt % was required to be able to get good polymerisation. All subsequent results were obtained with this critical amount of water included but its role was not discussed in the thesis. **Table 5.4** lists the pH values for 3 DESs with and without 10 wt% water. Ethaline and Reline contained 1 M H<sub>2</sub>SO<sub>4</sub> and 0.2 M aniline, the Oxaline liquid just contained aniline.

**Table 5.4:** pH values of a variety mixtures of DESs, 1M H2SO4 and 0.2 M aniline,\*Without H2SO4

Type of DESs	pH of Mixture with aniline in neat DESs	pH of Mixture aniline in DES/10% water
Ethaline	$0.98\pm0.048$	$0.95\pm0.048$
Glyceline	$1.01\pm0.026$	$0.99\pm0.018$
Oxaline*	$1.39\pm0.08$	$1.36\pm0.019$

Surprisingly, it can be seen that the pH values of the two liquids do not change significantly. This shows that either the acid does not partition into the aqueous phase or more likely that there is sufficient water in the liquid (introduced with the acid) to have already enhanced acid dissociation. It should also be noted that the addition of 10 wt% water will also dilute the acid slightly.

# 





Oxaline



Water/ H<sub>2</sub>SO<sub>4</sub>









*Figure 5.17*: Shows the formation solid phase in DESs/ water mixtures, water and pure oxaline.

One factor which Ismail did not discuss was the phase behaviour of the DES/H<sub>2</sub>SO<sub>4</sub>/ aniline/water mixtures. DES/H<sub>2</sub>SO<sub>4</sub>/ aniline mixtures are homogeneous when the DES is Ethaline, Reline and Glyceline, however when water is added to them a solid phase is formed. This slowly homogenises upon extended stirring and heating, but this is relatively slow. In pure Ethaline is aniline miscible and no solid phase is formed when the the

# After stirring

aqueous sulfuric acid is added to the mixture. However, when 10% wt water is added to the mixture it initially becomes cloudy as it did a pure sulfuric acid. The solid phase is almost certainly due to the formation of the anilinium salt but there is no data as the solubility of these in the literature. The solid phase also forms when aniline is added to Oxaline with and without water. This phase change is shown in **Figure 5.17**.

The solubility of aniline in water is 36g /L (0.38 mol L<sup>-1</sup>) so the experiments were run below the theoretical solubility limits. However, when the aniline is present in acidic solution the anilinium salt e.g. in H<sub>2</sub>SO<sub>4</sub>, PhNH<sub>3</sub>, HSO<sub>4</sub> is formed.

Al-Murshedi showed that the addition of 10 wt% water decreased the viscosity of Ethaline from 46 to 29 cP whereas that for Oxaline the viscosity decreased from 212 to 183.1 cP. It would therefore be expected that the voltammetry of aniline with and without water added to the DES would not change significantly. **Figure 5.18** shows that the opposite is in fact the case. Ethaline and Glyceline show a significant change in the shape of the voltammograms when water is added. This shows that water has a significant effect on the mechanism of polymerisation which cannot be explained just by changes in solution pH. Since the concentration and type of anion remains constant, this can also not be considered a factor in the growth of PANI.

The study by Al-Murshedi showed that the addition of 10 wt% water not only decreased the viscosity of DESs but diffusional and dynamic light scattering experiments showed that the liquids themselves were heterogeneous on the nm scale. It was proposed that DESs form emulsions on the  $10^{-7}$  m scale. This could also be the case with the DES/ water/ H<sub>2</sub>SO<sub>4</sub>/ aniline mixtures. To investigate this phenomenon further dynamic light scattering was carried out on the DES/ aniline mixtures with and without water and on the aqueous sulfuric acid mixtures. The results of this are shown in **Figure 5.18**.

The data above appear to be contradictory in that neither pH nor viscosity appear to have an over-riding control on the polymer growth. It can, however, be seen that polymers tend to grow in systems where a phase change occurs on mixing the components. It could be argued that the role of the water is to control the separation of the anion and cation in the anilinium complex and to assist the deprotonation of the anilinium cation in the final step of **Figure 5.6**.



**Figure 5.18:** Cyclic voltammograms of 0.2M aniline recorded at 0.5mmPt electrode in a)Ethaline/water b) Ethaline c) Glyceline d) Glyceline/ water e) Oxaline f)Oxaline.2H<sub>2</sub>O respectively at 20 mV/s and 20C°. (a-d) contained 1 M H<sub>2</sub>SO<sub>4</sub>.



 $Water + 1 M H_2 SO_4 + 0.2 M aniline$ 

*Figure 5.19*: Dynamic light scattring for anilne in water, Ethaline, Oxaline and Oxaline. 2H<sub>2</sub>O

**Figure 5.19** shows that when aniline is added to sulphuric acid a separate phase is formed with dimensions of approximately 100 to 200 nm. To some extent this is not surprising since aniline or anilinium sulfate will be relatively hydrophobic. When aniline and sulfuric acid were added to Ethaline a solution was made with no structures greater than 35 nm found in solution, however when 10 wt% water was added to the solution a phase with an average dimension of 400 nm. The dispersed phase could potentially be a solid phase; however, it is unlikely that polymerisation could occur if the monomer was not mobile. Where, the role of water in ionic liquids has been discussed by several groups.<sup>78, 79</sup> it has been suggested that nano-domains of water exist rather than the water being homogeneously mixed with the ionic liquid<sup>80</sup> and DES.<sup>81</sup>

The addition of aniline to Oxaline without additional water also produced an emulsion with dimensions of the dispersed phase of 410 nm. The addition of 2 mole equivalents of water maintained an emulsion with a dispersed phase of similar dimensions (380 nm). This shows that the systems in which PANI grows efficiently are in fact emulsions. This suggests for the first time that PANI is an emulsion polymerisation rather than a solution polymerisation. This explains why PANI will not grow from Ethaline, Glyceline and Reline, because the aniline is evenly distributed in a solution rather than forming an emulsion.

