Article:

Reid, Joshua Elias Samuel James, Shimizu, Seishi orcid.org/0000-0002-7853-1683 and Walker, Adam J. (2020) Connecting precursors to a protic ionic liquid: Effects of hydrogen bond synergy in acid-base binary mixtures on the solvent-solute interactions. JOURNAL OF MOLECULAR LIQUIDS. 111746. ISSN: 0167-7322

https://doi.org/10.1016/j.molliq.2019.111746

Connecting Precursors to a Protic Ionic Liquid: Effects of Hydrogen Bond Synergy in Acid-Base Binary Mixtures on the Solvent-Solute Interactions

Joshua E. S. J. Reid[1,2,3*], *Seishi Shimizu*[1] *and Adam J. Walker*[2,3*]

[1]York Structural Biology Laboratory, Department of Chemistry, University of York,
Heslington, York YO10 5DD, United Kingdom.

[2]TWI Ltd., Granta Park, Great Abington, Cambridge CB21 6AL, United Kingdom. (former address)

[3]Bioniqs Ltd., BioCity Nottingham, Pennyfoot Street, Nottingham, NG1 1GF, United Kingdom.
(present address)

Keywords: Hydrogen Bonding / Acetic Acid / Amine / Binary Mixture /Solvatochromic Dyes / Solvation Environment/ Protic Ionic Liquids

Corresponding Author:

Joshua E. S. J. Reid

York Structural Biology Laboratory, Department of Chemistry, University of York, Heslington, York,
YO10 5DD, United Kingdom

Email: jr649@york.ac.uk

Adam J. Walker

Bioniqs Ltd., BioCity Nottingham, Pennyfoot Street, Nottingham, NG1 1GF, United Kingdom.

Email: adam.walker@bioniqs.co.uk

Abstract

How does the solvation behaviour of a protic ionic liquid (PIL) relate to their precursor Brønsted acid and base? By studying how the solvent-solute interactions in a binary mixture of a Brønsted acid and base changes with respect to composition, a rational connection between precursor and PIL can be made. Using acetic acid and *N,N*-dimethylethanolamine as model precursors, we demonstrate here that the change in solvent-solute interactions, as inferred from the Kamlet-Taft solvatochromic parameters, are drastically different from additivity approximation based on the simple sum of precursors. Indeed, the apparent hydrogen bond basicity of these mixtures can either be greater than or lesser than either precursor, and the apparent hydrogen bond acidity of these mixtures are dependent on the solvatochromic probe used. Nevertheless, the change in polarizability correlates well with the extent of proton transfer taking place, as inferred from infrared spectroscopy, and can be used as a measure for precursor non-additivity in PILs. Our findings shed light on how the solvation properties of PILs connect to their precursor materials and showcase a new strategy to expand the tuneability of the solvent properties in PIL-based systems.

.

1. Introduction

Development of alternative reaction media has become more and more widespread in the pursuit of more sustainable chemistry.[1–4] A promising class of such alternative media is protic ionic liquids (PILs), broadly classified as liquid materials formed from the proton transfer reaction between a Brønsted acid and base.[5–7] The synthesis of PILs by the direct mixing of a suitable acid and base to produce a liquid materials means they are a wide number of possible PILs that can be prepared for a relatively low cost in comparison to aprotic ionic liquids with similar structures.[5,7–9]

In terms of sustainability, a number of PILs have been shown to exhibit favourable toxicology,[10,11] mutagenicity[12] and biodegradation[13] screening results. Moreover, that PIL precursors such as carboxylic acids and tertiary amines can be derived from renewable feedstocks adds to its potential sustainability credential. .[14,15] The vast majority of PIL application are as alternative solvents[5–7] for biocatalysis,[16–19] natural product extraction,[20–22] and biomass processing.[23–28] To fulfil its potential, solvent choice and optimization should be made in a rational manner, for which an understanding is indispensable as to what governs the solvation environments. Despite extensive research on what governs the solvent properties of ionic liquids in general,[29–32] distinctly different chemistry exhibited by analogous protic and aprotic ionic liquids still poses challenge in the understanding and prediction of PIL solvent environments.[33–36]

