

Brønsted Acidity in Deep Eutectic Solvents and Ionic Liquids

Andrew P. Abbott, Sahar S. M. Alabdullah, Azhar Y. M. Al-Murshedi, and Karl S. Ryder

Materials Centre, Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK.

Despite the importance of ionic liquids in a variety of fields, little is understood about the behaviour of protons in these media. The main difficulty arises due to the unknown activity of protons in non-aqueous solvents. This study presents acid dissociation constants for nine organic acids in deep eutectic solvents (DESs) using standard pH indicator solutes. The pK_{In} value for bromophenol blue was found by titrating the DES with triflic acid. The experimental method was developed to understand acid-base properties of deep eutectic solvents, and through this study it was found that the organic acids studied were slightly less dissociated in the DES than in water with pK_a values between 0.2 and 0.5 higher. pK_{In} values were also determined for two ionic liquids [Bmim] [BF₄] and [Emim] [acetate]. The anion of the ionic liquid changes the pH of the solution by acting as a buffer. [Emim] [acetate] was found to be more basic than water. It is also shown that water significantly affects the pH of ionic liquids. This is thought to arise because aqueous mixtures with ionic liquids form heterogeneous solutions and the proton partitions into the aqueous phase. This study also attempted to develop an electrochemical pH sensor. It was shown that a linear response of cell potential vs. $\ln a_{H^+}$ could be obtained but the slope for the correlation was less than that obtained in aqueous solutions. Finally it was shown that the liquid junction potential between two reference electrodes immersed in different DESs was dependent upon the pH difference between the liquids.

Keywords: Deep eutectic solvents, ionic liquids, pH, bromophenol blue, glass electrode, pK_{In} .

Introduction

Chemistry in ionic liquids 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 zwitter ionic liquids however, comparatively little is understood about how their acidity compares with aqueous solutions.^{1,2} In an analogous way, deep eutectic solvents, DESs, which are eutectic mixtures of quaternary ammonium salts and hydrogen bond donors can be tailored by the functionality of either components and basic and acidic versions have been made and characterised.^{3,4} 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.

MacFarlane *et al.*⁵ studied traditional indicator molecules such as bromocresol purple and Alizarin red S to show that liquids such as [Emim] [acetate] are relatively basic. The authors proposed that the pK_a value of an acid (HX) in an ionic liquid $[R_4N^+][S^-]$ containing a weak anion $[S^-]$ could be approximated by taking the ratio of the aqueous pK_a values of the acid and salt in water i.e.

$$pK_a^{[R_4N][S]}(HX) = pK_a^{aq}(HX) / pK_a^{aq}(HS) \quad (1)$$

Using this approach they showed that strong acids in water, such as HCl, HOTf, HNO₃ and HClO₄, should be totally dissociated in ionic liquids. They also showed that ionic liquids acted as buffers when acids and bases were added to them but they did not quantify pK_a or pH values. Kanzaki *et al.*⁶ used an electrochemical cell to measure the pH of the protonic ionic liquid ethylammonium nitrate (EAN) using the cell



Where || was a glass membrane. They dissolved different organic acids in EAN and found that the pK_a 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.*⁷ used the Hammett acidity scale to characterise the acidity of the [BHim][HSO₄]-H₂SO₄ 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.⁸ Mihichuck *et al.*

showed that there was a good correlation between the Hammett acidity scale and the pH for H[NTf₂] in [Bmim][NTf₂].⁹

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.*¹⁰ and supported by quantum chemical calculations. They also characterised the superacidity of the HBr/AlBr₃ system using NMR spectroscopy and related this to other acids using the absolute pH scale.¹¹

In this study we present the use of bromophenol blue to determine the pK_a values of organic acids in ionic liquids and deep eutectic solvents. We present the first pK_{in} values in ionic liquids and DESs and show that the pK_a values of organic acids in DESs and ionic liquids are closely correlated with those in aqueous solutions. It is also shown that a glass electrode does not behave in a strictly Nernstian manner in ionic liquids. The cell potential can, however be correlated with acid concentration and calibration can produce a potential which can be used to produce an analytical signal which gives a measure of relative pH .