It could be questioned why Oxaline forms an emulsion while the other DESs do not. Results from the Abbott group show that the transferral of species from an oil phase to a DES is governed by the surface tension of the liquid. A high surface tension leads to a high cohesive energy density meaning that the solution species have large interactions between themselves so it is difficult to dissolve a molecule in the liquid as it requires a large amount of energy to break up the hydrogen bonds between the HBD and the HBA. This means that it is easier for the dispersed phase to accumulate together rather than dispersing in the continuous phase. Since Oxaline has the highest surface tension of any of these DESs it is not surprising that it forms emulsions. When water is added to the other DESs, it increases the surface tension, increasing the tendency to form emulsions.

This may help to explain the disparity in charge between PANI grown in aqueous solutions and DESs. **Figure 5.20** shows the charge for PANI grown in aqueous solutions of different pH compared with solutions in DESs with 10 wt% water added.



**Figure 5.20:**  $Q^+$  after 15 cycles for solutions of 0.2 M aniline in aqueous solutions of sulfuric acid at different concentrations compared with DESs/10% water.

**Table 5.5** Shows the charge for oxidation for PANI after 15 cycles for solutions of 0.2 M aniline in DESs containing 10% water and 1 M H<sub>2</sub>SO<sub>4</sub>. The table also shows the viscosity of the liquids and the size of the dispersed phases.

	$Q^+$ / C	Viscosity / cP	<i>d</i> / nm	$D / \text{cm}^2 \text{ s}^{-1}$
water	0.11	1.97	240	4.8 x 10 <sup>-13</sup>
Ethaline	1.05x10 <sup>-3</sup>	34	398	1.6 x 10- <sup>14</sup>
Glyceline	1.07x10 <sup>-4</sup>	300	110	6.6 x10- <sup>15</sup>

**Table 5.5:** Charge for the oxidation for PANI after 15 cycles for solutions of 0.2 Maniline in DESs containing 10% water and 1 M H2SO4. The table also shows theviscosity of the liquids and the size of the dispersed phases.

Assuming the growth of PANI is diffusion controlled. The diffusion coefficient, D, is given by the Stokes–Einstein equation;

$$D = k_B T / 6\pi \eta r \tag{5.1}$$

Where  $\eta$  is the dynamic viscosity, *r* is the radius of the spherical particle, *T* is the absolute temperature and  $k_B$  is the Boltzmann constant. If the growth of the polymer is diffusion

controlled then the charge for polymer growth should be proportional the diffusion coefficient. The data in **table 5.5** are not evenly distributed and so it is difficult to claim categorically that data correlate but the data show that there may be some correlation between parameters.

An emulsion polymerisation process would mean that a droplet of monomer would approach the electrode surface and given that it will wet the surface well, it will all be converted to polymer. Assuming that the droplet contains pure aniline monomer then a droplet of 200 nm radius will have a volume of  $3.4 \times 10^{-14}$  cm<sup>3</sup> which is equivalent to  $3.4 \times 10^{-14}$  g or  $4.0 \times 10^{-16}$  moles of aniline. This is too much to grow into a single polymer chain which typically contains 1000 to 5000 monomer units so it could mean that when a droplet lands on the electrode surface it could start a number of chains growing next to each other and produce a particle of polymer which could have dimensions similar to those of the droplet. It is likely that the polymer chain will stop growing when the monomer in the droplet is used up. If this were the case then this should manifest itself in the structure of the growing polymer. **Figure 5.21** shows some SEM and AFM images of PANI grown from DES/H<sub>2</sub>SO<sub>4</sub> using Glyceline and Oxaline as the DESs.



*Figure 5.21: AFM images (top) and SEM images below of PANI electrodeposited from 0.8M aniline dissolved in (a) and (c) Glyceline and (b) and (d) Oxaline on a Pt electrode. Both solutions contain 1.0 M H<sub>2</sub>SO<sub>4</sub> and 10 wt% water.<sup>5</sup>* 

It can clearly be seen that the PANI deposits are made up of small particles and these are within the size range of the droplets shown in **Figure 5.19.** This reinforces the idea that PANI polymerisation is an emulsion polymerisation process. This mechanism seems logical because if PANI formation was a solution polymerisation process then a growing polymer would need thousands of single monomer units to diffuse to the electrode surface before a termination event occurred, which in an aqueous solution in unlikely. A more plausible mechanism is that a monomer droplet arrives at the electrode surface and is all rapidly converted to polymer. This mechanism suggested the morphology observed in **Figure 5.21**. The morphology of the PANI film is quietly similar to the PANI films grown in other solvents reported in the literature.<sup>82</sup> it would be useful to perform DLS on these solutions to see if there is an emulsion or not that formed in all liquids. This would be an important observation because it would imply that PANI polymerisation occurred via an emulsion polymerisation mechanism or there is another process that could happen in these non-aqueous systems.

The importance of the pH study is that it has been able to show that the previous hypothesis that PANI polymerisation in DESs was controlled by pH is incorrect. Knowledge of the biphasic nature of aqueous DES mixtures has shown why water is so critical at enabling polymerisation in DESs. This has resulted in checking the phase behaviour of aniline in aqueous solutions and it has shown that aqueous solutions of aniline in sulfuric acid are also emulsions and it is the emulsion which appears to control the morphology of the growing conducting polymer.