There is still a lack of consensus even on

- how anion and cation structure variation in PILs can change the solvent-solute interactions, and
- how such interaction change can be inferred from solvatochromic parameters. [8,37–40]

We have recently shown that additional hydrogen bond donating capability of the cation of the PIL *N,N*-dimethylethanolammonium acetate, [DMEtAH][OAc], results in significantly greater ionic character, which leads to a greater dipolarity-polarizability and lesser hydrogen bond basicity of the PIL compared to similar PILs without additional hydrogen bond donating capabilities.[8,9] This shows that both ionic character and hydrogen bonding are crucial for the PIL solvation capacity. In addition, recent observations that solvation environment can strongly be affected by cosolvents,[41–44] indicating the importance of competitive solvation between PIL and co-solvents.[43,45]

The connection between a PIL and its corresponding precursors are often overlooked, and are treated as novel green solvents as opposed to mixtures of well-established acids and bases.[46,47] Previously, we have shown that there is a connection between the properties of PILs and the structures of their precursor materials.[8,9] However this connection is still not well understood due to the lack of a clearly-established connection between PILs and Brønsted acid-base binary mixtures. [46–48] That does not mean the lack of previous attempts exploring this connection, but the topics mostly focus on electrochemical properties and ion mobility or ionicity.[49,50] Recent work on the mixing behaviour of the

PIL *n*-butylammonium acetate with its corresponding precursor acid and base suggested association of the precursors with the PIL; the solvent properties were found to be strongly dependent on the acid:base ratio from solubility studies with a range of solutes.[51] Otherwise, there is no reported literature exploring how the general solvation capabilities change with composition in these types of systems.

By studying the composition derivative of the solvation behaviour in terms of solvent-solute interaction parameters in acid-amine binary mixtures, a deeper understanding can be found as to how precursor structure relates to the solvation capabilities of a PIL. We have therefore chosen to study the solvent-solute interactions in the binary system of acetic acid (HOAc) and *N,N*-dimethylethanolamine (DMEtA). By using a selection of solvatochromic dyes, the Kamlet-Taft solubility parameters for hydrogen bond acidity (α), hydrogen bond basicity (β) and non-specific polarizability (π) have been determined as a function of composition.[8] Furthermore, we report Gutmann Acceptor Number (AN) values as a function of composition to compare against the values of α obtained using solvatochromic dyes with ^{31}P NMR measurements of the probe solute, triethylphosphine oxide. We emphasise here that our goal is to rationalise the relative change in solvent-solute interactions between a binary acid-amine mixture, including the equimolar composition of the PIL, and the corresponding precursor acid and amine.

2. Materials and Methods

The acetic acid (≥99.5%) and *N,N*-dimethylethanolamine (≥99.5%,) used in the preparation of the binary mixtures were supplied by Sigma Aldrich UK, and were not further purified. The solvatochromic dyes, 4-nitroaniline, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate, 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate, 1-ethyl-4-(methoxycarbonyl)pyridinium iodide and Nile red were supplied by Sigma Aldrich UK, and were not further purified. *N,N*-diethyl-4-nitroaniline was supplied by Fluorochem Ltd. And was not further purified. The ^{31}P NMR probe solute triethylphosphine oxide was supplied by Sigma Aldrich UK and was not further purified.

2.1. Preparation of acid-amine binary mixtures

The acid-amine binary mixtures were prepared using an adapted method from Walker.[5] A flask purged with N_2 was charged with *N,N*-dimethylethanolamine and placed in an ice bath. Acetic acid was added to the flask dropwise while stirring. After complete addition, the reaction was left to stir for 24 h, to ensure mixing of precursors was complete. Because of the known effect of low concentrations of water on the structure of PILs and ILs in general,[36,52] water content in each PIL was determined using one component Karl-Fischer titration using a Metrohm 890 Titrando with 803 Ti Stand apparatus. The mass of precursors and subsequent water content for each mixture is summarized in the supporting information document (SI. 1). A second batch of mixtures were prepared for repeat measurements of the solvatochromic dyes and the ^{31}P NMR measurements, with the corresponding preparation information and water content also summarized in the supporting information document (SI. 2).