Experimental

Synthesis of Deep Eutectic Solvents: 2 EG: 1 ChCl and 2 glycerol: 1 ChCl were prepared by mixing choline chloride (Sigma-Aldrich 99 %) with the hydrogen bond donor (ethylene glycol glycerol or urea (all Sigma-Aldrich ≥ 99 %)) 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 other chemicals are shown in **Table 1**; all were used without further purification.

Table 1: Sources and purity of chemicals used in this study

Compound	Source	Purity %
Triflic acid	Fisher	≥ 99
Oxalic acid	Sigma-Aldrich	98
salicylic acid	Sigma-Aldrich	99
Succinic acid	Fisher	≥ 99
Citric acid	Sigma-Aldrich	≥ 99
Benzoic acid	Sigma-Aldrich	> 98.9
Lactic acid	Fisher	≥ 99
Propanoic acid	Fluka	≥ 98
Butanoic acid	Fluka	≥ 98
[Bmim] [BF ₄]	Aldrich	$\geq 98\%$
[Emim] [OAc]	Sigma-Aldrich	$\geq 98\%$
Bromophenol blue	Amresco	> 98.9
Acetic acid	Fluka	≥ 99
Silver chloride	Sigma-Aldrich	≥ 99

The pK_a value of the bromophenol blue indicator were determined using a UV-vis spectrophotometric method. Solutions of bromophenol blue ($6.60 \times 10^{-5} \text{ mol kg}^{-1}$) were made up in each of the ionic liquids and DESs. The solution was split into 3; one was used as made, one was made up to 0.1 mol kg^{-1} triflic acid solution, and the third to 0.1 mol kg^{-1} with methylamine. These were able to convert the indicator to the fully protonated and deprotonated forms respectively. A Shimadzu UV- visible spectrophotometer 1601 was used for the experiments. The path length for the quartz cell was 10 mm. The spectra were measured in the range 350 to 750 nm. The absorbance maxima of B.P.B were at approximately 602 nm (deprotonated) and 428 nm (protonated).

The water content of all liquids was measured using TG and were found to be 2.10 (2 EG: 1 ChCl), 0.72 (2 urea: 1 ChCl), 1.64 (2 Glycerol: 1 ChCl), 1.48 [Emim] [OAc] and 0.043 wt% [Bmim] [BF₄].

The pH electrode was a Jenway 3510 module number 924 005. Solutions of HOTf containing 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} , 10^{-6} , $10^{-7} \text{ mol kg}^{-1}$ were made up in distilled water. This was repeated using a 50:50 wt % mixture of 2EG: ChCl and water and finally in pure 2EG: ChCl. For each measurement the cell voltage was measured after the solution was stirred for 20 minutes and the electrode was left to equilibrate in an unstirred solution for 3 minutes before the cell voltage was measured.

The liquid junction potentials were measured by chronopotentiometry using an Autolab Type III potentiostat with GPES software. The reference electrodes on either side of the liquid junction were a silver electrode in contact with 0.01 mol kg^{-1} AgCl in one of four DESs; 2 EG: 1 ChCl, 2 glycerol: 1 ChCl, 2 urea: 1 ChCl, 2 oxalic acid: 1 ChCl

Ag | AgCl ($a=0.01 \text{ mol kg}^{-1}$) (DES1) || 2 AgCl ($a=0.01 \text{ mol kg}^{-1}$) (DES2) | Ag

The size of droplets formed when water was mixed in the ionic liquids was determined using a Malvern instruments, Zetasize Nano dynamic light scattering apparatus. To each ionic liquid 5 wt% water was added and each mixture was stirred for 10 minutes before filtration through a $0.22 \mu\text{m}$ Nylon filter to remove any solid particles from the liquids under investigation.

Results

In this study, two methods of determining proton activity are tested; indicator solutes and electrochemical sensors. The first of these methods uses the classical spectroscopic method to characterise the pH of an acid based upon the relative amounts of protonated and deprotonated indicator solute. The pH can be determined by measuring the ratio of absorbances for the protonated and deprotonated forms of the indicator.¹²

$$pK_{In} = pH + \log_{10} \frac{[In^-]}{[HIn]} \quad (2)$$

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| H₂ |H⁺_{DES}) was measured as a function of acid molality.¹³ 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).¹⁴ It was found that over 6 orders of magnitude concentration the H₂/H⁺ redox couple exhibited Nernstian behaviour up to a molality of 1 mol kg⁻¹. It was assumed from this that the acid was effectively totally dissociated over this concentration range and behaved as an ideal solution.