## 5.5 Conclusion

This chapter has investigated the effect of pH on the solubility of metal oxides and the kinetics and mechanism of making the conducting polymer, polyaniline, in DESs. While these systems have been studied previously the effect of pH has only been discussed in a qualitative way.

In the first part of this study the solubility of a range of metal oxides was investigated in a variety of acidic and neutral DESs. It was shown previously that metal oxides dissolved in Oxaline better than in Ethaline or Reline. This study has shown that using more acidic DESs enables a higher metal ion solubility. In less acidic liquids, solubility changes more erratically with the type of oxide and DES due to changes in speciation in solution.

The second part of the study investigated the polymerisation of aniline in both aqueous and DES solutions. It was found that in aqueous solutions the charge for polymer growth correlated strongly with solution pH, however it was also found that there was an anion effect. Addition of a constant concentration of NaCl to the solution resulted in a smaller change in charge with pH.

It was confirmed that PANI would only grow in Oxaline, even with the addition of sulfuric acid to the other DESs. It was also found that the addition of water to the DESs enabled PANI growth. These observations could not be explained in terms of viscosity or pH. Recent results have shown that DES-water mixtures form emulsions and this idea was tested with the DES/ H<sub>2</sub>SO<sub>4</sub>/ aniline/ water mixtures using dynamic light scattering. It was found that in the absence of water, DES/ H<sub>2</sub>SO<sub>4</sub>/ aniline mixtures were homogeneous and it was only when water was added that an emulsion formed. The exception to this was Oxaline where an emulsion formed without the addition of water. The reason for this has previously been suggested to occur due to the high surface tension of Oxaline.

It was suggested that if the polymerisation of PANI occurred via an emulsion mechanism then this could affect the morphology of the PANI deposits obtained. Analysis of the SEM and AFM images of PANI grown from DES/ H<sub>2</sub>SO<sub>4</sub>/ aniline/ water mixtures showed that the polymer was made up of small particles of polymer which were in the same size range as the droplets found by dynamic light scattering. This could be interpreted as evidence that PANI growth occurs by a suspension polymerisation mechanism. This is the first time that this mechanism has been proposed. This insight would not have been possible unless the pH of the DES/ water mixtures could have been quantified and ruled out of the polymerisation mechanism.

## **5.6 References**

- 1. A. P. Abbott, G. Capper, D. L. Davies, K. J. McKenzie and S. U. Obi, *Journal of Chemical & Engineering Data*, 2006, **51**, 1280-1282.
- M. Krystof, M. Pérez-Sánchez and P. Domínguez de María, *ChemSusChem*, 2013, 6, 630-634.
- 3. D. Lindberg, M. de la Fuente Revenga and M. Widersten, *Journal of biotechnology*, 2010, **147**, 169-171.
- E. A. Drylie, D. S. Wragg, E. R. Parnham, P. S. Wheatley, A. M. Slawin, J. E. Warren and R. E. Morris, *Angewandte Chemie International Edition*, 2007, 46, 7839-7843.
- 5. H. K. Ismail, Department of Chemistry, 2017.
- D. Carriazo, M. C. Serrano, M. C. Gutiérrez, M. L. Ferrer and F. del Monte, *Chemical Society Reviews*, 2012, 41, 4996-5014.
- F. del Monte, D. Carriazo, M. C. Serrano, M. C. Gutiérrez and M. L. Ferrer, *ChemSusChem*, 2014, 7, 999-1009.
- J. D. Mota-Morales, M. C. Gutiérrez, I. C. Sanchez, G. Luna-Barcenas and F. del Monte, *Chemical Communications*, 2011, 47, 5328-5330.
- J. D. Mota-Morales, M. C. Gutiérrez, M. L. Ferrer, R. Jiménez, P. Santiago, I. C. Sanchez, M. Terrones, F. Del Monte and G. Luna-Bárcenas, *Journal of Materials Chemistry A*, 2013, 1, 3970-3976.
- H. Zhao and G. A. Baker, *Journal of Chemical Technology and Biotechnology*, 2013, 88, 3-12.
- 11. J. Wang, Analytical electrochemistry, John Wiley & Sons, 2006.
- 12. W. H. Kruesi and D. J. Fray, *Metallurgical Transactions B*, 1993, 24, 605-615.
- 13. D. Fray and G. Chen, *Materials science and technology*, 2004, **20**, 295-300.
- 14. K. Grjotheim, C. Krohn, M. Malinovský, K. Matiašovský and J. Thonstad, *Google Scholar*.
- 15. S. Dai, Y. Shin, L. Toth and C. Barnes, *Inorganic chemistry*, 1997, **36**, 4900-4902.
- 16. H.-L. Huang, H. P. Wang, E. M. Eyring and J.-E. Chang, *Environmental Chemistry*, 2009, **6**, 268-272.
- 17. M. N. Kobrak, Advances in Chemical Physics, 2008, 139, 85-138.
- A. P. Abbott, G. Frisch and K. S. Ryder, *Annual Reports Section*" A"(Inorganic Chemistry), 2008, 104, 21-45.