2.2. Solvatochromic dyes experiments

The solvatochromic parameters α, β and π* were calculated based on the observed wavelength of maximum absorption, λ_{max}, of four solvatochromic dyes; 4-nitroaniline (NA), *N,N*-diethyl-4-nitroaniline, (DE-NA) and 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (BD) and 1-ethyl-4-(methoxycarbonyl)pyridinium iodide (Z salt). The UV-Visible spectra in the region of 300 – 800 nm, with a 0.1 nm resolution, was recorded using a Thermo Scientific Evolution 60S UV-Visible Spectrophotometer using quartz silica 1 cm path length cuvettes. A small quantity of dye (c.a. 2-5 mg) was dissolved in 1 cm^3 of PIL and was subsequently diluted to achieve a relative absorption value between 1 – 1.5. The wavelength is then converted from nm to 10^3 cm^{-1} for all necessary calculations. To calculate the solvatochromic parameters, the following equations were used;[29,38,53,54]

$$\alpha = [-0.182(10.91 - \lambda_{max}\mathrm{RD}) - \ 0.72\pi^*] \tag{1}$$

$$\beta = \frac{(1.035\lambda_{max}\mathrm{DE}+2.64- \lambda_{max}\mathrm{NA})}{2.80} \tag{2}$$

$$\pi^* = 0.314(27.52 - \ \lambda_{max}\mathrm{DE}) \tag{3}$$

As λ_{max}RD cannot be measured directly in all acid-amine binary mixtures (due to the protonation of the dye at high acid mole fractions), this value is inferred indirectly from the λ_{max} of both BD and Z Salt solvatochromic dyes (in cm^{-1}) in the following relation;[55–57]

$$\lambda_{max}\text{RD} = 1.3423\lambda_{max}\text{BD} - 76.842 \qquad R^2 = 0.9818 \qquad (4)$$

$$\lambda_{max}\text{RD} = \frac{28591}{-0.1293\lambda_{max}\text{Z salt}+98.0191} \qquad R^2 = 0.9953 \qquad (5)$$

The values of λ_{max} for each dye (and any repeat measurements reported) are summarised in the supporting information document (SI 3). The subsequent values of each Kamlet-Taft parameter calculated from these values are summarised in the supporting information document (SI 4). Due to dye availability, only the measurements of λ_{max}NA and λ_{max}DE could be repeated reliably. The subsequent error margins for the values of β and π^* calculated are represented as 1 standard deviation of three measurements.

2.3. ^{31}P NMR Spectroscopy

Samples were prepared in a glove box environment due to the hygroscopic nature of the probe solute, triethylphosphine oxide (tepo). Solutions of tepo were prepared at approximately 10 mol%, 5 mol% and 2.5 mol% concentrations in the pure acid and amine, their respective mixtures and hexane. Solutions were left to dissolve for 24 hours to ensure complete dissolution. The solutions were then transferred into a 5mm borosilicate NMR tube with a co-axial insert filled with $CDCl_3$ as an external lock. ^{31}P NMR spectra were obtained at 161.98 MHz using a Bruker 400 MHZ Ultrashield Plus spectrometer with a BBFO probe. An aqueous solution of Phosphoric acid (85 wt%) was used as an external reference. All samples were measured at 298.2 K. The values of ^{31}P NMR chemical shift at different concentrations were used to extrapolate the chemical shift at infinite dilution, δ_{inf}, for each mixture, the pure acid and amine and hexane. The difference in δ_{inf} between a sample and hexane is used to determine the AN of that sample (hexane is used as a reference, δ_{inf} (hexane) = 0). The AN number for each samples was determined using the following equation:[58]

$$\text{AN} = 2.348(\delta_{inf}\,(\text{sample}) - \delta_{inf}(\text{hexane})) \qquad (6)$$

2.4. Attenuated Total Reflectance-Infrared Spectroscopy (ATR-IR)

The ATR–IR spectra of all precursor materials and mixtures were recorded at room temperature using an A_2 Technologies (Agilent) ExoScan Fourier–Transform Infrared Spectrometer fitted with a Germanium crystal attenuated total reflectance interface. All measurements were performed within the infrared region between 3500 and 800 cm^{-1}. A background signal was recorded 32 times to produce a single averaged background spectrum. The sample was then placed directly on to the interface for immediate measurement of 32 scans and then averaged to produce a single sample spectrum. The interface was cleared using a dry paper towel and propan–2–ol. Once the interface was cleaned sufficiently to return the beam to the background baseline, the instrument was ready for subsequent measurements. Each sample was recorded three times for a total of 96 scans, averaged to produce the final ATR–IR spectrum.