For this study the aim was to determine the acidity of a variety of simple organic carboxylic acids in a range of ionic liquids and deep eutectic solvents. In aqueous solutions, most of these would have pK_a values in the range 2.5 to 5.5. To quantify the pK_a of these acids, bromophenol blue (BPB) was chosen as an indicator as it is approximately in the middle of this range (pK_{In} in water is 4.0).

The spectroscopic method is also slightly complicated because the extinction coefficient of the protonated and deprotonated forms need to be considered. For each ionic liquid and DES the extinction coefficient was measured for the protonated and deprotonated forms using 4 different concentrations of bromophenol blue.

Figure 1 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^{-1} and it can be seen that the indicator is largely protonated at the higher concentration and partially dissociated at the lower concentration.

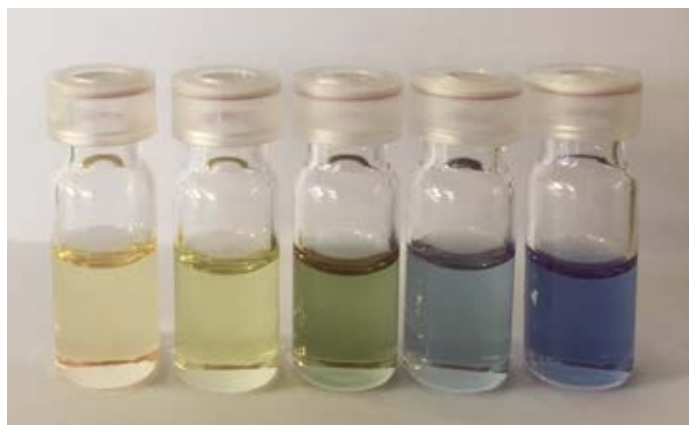


Figure 1: solutions of bromophenol blue in 2 EG: 1 ChCl containing different molalities of triflic acid ranged from (l to r) 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} and 10^{-8} mol kg^{-1}

Figure 2a shows the absorbance spectra of 9 solutions of different triflic acid molalities and **Figure 2b** 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.* $\text{pH} = -\log_{10} a_{\text{H}^+}$. Using the assumption of MacFarlane in equation 1 this appears to be a reasonable approximation.² **Figure 2b** shows a plot of absorbance vs effective pH on a molal scale assuming complete dissociation of the acid. This is effectively a titration curve for the indicator and the $\text{p}K_{\text{In}}$ 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.⁶ The $\text{p}K_{\text{In}}$ of the BPB is 3.74 ± 0.012 in 2 EG: 1 ChCl which is slightly lower than that in water (4.0)¹⁵ which would be logical as the liquid will be a slightly weaker base than water.

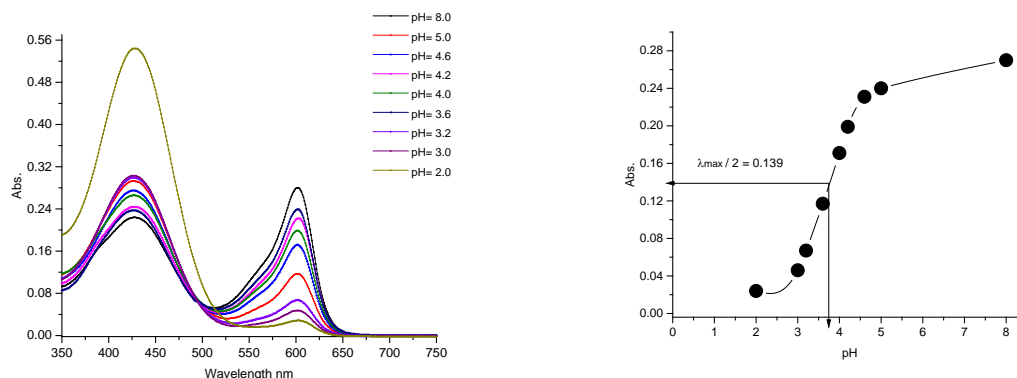


Figure 2: (a) The absorbance of spectra of different BPB with different concentrations of triflic acid in 2 EG: 1 ChCl (b) absorbance of the peak at 600 nm as a function of relative pH.