- 19. C. Hardacre, Annu. Rev. Mater. Res., 2005, 35, 29-49.
- 20. J.-M. Lee, S. Ruckes and J. M. Prausnitz, *The Journal of Physical Chemistry B*, 2008, **112**, 1473-1476.
- A. Oehlke, K. Hofmann and S. Spange, *New Journal of Chemistry*, 2006, **30**, 533-536.
- 22. I. Correia and T. Welton, *Dalton Transactions*, 2009, 4115-4121.
- S. Wellens, T. Vander Hoogerstraete, C. Möller, B. Thijs, J. Luyten and K. Binnemans, *Hydrometallurgy*, 2014, 144, 27-33.
- 24. M. Chuan, G. Shu and J. Liu, *Water, Air, and Soil Pollution*, 1996, **90**, 543-556.
- 25. M. McBride, in *Advances in soil science*, Springer, Editon edn., 1989, pp. 1-56.
- 26. S. Ziemniak, *Journal of solution chemistry*, 1992, **21**, 745-760.
- J. Koryta, J. Dvořák and L. Kavan, *Principles of electrochemistry*, John Wiley & Sons Inc, 1993.
- A. Ravve, *Principles of polymer chemistry*, Springer Science & Business Media, 2013.
- C. K. Chiang, C. Fincher Jr, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis,
   S. C. Gau and A. G. MacDiarmid, *Physical review letters*, 1977, **39**, 1098.
- W.-S. Huang, B. D. Humphrey and A. G. MacDiarmid, Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1986, 82, 2385-2400.
- R. B. Seymour and C. E. Carraher, *Polymer chemistry*, Marcel Dekker New York, 2000.
- 32. L. H. Sperling, *Introduction to physical polymer science*, John Wiley & Sons, 2005.
- 33. J. De Albuquerque, L. Mattoso, R. Faria, J. Masters and A. MacDiarmid, *Synthetic Metals*, 2004, **146**, 1-10.
- 34. F. Rodriguez, C. Cohen, C. K. Ober and L. Archer, *Principles of polymer systems*, CRC Press, 2014.
- 35. S. Lu, R. Cong, S. Zhu, X. Zhao, J. Liu, J. S. Tse, S. Meng and B. Yang, ACS applied materials & interfaces, 2016, **8**, 4062-4068.
- W. W. Focke, G. E. Wnek and Y. Wei, *Journal of Physical Chemistry*, 1987, 91, 5813-5818.
- S.-Y. Hong and S.-M. Park, *The Journal of Physical Chemistry B*, 2005, 109, 9305-9310.

- 38. P. J. Flory, *Principles of polymer chemistry*, Cornell University Press, 1953.
- 39. R. Prakash, *Journal of applied polymer science*, 2002, **83**, 378-385.
- 40. G. Asturias, A. MacDiarmid, R. McCall and A. Epstein, *Synthetic Metals*, 1989, 29, 157-162.
- 41. A. Ray, A. Richter, A. MacDiarmid and A. Epstein, *Synthetic Metals*, 1989, **29**, 151-156.
- 42. L. Duić and Z. Mandić, *Journal of Electroanalytical Chemistry*, 1992, **335**, 207-221.
- H. D. Nguyen, T. H. Nguyen, N. V. Hoang, N. N. Le, T. N. N. Nguyen, D. C. T. Doan and M. C. Dang, *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 2014, 5, 045001.
- 44. Q. Pei and X. Bi, *Synthetic metals*, 1989, **30**, 351-358.
- 45. Y. Cao, J. Qiu and P. Smith, *Synthetic Metals*, 1995, **69**, 187-190.
- 46. H. Tang, A. Kitani and M. Shiotani, *Electrochimica acta*, 1996, **41**, 1561-1567.
- 47. R. Cordova, M. Del Valle, A. Arratia, H. Gomez and R. Schrebler, *Journal of Electroanalytical Chemistry*, 1994, **377**, 75-83.
- 48. A. Diaz and J. Logan, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 1980, **111**, 111-114.
- 49. Z. Mandić, L. Duić and F. Kovačiček, *Electrochimica acta*, 1997, **42**, 1389-1402.
- 50. Q. Hao, W. Lei, X. Xia, Z. Yan, X. Yang, L. Lu and X. Wang, *Electrochimica Acta*, 2010, **55**, 632-640.
- C. D'Agostino, L. F. Gladden, M. D. Mantle, A. P. Abbott, I. A. Essa, A. Y. Al-Murshedi and R. C. Harris, *Physical Chemistry Chemical Physics*, 2015, 17, 15297-15304.
- 52. A. P. Abbott, A. Y. Al-Murshedi, O. A. Alshammari, R. C. Harris, J. H. Kareem,
  I. B. Qader and K. Ryder, *Fluid Phase Equilibria*, 2017, 448, 99-104.
- 53. C. S. Brazel and R. D. Rogers, *Ionic liquids in polymer systems: solvents, additives, and novel applications*, ACS Publications, 2005.
- 54. J. Dupont, T. Itoh, P. Lozano and S. Malhotra, *Environmentally friendly syntheses using ionic liquids*, CRC Press, 2014.
- 55. H. Liu, Y. Liu and J. Li, *Physical Chemistry Chemical Physics*, 2010, **12**, 1685-1697.
- 56. M. C. Li, C. A. Ma, B. Y. Liu and Z. M. Jin, *Electrochemistry Communications*, 2005, **7**, 209-212.