3. Results and Discussion

The three Kamlet-Taft solubility parameters for hydrogen bond acidity (α), hydrogen bond basicity (β) and dipolarity-polarizability (π*) and Gutmann Acceptor Number (AN) values were determined at 298.15 K over the whole composition range. These empirical parameters are well established in the study of solvent-solute interactions in liquid mixtures.[30,40,58–60] In general, the solvent-solute interactions are strongly dependent on composition, and each parameter changes in a different manner with respect to composition. Solvatochromic dyes offer a very striking way of observing how the solvent environment changes with composition, as demonstrated in Figure 1.

Figure 1: The solvatochromic shift of the dye 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate in DMEtA (far left), HOAc (far right) and their corresponding mixtures, with increasing acid mole fraction going from left to right.

3.1. Hydrogen Bond Acidity; the α parameter

The α parameter has been used extensively to describe specific hydrogen bond donor capabilities of a solvent. The greater the α parameter, the greater the hydrogen bond donor capability of that solvent. Typically, this value is inferred from the solvatochromic shift of the dyes 4-nitroaniline (used to determine π*) and 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate, also known as Reichardt's dye (RD). However, for pure HOAc and the acid-rich compositions studied, we are unable to observe a peak for RD due to the protonation of the dye in the acidic systems. This issue is well-known,[61] and alternative means of determining the α parameter have been proposed.

One example was based on the determination of the polarity parameter established by Kosower referred to as the Z parameter,[55,56] and then use a linear relation between Z and the Et(30) to indirectly calculate α.[61] Another example was based on using a dye with an analogous structure to RD, referred to as BD, which is less basic and therefore less susceptible to being protonated,[57] and using a linear relation between the λ_{max} of RD and BD to indirectly calculate α. As neither of these strategies appeared to be a superior technique over the other, we first obtained the values of λ_{max} for BD and Z-salt to compare against λ_{max} of RD (up to the equimolar composition) (Figure 2). The inherent difference in how each probe solute interacts with the solvent mixture may lead to a significant change in the local solvation environment relative to the bulk solvation environment for each probe.[62,63]