One interesting aspect of using DESs is that the ionic strength can be changed by varying the ratio of quaternary ammonium salt to hydrogen bond donor. **Table 2** 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. This is logical because the chloride anions are relatively basic compared to the glycol molecules. In comparison, the DES 2 glycerol: 1ChCl has a pK_{In} value of 3.89 ± 0.28 even though it contains the same chloride concentration as 2 EG: 1 ChCl. It can be seen that the HBD does have an effect on the acidity of the DES. We previously showed that the protons in 2 EG: 1 ChCl are more labile than in 2 glycerol: 1ChCl despite the similarities in their pK_a values in water (ethylene glycol (14.22) and glycerol (14.15)).¹⁶

Table 2: pK_{In} for bromophenol blue in some DESs. Error bars are standard deviations of 5 measurements.

Solvent	water	2 EG: 1 ChCl	3 EG: 1ChCl	4 EG: 1ChCl	ethylene glycol
pK_{In}	3.99 ± 0.05	3.61 ± 0.02	3.55 ± 0.04	3.39 ± 0.13	3.23 ± 0.09

Once the pK_{In} was determined it was possible to calculate pK_a for a variety of carboxylic acids in 2 EG: 1 ChCl. The pK_a values for 9 carboxylic acids are shown in **Figure 3**. 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. The same approach was used for the same acids in water and values were very similar to those reported in the literature.

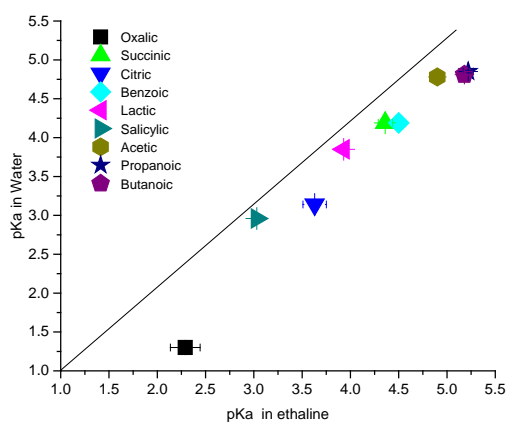


Figure 3: Comparison the average pK_a values of 9 carboxylic acids in 2 EG: 1 ChCl and water. Error bars are standard deviations of 5 data points.

For most of the acids tested the pK_a value in 2 EG: 1 ChCl was approximately 0.5 larger than that in water. **Table 3** shows that this is very like the difference between the pK_{in} values for the two liquids (0.39). 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^{-1} c.f. water concentration which is 55.6 mol kg^{-1}).

pK_a values for carboxylic acids in other ionic liquids

The approach used above to calculate pK_{in} for 2 EG: 1 ChCl was used for some other ionic liquids and the results are shown in **Table 3**.

Table 3: pK_{in} for bromophenol blue in some ionic liquids. Error bars are standard deviations of 5 data points.

	[C ₄ mim][OTf]	[Bmim][BF ₄]	[Emim][OAc]	Water
pK_{in} (BPB)	3.38 ± 0.15	3.84 ± 0.10	3.92 ± 0.09	4.0
	HOTf	HB ₄ F	HOAc	H ₂ O
$pK_a^{ref\ 2}$	c.a. -2.8	-0.44	4.75	14

Table 3 shows 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.²

Using the pK_{in} data in **Table 3**, the pK_a values of 4 acids; acetic, succinic, lactic and salicylic acid were determined for [Emim][OAc] and [Bmim][BF₄] and a related DES, 2 glycerol: 1ChCl. MacFarlane used OAc⁻ and BF₄⁻ salts as examples of weakly basic and basic anions respectively and estimated the pK_a of the ionic liquids.² The BF₄⁻ salts are also thought to be acidic due to hydrolysis of the anion by traces of water¹⁷ so it was thought to be a useful system to quantify and see how the practical pK_a compares with the predicted value.² **Figure 4** 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.