- 57. Y. Jiang, A. Wang and J. Kan, Sensors and Actuators B: Chemical, 2007, **124**, 529-534.
- 58. J. Kan, X. Pan and C. Chen, *Biosensors and Bioelectronics*, 2004, **19**, 1635-1640.
- D. Nicolas-Debarnot and F. Poncin-Epaillard, *Analytica Chimica Acta*, 2003, 475, 1-15.
- 60. M. Gvozdenović, B. Jugović, J. Stevanović, T. Trišović and B. Grgur, 2011.
- 61. B. Wang, J. Tang and F. Wang, *Synthetic Metals*, 1987, **18**, 323-328.
- 62. B. Wang, J. Tang and F. Wang, *Synthetic Metals*, 1986, **13**, 329-334.
- D. Sazou and C. Georgolios, *Journal of Electroanalytical Chemistry*, 1997, 429, 81-93.
- 64. G. Morales, M. Miras and C. Barbero, *Synthetic metals*, 1999, **101**, 686.
- 65. T. Osaka, T. Nakajima, K. Naoi and B. B. Owens, *Journal of The Electrochemical Society*, 1990, **137**, 2139-2142.
- W. Lu, A. G. Fadeev, B. Qi, E. Smela, B. R. Mattes, J. Ding, G. M. Spinks, J. Mazurkiewicz, D. Zhou and G. G. Wallace, *Science*, 2002, 297, 983-987.
- 67. L. Nyholm and L. M. Peter, *Journal of the Chemical Society, Faraday Transactions*, 1994, **90**, 149-154.
- 68. C. Odin, M. Nechtschein and P. Hapiot, *Synthetic metals*, 1992, 47, 329-350.
- 69. S. R. Moraes, D. Huerta-Vilca and A. J. Motheo, *European polymer journal*, 2004, **40**, 2033-2041.
- O. S. Hammond, D. T. Bowron and K. J. Edler, *Angewandte Chemie*, 2017, **129**, 9914-9917.
- S. Khandelwal, Y. K. Tailor and M. Kumar, *Journal of Molecular Liquids*, 2016, 215, 345-386.
- S. Wang, J. Liu, R. Hembre, S. Barnicki, P. Goodrich, T.-L. Hughes, D. W. Rooney, C. Sink, J. Jacquemin and C. Hardacre, *Journal of Chemical & Engineering Data*, 2017, 62, 653-664.
- 73. C. R. Ashworth, R. P. Matthews, T. Welton and P. A. Hunt, *Physical Chemistry Chemical Physics*, 2016, **18**, 18145-18160.
- 74. J. E. Reid, R. J. Gammons, J. M. Slattery, A. J. Walker and S. Shimizu, *The Journal of Physical Chemistry B*, 2017, **121**, 599-609.
- A. P. Abbott, G. Frisch and K. S. Ryder, *Annual Review of Materials Research*, 2013, 43, 335-358.

- A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *Journal* of the American Chemical Society, 2004, **126**, 9142-9147.
- 77. A. P. Abbott, S. S. Alabdullah, A. Y. Al-Murshedi and K. S. Ryder, *Faraday discussions*, 2018, **206**, 365-377.
- 78. H. Katayanagi, K. Nishikawa, H. Shimozaki, K. Miki, P. Westh and Y. Koga, *The Journal of Physical Chemistry B*, 2004, **108**, 19451-19457.
- M. G. Freire, C. M. Neves, P. J. Carvalho, R. L. Gardas, A. M. Fernandes, I. M. Marrucho, L. M. Santos and J. A. Coutinho, *The Journal of Physical Chemistry B*, 2007, **111**, 13082-13089.
- K. Saihara, Y. Yoshimura, S. Ohta and A. Shimizu, *Scientific Reports*, 2015, 5, 10619.
- E. A. Cade, J. Petenuci III and M. M. Hoffmann, *ChemPhysChem*, 2016, **17**, 520-529.
- 82. H.-y. Ma, Y.-w. Li, S.-x. Yang, F. Cao, J. Gong and Y.-l. Deng, *The Journal of Physical Chemistry C*, 2010, **114**, 9264-9269.

# **Chapter 6: Conclusions and Suggestions for Further work**

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### Chapter six: Conclusion & suggestions for future work

## 6.1 Conclusion

This study has brought about a better understanding of proton activity in ionic liquids and deep eutectic solvents (DES). This study has stuck to the definition of  $pH = -log_{10}$  [H<sup>+</sup>]. The values were determined by two methods, a spectroscopic method and a glass electrode. The values obtained are not intended to give absolute values of pH but they give useful comparative methods of assessing proton activity. The final part uses the data in two applications to see whether the values give a reasonable assessment of solution based processes which are thought to be sensitive to proton activity.

## 6.1.1 Spectroscopic method of measuring acidity in DESs and ILs

Indicator molecules have long been used as sensors of proton activity. Although they have been used in a qualitative indicator of pH in ionic liquids, they have not been used to quantify pH due to the difficulty of determining the  $pK_{In}$  value in DESs. This work has assumed that triflic acid is fully dissociated in DESs and ILs (an assumption supported by experimental measurements) to determine  $pK_{In}$  by a titimetric method. Using this approach which is analogous to the aqueous method  $pK_{In}$  was found for bromophenol blue in a variety of DESs and ILs.

The validity of this approach was examined by comparing the values of pKa for organic acids in water with the values determined using an aqueous pH electrode. The pKa values were also compared with the aqueous literature values and all three were found to agree within experimental error showing the validity of this approach.

Dissociation constant of nine carboxylic acids were measured in a DES by the developed spectroscopic indicator method. It was found that the pKa values were higher in DESs than in water showing that water acted as a better base than Cl in Ethaline. A good linear correlation between the pKa values in the two liquids was observed with a constant difference of about 0.5 pKa units which would seem appropriate given the differences in concentration and strength of the base in the two liquids. Most importantly it was shown that this difference between the aqueous solution values and that of the DES could be accounted for by assuming that the chloride acted as a buffer solution. In doing this, very good agreement was obtained between the theoretical value in an aqueous solution of acid with an equivalent concentration of chloride ions in it and the values measured in the DES using the indicator method.

The indicator method was used to measure the acidity of different ionic liquids as a function of the basicity of the anion. The experimental values show the impact of different hydrogen bond donors on the acidity of DESs. It was found that the basicity of the DESs increased in the order Ethaline < Glyceline < Reline. These acidity values were compared with two types ionic liquids with Bmim BF<sub>4</sub> and Emim acetate and as expected acetate was more basic than BF<sub>4</sub><sup>-</sup>.