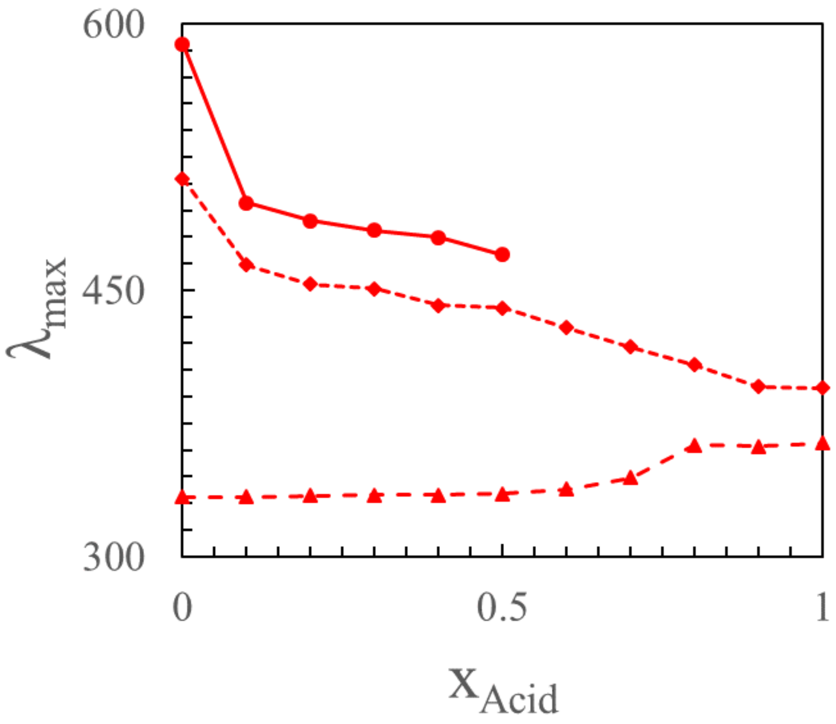

Figure 2. Dependence of the λ_{max} for the dyes RD (solid line, circle), BD (dotted line, diamond) and Z-Salt (dashed line, triangle) on mole fraction of acid in the DMEtA-HOAc binary mixture.

From figure 2, we show that the trend in amine-rich compositions for RD and BD are much more alike than for RD and Z-salt. Furthermore, the values of λ_{max} (Z-salt) are at a lower wavelength than the available literature data comparing the values of λ_{max} (Z-salt) to λ_{max} (RD). As such, we do not feel that extrapolating the literature correlation to include these experimental data points is an appropriate means of inferring values of α. The values of λ_{max} (BD) and λ_{max} (RD) have been used to determine the values of α for the systems studied (Figure 3).

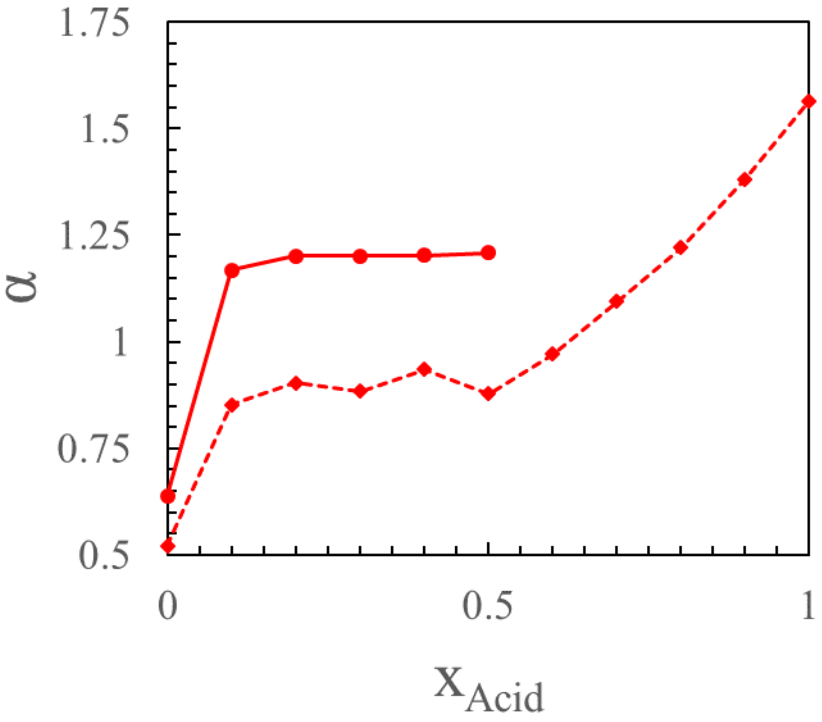

Figure 3. Dependence of the α hydrogen bond donor parameter calculated from RD (solid line, circle) and BD (dotted line, diamond) on mole fraction of acid in the DMEtA-HOAc binary mixture.

From Figure 3, we can see that both values of α follow a similar trend over the amine-rich mixtures, despite the absolute values being distinctly different. The difference in the absolute values can largely be drawn to the limited training set available: while the values used covered the wavelength range of the binary mixtures in this study, they didn't include a significant number of strong hydrogen bond donor or acceptor solvents, which may have yielded a better correlation to apply to our binary mixtures. Nevertheless, the relative changes in α as a function of composition can still yield a great deal of information about these systems.