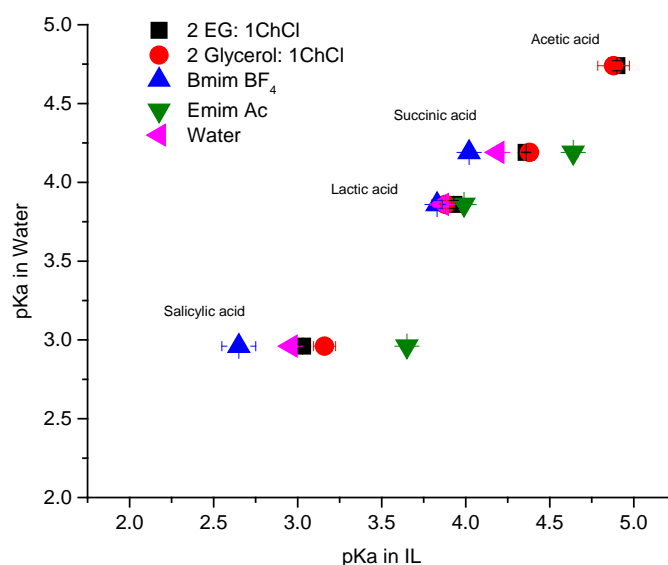


Figure 4 Correlation of pK_a values of acetic, succinic, lactic and salicylic acid in 4 ionic liquids and DESs compared to the values in water. Error bars are standard deviations of 5 data points.

It can be seen that the pK_a values of all the acids are largest in [Emim][OAc] and smallest for [Bmim][BF₄]. MacFarlane *et al.* predicted that the acids should be less dissociated in [Bmim][BF₄] should be lower than those observed in aqueous solutions due to its moderately weak basicity.² The pK_a values for the acids in [Bmim][BF₄] are, however, lower than might be

expected due to the presence of water which is known to hydrolyse the anion to HF and BF₃ 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_{In} values in **Table 2**.

It is difficult to remove the presence of all water from the samples so hydrolysis of [Bmim] [BF₄] is not surprising. To show the effect of water on [Bmim] [BF₄] 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 ± 0.012 . The addition of 1 wt % water caused the pK_{In} to decrease to 3.66 ± 0.034 and with 5 wt % water this fell further to pK_{In} 3.59 ± 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.^{18,19,20} Recently, it has been suggested that nano-domains of water exist rather than the water being homogeneously mixed with the ionic liquid²¹ and DES.²²

To demonstrate that this is indeed the case, dynamic light scattering was carried out with ionic liquids and DESs containing 5 wt% water. **Table 4** shows the average droplet size and distribution for [Bmim] [BF₄], [Emim] [OAc], 2 glycerol: 1ChCl and 2 EG: 1 ChCl. Clearly, far from creating homogeneous solutions the water forms nanodomains. These are largest in 2 EG: 1 ChCl with an average diameter of 311 nm. This is effectively a microemulsion with a droplet containing approximately 4×10^8 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.¹⁶ At low water content (<2.5 wt %) the OH protons on Ch⁺ 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.

The observation that microemulsions 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] [BF₄] 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.^{23,24,25}

Table 4: Average aqueous dispersed phase size for 5 wt % water in 2 ILs and 2 DESs. Error bars are standard deviations of 7 data points.

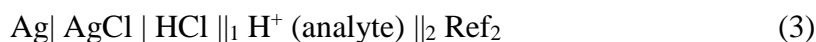
Bulk phase	Dispersed phase size (nm)
2 EG: 1 ChCl	311 \pm 18
2 glycerol: 1ChCl	105 \pm 12
[Bmim] [BF ₄]	96 \pm 4.0
[Emim][OAc]	72 \pm 8.0

The light scattering experiment with 5 wt% water in 2 EG: 1 ChCl was repeated with 0.01 mol kg⁻¹ triflic acid and it was found that the particle size was 239 \pm 20.8 nm which is similar to that without acid which suggests that the acid does not significantly affect the zeta potential and hence the size of the droplet.

pH measurement using an electrochemical sensor

Clearly a common way of measuring *pH* is to use an electrochemical cell. This approach was studied by Kanzaki *et al.*⁶ who created a hydrogen electrode to measure the *pH* of organic acids in ethylammonium nitrate. While the H⁺/H₂ couple appears to be Nernstian in these solutions the issue which needs to be reviewed is the performance of the glass membrane and the meaning of a liquid junction potential in an ionic liquid.