The *pKa* of acidic DESs and protonic ionic liquids were determined for the first time. It was found that protic DESs mixtures of oxalic acid and ChCl were more acidic than those based on citric or malonic acid. The *pK*<sub>In</sub> values were quite high considering that they are weak acids but can be understood when the high concentration of acid is taken into account. Comparison of the acidity of the acids in water at the same concentration gave comparable results.

The effect of water on the pH of ionic liquids and DESs was also studied. It was found that the pKa value of carboxylic acids increased as the water content increased. It required a molar excess of water to ChCl: before the pKa changed significantly.

The data offered in this study show pH and pKa values in ionic liquids and DESs which are consistent with the approximate proton activity in DESs that would be expected given their ionic concentration and base strength.

## 6.1.2 Electrochemical method of measuring acidity in DESs and ILs

While the spectroscopic method provides an effective method of determining pH and pKa it is relatively slow and requires extensive calibration. A more commonly used and faster method of determining pH is using a glass electrode. Firstly, it was shown that the response of a standard commercial aqueous glass electrode could be used to measure a cell potentail in an acidic DES. Clearly the pH function did not give meaningful results due to the unknown liquid junction potentials but using standard concentrations of triflic acid in Ethaline gave an almost Nernstian slope in a DES with minimal water incorporated. The Nernstian slope increased as more water was added to the DES becoming Nernstian in an aqueous solution. It was proposed that the deviation fromNernstian response was possibly due to dehydration of the silica layer close to the solution interface. While the response was non-Nernstian it was nevertheless linear and gave pH values for an organic acid in a DES which corresponded to those observed in solution using the bromophenol blue indicator.

A methodology was developed to give reproducible results with an aqueous pH probe whereby the electrode was rinsed in an Ethaline solution containing NaCl in between measuremnts to re-equilibrate the sodium ions in the glass membrane. Failure to do so resulted in irreproducible results. It was also found that the probe took longer to reach equilibrium (typically about 20 s) than it did in water which may be expected given the higher viscosity of the DES. This ensured that cell potentials were reproducible with only small error bars on each recorded measurements.

The liquid junction potential also investigated in this section of work it was found that in an electrochemical cell is pH dependent due to the preferential transport of protons compared to large organic cations. The liquid junction potentials between different DESs were determined and it was shown that these relied on the proton activity in the different DESs. The major difference was found between Reline and Oxaline. In the former the mobile cation is  $Ch^+$  where as in Oxaline the H<sup>+</sup> ion has much greater mobility.

A new, non-aqueous glass electrode was constructed by dismantling an aqueous glass electrode and filling the two cells with Ag/AgCl in Ethaline reference electrode. It was found that this did have a Nernstian response showing that the glass membrane could function with only the traces of water naturally incorporated in the DESs.

It can be concluded that the electrochemical method was successfully improved to quantify variety of DESs and ILs. It was shown that the key effect of the proton activity induced by the type of anion for ionic liquids act as a conjugated base in the liquid. The order of acidity is affected by the electronegativity of the anion, by the following order  $F^-$  > HSO<sub>4</sub> > Cl<sup>-</sup>> Ac suggesting some correlation with hydrogen bond strength.

## 6.1.3 Effect of pH on process thermodynamics and kinetics

Proton activity is a major factor in the thermodynamics and kinetics of many chemical processes. In this study two processes were investigated to see whether the pH methods developed in chapters three and four could provide any insight into firstly the dissolution of metal oxides in DESs and secondly into the kinetics of polyaniline polymerisation in DESs.

Previous studies had shown that metal oxides dissolved better in Oxaline than Ethaline and this was thought to be due to differences pH. Using recent data by Pateli who extended the range of acidic DESs used, it was found that solubility for a range of metal oxides decreased in the order Oxaline > Maline > Lactiline. For the Ethaline and Reline the solubility of metal oxides was less well correlated with pH. This showed that in more netral solutions the proton has little effect on the solubility and it is more the specific interaction of the HBD with the metal which is important in controlling solubility. This section shows that the pH values show the expected indicative trends but they are also useful in demonstrating the ability of the HBD to act as a specific ligand for certain metals.

In the final part of the study the work of Ismail on the polymerisation of aniline in DESs was correlated with solution pH. It was postulated that PANI would not grow in DESs of neutral pH and that sulfuric acid had to be added for polymerisation to occur. When the pH values of the solutions were measured, it was found that despite having a low pH PANI would not grow from Ethaline with sulfuric acid unless water was added. This did not change the pH or viscosity significantly. Confusingly, PANI would grow from Oxaline which was less acidic and much more viscous. The addition of water did not affect PANI growth from Oxaline. It appeared that the mechanism was not in fact dependent on pH. It was observed that PANI only grew from systems where aniline appeared to form an emulsion on first addition. All of these systems required vigorous stirring at elevated temperature to form a clear liquid.

It was postulated that aniline formed emulsions when mixed with some DESs and not with others and the addition of water brought about emulsion formation. This was confirmed using dynamic light scattering and it was shown that droplets in the range 200 to 400 nm were formed. This study showed that in all probability the electropolymerisation of aniline in aqueous and DES solutions occurs by an emulsion polymerisation mechanism and this results in the observed morphology which is spheres of polymer of the approximate dimensions of the aniline droplets in solution. The reason that aniline grows from an aqueous solution is that it is an emulsion and the reason that it does not grow in Ethaline, even when acidified is because it forms a homogeneous solution. This conclusion could only be drawn when the pH could be quantified and eliminated as the cause of non-polymerisation.

### 6.2 Suggestions for Future work

This thesis has illustrated the pH scales of variety of deep eutectic solvents. Measuring pH is essential not only in finding the chemical characteristics of DESs but also as the initial step toward managing chemical reactions. In electrochemical processes, the pH

function can be use to investigate the speciation of many metals dissolved in DESs. For instance, Pourbaix Diagrams are plots of potential vs pH and they help to explain solubility and corrosion. To date no such plots exist in media other than aqueous solutions.