What is interesting is the very large increase in α from both dyes going from the pure amine to the 0.1 acid mole fraction mixture. This implies that the addition of a small amount of HOAc creates a substantially stronger hydrogen bond donor solvation environment. It is very likely that at these amine-rich compositions, the HOAc would become deprotonated and form the PIL, [DMEtAH][OAc]. We have previously shown that hydrogen bond donor interactions can stabilise the formation of PILs, so it would be expected that any amine present in acid-rich compositions will be protonated and form ionic species.[8] It may be that BD exhibits a preferential solvation with the PIL over the free amine in these mixtures. Given by how the values of α remain relatively unchanged in all amine-rich binary mixtures, it is highly plausible that BD is preferentially solvated by the PIL in the amine-rich compositions. From the equimolar composition to pure acid, there is a gradual almost linear increase in the values of α observed. This implies an almost systematic change of the hydrogen bond donor capability of the solvent system, likely due to a decrease in the number of PIL-BD interactions and a corresponding increase in the number of HOAc-BD interactions.

3.2. Hydrogen Bond Acidity; Gutmann Acceptor Number

Initially, we wanted to compare between multiple different solvatochromic dyes used to calculate the α Kamlet-Taft parameter. However, with the lack of appropriate literature data to calculate α from the λ_{max} (Z salt) values our values couldn't be utilised. In light of this, we sought to use an alternative technique to discuss solvent-solute hydrogen bond acidity. A recent study by McCune demonstrated the use of Gutmann Acceptor Number (AN) values to discuss how acidity changes for mixtures of ionic liquids and Brønsted acids.[64] The AN values were determined by observing how the ^{31}P NMR chemical shift of the solute triethylphosphine oxide (tepo) changes, as a result of the interaction the solute has with a Brønsted acid.[58] By studying the AN values, we can compare against the values of α as obtained by UV/Vis spectroscopy to compare these measurements of solvent-solute hydrogen bond donor interactions.

From the values of AN obtained, we can observe there are some distinct composition dependent trends observed; in the acid-rich compositions AN values increase significantly with increasing acid mole fraction, from pure amine to 0.1 acid mole fraction we see a jump in AN values, which remains relatively unchanged up until the equimolar composition (Figure 4). These composition trends are very relatable to the trends observed with the values of α obtained from solvatochromic dyes, despite the differences between these two methods in terms of solute structure and analytical method. This reinforces the implication that, in amine-rich compositions, the solute preferentially interacts with the [DMEtAH][OAc] species over the free amine species.

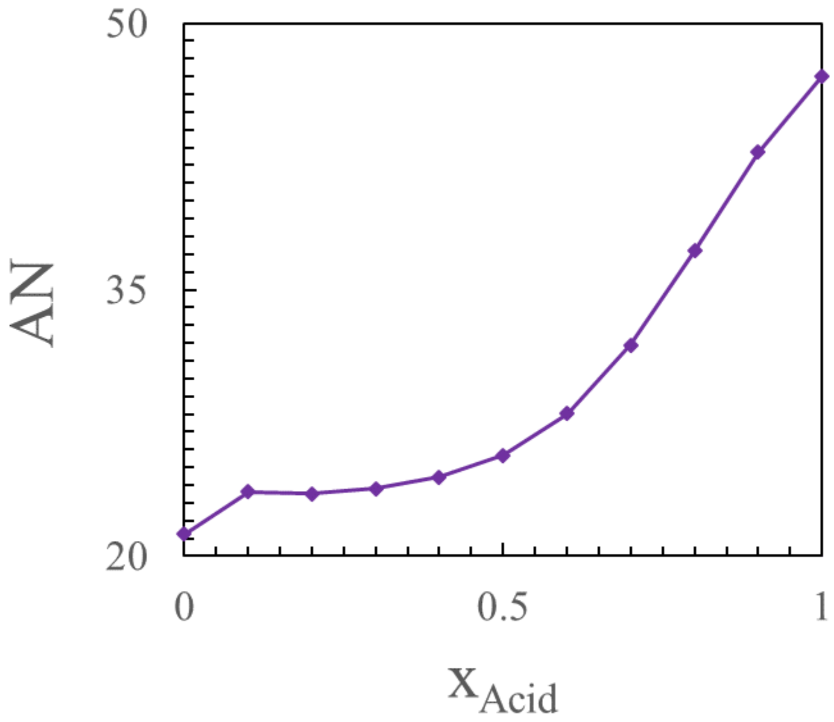

Figure 4. Dependence of the Gutmann Acceptor Number values on mole fraction of acid in the DMEtA-HOAc binary mixture.