The glass electrode functions by having a conducting glass membrane which 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:²⁶



Where ||₁ is the conducting glass membrane and Ref₂ 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;

$$E_{\text{cell}} = \text{constant} + \frac{RT}{F} \log_{10} a_{\text{H}^+} \quad (4)$$

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 by measuring the cell potential as a function of HOTf molality. **Figure 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 ± 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% 2 EG: 1 ChCl . 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 ± 2.4 mV. Repeating the experiment using pure 2 EG: 1 ChCl results in a linear correlation but the slope of the line was -52 ± 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.

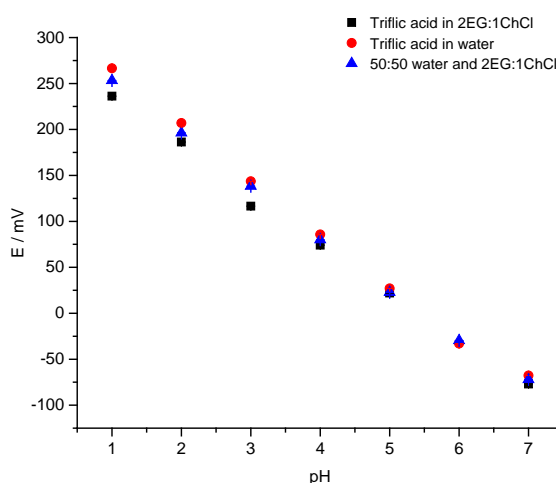
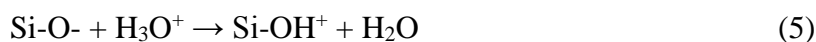


Figure 5: Correlation of cell potential with relative pH for triflic acid in (a) water (b) 2 EG: 1 ChCl and (c) a 50:50 wt mixture of a and b. Error bars are standard deviations of 3 data points.

The discrepancies in the slopes of **Figure 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



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. Using this plot the glass electrode was used to determine the relative pH of acetic and citric acid solutions in 2 EG: 1 ChCl and these data were used to calculate the pK_a values. A pK_a of 3.21 ± 0.05 was determined for citric acid compared to 3.63 ± 0.12 shown in **Figure 3** and a pK_a of 4.79 ± 0.14 was determined for acetic acid compared to 4.90 ± 0.04 . This shows that both methods give comparable values of pK_a although the glass electrode produces slightly lower values than that using the indicator dye.

In addition to the 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;



Table 5: Cell potential of cell (6) where DES1 is 2 EG: 1 ChCl and DES is a n HBD:1 ChCl Error bars are standard deviations of 3 measurements.

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

Table 5 shows the liquid junction potentials, E_{LJP} , for 4 DESs in contact with each other. It can be seen that the E_{LJP} values increase with increasing acidity. Although all 4 DESs have the same ionic species (Ch^+ and Cl^-) the proton will have a higher mobility than Ch^+ and this will set up an LJP as the migration of the proton will be easier than that of Ch^+ . 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 during synthesis of the DES.

This is therefore an issue that needs to be addressed when using ionic liquids of different relative proton activities in contact with each other *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 (3).

Conclusions

This study has shown bromophenol blue can be used as a probe for quantifying the pK_a values of organic acids in ionic liquids and deep eutectic solvents. The pK_{in} values were determined using a titration method using UV-vis spectroscopy. It was found that the pK_a values for 9 organic acids were constantly about 0.5 units higher than those found in water. This would be expected given the differences in concentration and strength of the base in the two liquids. The process was repeated for other ionic liquids and DESs and it was found that the liquid became more basic as the concentration of ChCl was increased in the DES. The acidity of ionic liquids was found to depend on the basicity of the anion. The unusually low pK_a value for [Bmim][BF₄] 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 BF₄⁻ based IL and highest in the acetate-based liquid.

The behaviour of a glass electrode was determined in DESs of different water content and it was shown that while the potential – pH plot was Nernstian at high water content the slope decreased as the amount of water decreased. It was proposed that the non-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. 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.

Acknowledgements

SSMA and AYMA would like to thank the Ministry of Higher Education in Iraq for funding studentships and Al-Nahrain University and the University of Kufa for allowing study leave to carry out this research.