While two techniques have been used to quantify several DESs and a few ILs, it would be important to extend the study in Chapter 3 to imidazolium salts with different anions e.g.  $HSO_4^-$ ,  $OTf^-$ ,  $Tf_2N^-$ , and  $Cl^-$ . It would also be useful to quantify the effect and phase behaviour of water. It may be useful to use other techniques such as NMR to determine whether weak acids partition differently in IL-water mixtures and whether this affects the acidity of the mixture.

While the use glass membranes has been shown to be viable in DESs, it would be important to extend this study to understand the mechanism of the proton sensing in this device. The role of water is no doubt important in shuttling protons between the liquid and the glass. Ultra-dry studies may be difficult with many of the acids of interest but it would be interesting to see whether the device is unable to sense protons if the liquid has negligible water available. It is important to continue the analytical studies to optimise the conditions for use and the time taken to reach equilibrium. It would therefore be important to develop a buffer system that worked in ILs and DESs so that the electrode could be easily standardised.

An area where pH investigations would be interesting would be in studying the stability of enzymes in ILs and DESs. It has been found that a variety of enzymes are stable for extended periods in certain ionic environments, particularly when traces of water are present. It would be interesting to see if the stability was related to local pH conditions. Enzymes are particularly sensitive to ionic strength changes particularly when protons are involved as these can affect secondary and tertiary folding of protein chains.

# 6.3 Appendix

# 6.3.1 Appendix for UV-Vis spectroscopy experiments

The acidity of oxalic acid in Ethaline:



Figure 6.1: different concentration of oxalic acid in Ethaline with Bromophenol blue

Molarity of	Abs. of	Abs. of	pH in	pH in water	pH in
Oxalic	acid	base	Ethaline	by pH	theoretical
acid/mM				probe	
0.032	0.344	0.076	3.55	2.86	2.96
0.040	0.349	0.068	3.50	2.87	2.81
0.060	0.356	0.055	3.40	2.76	2.72
0.080	0.370	0.033	3.17	2.70	2.66
0.100	0.385	0.021	2.95	2.65	2.61

*Table 6.1*: *The acidity of oxalic acid in Ethaline:* 

*Table 6.2: The comparison values of pKa water vs. Ethaline:* 

M of Oxalic	Ka in Water	Ka in water	Ka in	pKa in	pKa in
acid	literature	by pH	Ethaline	Ethaline	water
		probe			
3.2×10 <sup>-5</sup>	0.0591	0.0512	2.46×10 <sup>-3</sup>	2.609	1.29
4×10 <sup>-5</sup>	0.0591	0.0468	2.49×10 <sup>-3</sup>	2.603	1.33
6×10 <sup>-5</sup>	0.0591	0.0501	2.64×10 <sup>-3</sup>	2.578	1.30
8×10 <sup>-5</sup>	0.0591	0.0502	5.71×10 <sup>-3</sup>	2.240	1.30
1×10 <sup>-4</sup>	0.0591	0.0480	1.21×10 <sup>-2</sup>	1.920	1.31



**Figure 6.2**: *illustrates the extinction coefficient by mixing different concentration of B.P.B with the constant concentration of Oxalic acid.* 



*Figure 6.3*: *The Extinction coefficient of oxalic acid with B.P.B at 428 nm,602nm respectively.* 

 Table 6.3: The extinction coefficient of oxalic acid with B.P.B at 428 nm,602nm respectively:

Extinction coefficient	at 428 nm	At 602 nm	The ratio of extinction coefficient $\epsilon_2/\epsilon_1$
Oxalic acid with B.P.B	31763 M <sup>-1</sup> cm <sup>-1</sup>	$128381 M^{-1} cm^{-1}$	4.01
Error%	3.60 %	4.06	

# The acidity of Malonic acid in Ethaline:



Figure 6.4: Different concentration of malonic acid in Ethaline with B.P.B.

M of	Ka in Water	Ka in water	<i>Ka</i> in	<i>pKa</i> in	<i>pKa</i> in
Malonic	literature	by pH probe	Ethaline	Ethaline	water
acid					
8.68×10 <sup>-5</sup>	1.41×10 <sup>-3</sup>	1.32×10 <sup>-3</sup>	2.51×10 <sup>-5</sup>	4.60	2.88
1.73×10 <sup>-4</sup>	1.41×10 <sup>-3</sup>	1.00×10 <sup>-3</sup>	2.64×10 <sup>-5</sup>	4.57	2.99
2.60×10 <sup>-4</sup>	1.41×10 <sup>-3</sup>	1.39×10 <sup>-3</sup>	2.78×10 <sup>-5</sup>	4.56	2.85
3.40×10 <sup>-4</sup>	1.41×10 <sup>-3</sup>	1.22×10 <sup>-3</sup>	$4.24 \times 10^{-5}$	4.37	2.85
4.34×10 <sup>-4</sup>	1.41×10 <sup>-3</sup>	1.49×10 <sup>-3</sup>	3.77×10 <sup>-5</sup>	4.42	2.83

Table 6.4: The pKa of malonic acid water vs. Ethaline:

# The acidity of succinic acid in Ethaline



Figure 6.5 : different concentration of succinic acid in Ethaline with bromophenol blue
M of succinic acid	<i>Ka</i> in water literature	<i>Ka</i> in water by pH probe	<i>Ka</i> in Ethaline	<i>pKa</i> in Ethaline	<i>pKa</i> in water
$1.52 \times 10^{-4}$	6.89×10 <sup>-5</sup>	6.28×10 <sup>-5</sup>	4.76×10 <sup>-5</sup>	4.32	4.20
2.30×10 <sup>-4</sup>	6.89×10 <sup>-5</sup>	6.0×10 <sup>-5</sup>	3.95×10 <sup>-5</sup>	4.44	4.22
3.05×10 <sup>-4</sup>	6.89×10 <sup>-5</sup>	5.96×10 <sup>-5</sup>	3.54×10 <sup>-5</sup>	4.45	4.22
3.82×10 <sup>-4</sup>	6.89×10 <sup>-5</sup>	6.57×10 <sup>-5</sup>	4.09×10 <sup>-5</sup>	4.38	4.18
4.58×10 <sup>-4</sup>	6.89×10 <sup>-5</sup>	6.04×10 <sup>-5</sup>	5.45×10-5	4.26	4.21

Table 6.5: The pKa of succinic acid water vs. Ethaline:

### The acidity of Citric acid in Ethaline



Figure 6.6 : different concentration of citric acid in Ethaline with bromophenol blue.

M of Citric	Ka in water	Ka in water	<i>Ka</i> in	<i>pKa</i> in	<i>pKa</i> in
acid	literature	by pH probe	Ethaline	Ethaline	water
1.41×10 <sup>-4</sup>	7.10×10 <sup>-4</sup>	7.30×10 <sup>-4</sup>	1.66×10 <sup>-4</sup>	3.77	2.88
1.88×10 <sup>-4</sup>	7.10×10 <sup>-4</sup>	7.01×10 <sup>-4</sup>	1.66×10 <sup>-4</sup>	3.77	2.99
2.35×10 <sup>-4</sup>	7.10×10 <sup>-4</sup>	8.10×10 <sup>-4</sup>	2.02×10 <sup>-4</sup>	3.69	2.85
2.82×10 <sup>-4</sup>	7.10×10 <sup>-4</sup>	8.10×10 <sup>-4</sup>	2.56×10 <sup>-4</sup>	3.59	2.85
3.29×10 <sup>-4</sup>	7.10×10 <sup>-4</sup>	7.99×10 <sup>-4</sup>	3.60×10 <sup>-4</sup>	3.45	2.83

 Table 6.6: The pKa of citric acid water vs. Ethaline:

The acidity of benzoic acid in Ethaline:



Figure 6.7 : different concentration of benzoic acid in Ethaline with Bromophenol blue

The acidity of lactic acid in Ethaline:



Figure 6.8 : different concentration of lactic acid in Ethaline with bromophenol blue

The acidity of Salicylic acid in Ethaline:



Figure 6.9 : different concentration of salicylic acid in Ethaline with bromophenol blue

M of salicylic acid	<i>Ka</i> in water literature	<i>Ka</i> in water by pH probe	<i>Ka</i> in Ethaline	<i>pKa</i> in Ethaline	<i>pKa</i> in water
7.68×10 <sup>-4</sup>	1.07×10 <sup>-3</sup>	1.08×10 <sup>-3</sup>	9.42×10 <sup>-4</sup>	3.02	2.966
9.60×10 <sup>-4</sup>	1.07×10 <sup>-3</sup>	1.09×10 <sup>-3</sup>	9.06×10 <sup>-4</sup>	3.04	2.962
1.15×10 <sup>-3</sup>	1.07×10 <sup>-3</sup>	1.09×10 <sup>-3</sup>	8.69×10 <sup>-4</sup>	3.06	2.960
1.34×10 <sup>-3</sup>	$1.07 \times 10^{-3}$	$1.07 \times 10^{-3}$	9.39×10 <sup>-4</sup>	3.02	2.967

*Table 6.7:* The pKa of Salicylic acid water vs. Ethaline:

#### The acidity Data in water

### **Triflic acid**



*Figure 6.10:* The absorbance at different concentrations of *B.P.B* with triflic acid in water.



*Figure 6.11:* Slope for different peaks of B.P.B with triflic acid in water a) at 438 nm. b) At 592nm

# **Oxalic acid**



Figure 6.12: Shows different concentrations of B.P.B with Oxalic acid in water.



Figure 6.13: Slope for different peaks of B.P.B with .T.A a) at 438 nm. b) At 592nm.

Data for ILs Bromophenol blue indicator

**Bmim BF**<sub>4</sub>



*Figure 6.14:* Shows the absorbance at different concentrations of bromophenol blue in *Bmim BF*<sub>4</sub>.



Figure 6.15: Shows the absorbance at different concentrations of B.P.B with lactic acid in Bmim BF<sub>4</sub>.

Emim OAc



Figure 6.16: Shows the absorbance at different concentrations of B.P.B with lactic acid in EmimOAc

Methyl violet indicator



*Figure 6.17:* Shows the absorbance standardisation of methyl violet 2B in different *pHs* 

**Emim HSO<sub>4</sub>** 



Figure 6.18: The absorbance of spectra of different methyl violet with acidic, basic, pure Emim HSO<sub>4</sub>

Oxaline



*Figure 6.19:* The absorbance of spectra of different methyl violet with acidic, basic, pure Oxaline

Oxaline .2H2O



*Figure 6.20:* The absorbance of spectra of different methyl violet with acidic, basic, pure Oxaline.2H<sub>2</sub>O

# Data in Bromothymol blue indactor

Data EMIM Ac



*Figure 6.21:* The absorbance of spectra of different methyl violet with acidic, basic, pure Emim OAc



Figure 6.22: The absorbance of spectra of different methyl violet with succnic acid Emim OAc

Reline



*Figure 6.23:* The absorbance of spectra of different methyl violet with red line pH=10, blue line pH=4, blacke line pure reline

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