3.3. Hydrogen Bond Basicity; the β parameter

The β parameter has been widely used to characterise the hydrogen bond acceptor capability of a solvent.[53,65] The greater the β value, the greater the hydrogen bond acceptor capability of the solvent. The values of β were determined based on the λ_{max} of the dyes 4-nitroaniline (NA) and *N,N*-diethyl-4-nitroaniline (DE). While other pairs of solvatochromic dyes have been used to calculate β values, these two dyes are perhaps the most widely used, particularly in the study of solvent-solute interactions in ionic liquids.[29,38,40,53,65]

As expected, DMEtA has a greater β than that of HOAc. Upon mixing with HOAc, the β value increases, reaching a maximum at the 0.2 acid mole fraction. This is likely because all HOAc at these compositions becomes deprotonated to the acetate anion, which is a strong hydrogen bond acceptor. The combination of free DMEtA base and deprotonated acetate anion creates a highly hydrogen bond acceptor solvation environment. With increasing acid mole fraction, there is a fairly systematic decrease in β, reaching a minimum β value at the 0.9 acid mole fraction composition.

Interestingly, the acid mole fractions 0.7-0.9 all exhibit lower β values than pure acetic acid. In our previous work, we hypothesised that the hydroxyl functional group on the cation of the equimolar mixture of HOAc and DMEtA, namely the PIL [DMEtAH][OAc], can form a hydrogen bond with the acetate anion, thus stabilising the anion form.[8] Driven by local hydrogen bond interactions between the hydroxyl group of the amine/cation species towards acid/anion species, this interaction would reduce the availability of the carboxylic acid/carboxylate functional group to accept hydrogen bond interactions from a solute.

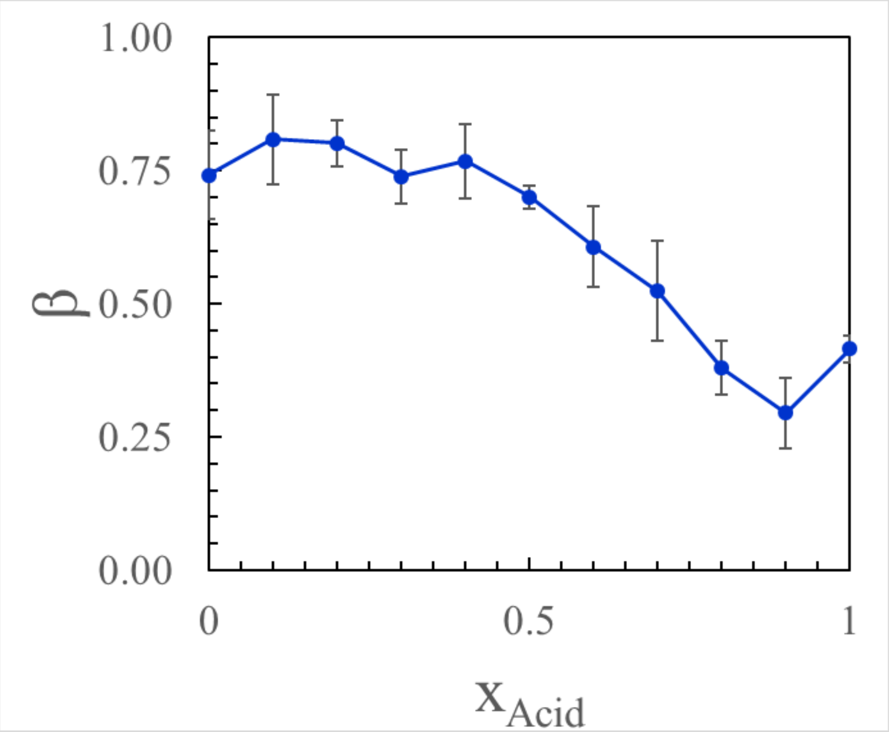

Figure 3. Dependence of the β hydrogen bond acceptor parameter on mole fraction of acid in the DMEtA-HOAc binary mixture.