References

- ¹ A. S. Amarasekara, *Chem. Rev.* 2016, **116**, 6133–6183
- ² D. R. MacFarlane, J. M. Pringle, K. M. Johansson, S. A. Forsyth and M. Forsyth, *Chem. Commun.*, 2006, 1905-1917
- ³ E. L. Smith, A. P. Abbott and K. S. Ryder, *Chem. Rev.* 2014, **114**, 11060-82
- ⁴ A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, R. Rasheed and V. Tambyrajah, *J. Am. Chem. Soc.* 2004, **126**, 9142-9147
- ⁵ D. R. MacFarlane, R. Vijayaraghavan, H. N. Ha, A. Izgorodin, K. D. Weaver and G. D. Elliott, *Chem. Commun.*, 2010, **46**, 7703-7705
- ⁶ R. Kanzaki, H. Kodamatani, T. Tomiyasu, H. Watanabe and Y. Umebayashi, *Angew. Chem. Int. Ed.* 2016, **55**, 6266 –6269
- ⁷ J. Gräsvik, J. P. Hallett, T. Q. To and T. Welton, *Chem. Commun.*, 2014, **50**, 7258-7261
- ⁸ H. Xing, T. Wang, Z. Zhou, Y. Dai, *J. Mol. Cat. A: Chem.* 2007, **264**, 53–59
- ⁹ L. M. Mihichuk, G. W. Driver and K. E. Johnson, *ChemPhysChem*, 2011, **12**, 1622-1632
- ¹⁰ D. Himmel, S. K. Goll, F. Scholz, V. Radtke, I. Leito and I. Krossing, *ChemPhysChem* 2015, **16**, 1428 – 1439
- ¹¹ F. Scholz, D. Himmel, L. Eisele, W. Unkrig, A. Martens, P. Schüter and I. Krossing, *Chem. Eur. J.* 2015, **21**, 7489-7502
- ¹² J. Reijenga, A. van Hoof, A. van Loon and B. Teunissen, *Anal. Chem. Insights*, 2013, **8**, 53–71
- ¹³ A. P. Abbott, G. Frisch, H. Garrett, J. Hartley, *Chem. Commun.*, 2011, **47**, 11876 – 11878
- ¹⁴ A. Trummal, L. Lipping, I. Kaljurand, I. A. Koppel, I. Leito, *J. Phys. Chem. A.* 2016, **120**, 3663-3669
- ¹⁵ M.J. O'Neil, (ed.) The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. Whitehouse Station, NJ: Merck and Co., Inc., 2006., 236
- ¹⁶ C. D'Agostino, L. F. Gladden, M. D. Mantle, A. P. Abbott, E. I. Ahmed, A. Y. M. Al-Murshedi, R. C. Harris *Phys. Chem. Chem. Phys.*, 2015, **17**, 15297-15304
- ¹⁷ M. G. Freire, C. M. S. S. Neves, I. M. Marrucho, J. A. P. Coutinho, and A. M. Fernandes, *J. Phys. Chem. A* 2010, **114**, 3744–3749
- ¹⁸ H. Rodríguez and J. F. Brennecke, *J. Chem. Eng. Data*, 2006, **51**, 2145–2155

-
- ¹⁹ M. G. Freire, C. M. S. S. Neves, P. J. Carvalho, R. L. Gardas, A. M. Fernandes, I. M. Marrucho, L. M.N. B. F. Santos, and J. A. P. Coutinho, *J. Phys. Chem. B* 2007, **111**, 13082-13089
- ²⁰ H. Katayanagi, K. Nishikawa, H. Shimozaki, K. Miki P. Westh and Y. Koga *J. Phys. Chem. B*, 2004, **108**, 19451–19457
- ²¹ K. Saihara, Y. Yoshimura, S. Ohta and A. Shimizu, *Sci. Rep.* 2015, **5**, 10619
- ²² E. A. Cade, J. Petenuci and M. M. Hoffmann, *ChemPhysChem* 2016, **17**, 520 – 529
- ²³ R. Sheldon, *Chem. Commun.*, 2001, **37**, 2399-2407
- ²⁴ Z. Yang, W. Pan, *Enzyme Microbial Tech.* 2005, **37**, 19–28
- ²⁵ Y. Kohno and H. Ohno, *Chem. Commun.*, 2012, **48**, 7119-7130
- ²⁶ K. L. Cheng and D-M Zhu, *Sensors*, 2005, **5**, 209-219