3.4. Dipolarity and Polarizability; the π* parameter

The π* parameter is one of many solvatochromic dyes that have been used to characterise non-specific polarity-polarizability solvent-solute interactions in solvents.[54,66] Like with both α and β, the greater the value of π*, the greater the dipolarity-polarizability of the solvent in question. While many dyes have been used to determine π*, we chose to use *N,N*-diethyl-4-nitroaniline alone to characterise the DMEtA system.

Both precursors exhibited very similar values of π*, with acetic acid having a value of 0.64 and *N,N*-dimethylethanolamine having a value of 0.59. What is immediately apparent is that all binary mixtures exhibit a greater value of π* than both precursors. From the pure amine, it appears as though π* increases consistently, reaching a maximum at the 0.6 acid mole fraction composition. At higher acid mole fractions, there is a slight decrease in π*, with a steep drop going from the 0.9 acid mole fraction to pure acetic acid.

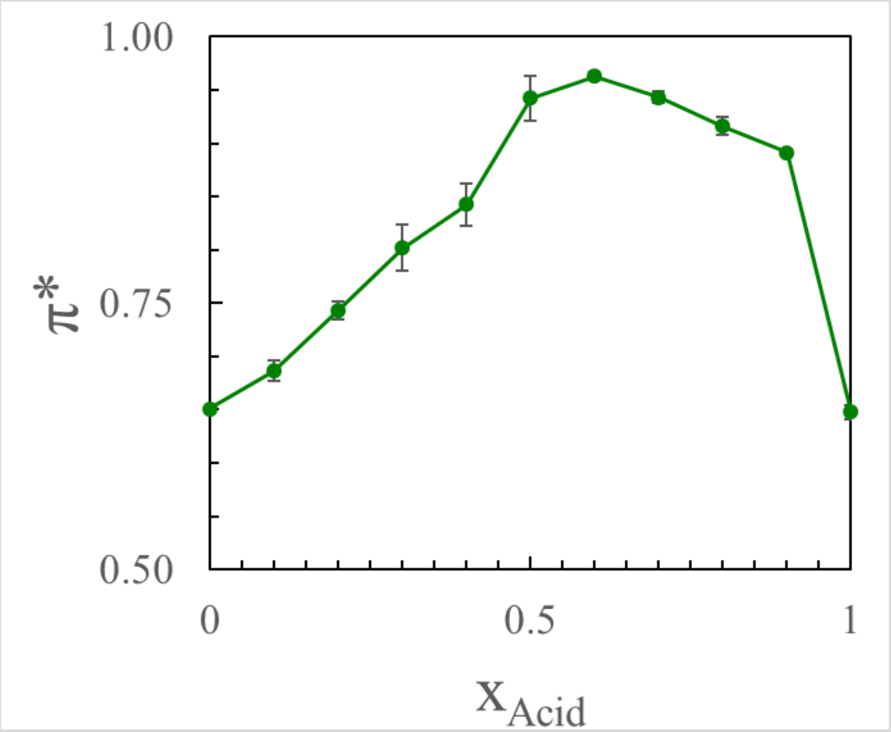

Figure 4. Dependence of the π* dipolarity-polarizability parameter on the acid mole fraction in the DMEtA-HOAc binary mixture.

In our previous work, we showed an excellent correlation between the π* parameter of three PILs with its ionic character, i.e. the extent of proton transfer from Brønsted acid to base.[8] The ionic character was determined from the relative ratio of absorbance peak areas of the carbonyl vibrations of the neutral carboxylic acid to the carboxylate vibrations of the anion. We have measured the Mid-IR spectra of these acid base mixtures to understand how well this correlation extends to non-equivalent mixtures of a Brønsted acid and base (Figure 5). While the same methodology cannot be applied to these systems, due to the absence of the neutral acetic acid peak in the spectra of some amine-rich mixtures, a qualitative comparison of the absorbances of these peaks can help to rationalise the extent of proton transfer in each mixture.

From the Mid-IR spectra, all compositions exhibit an absorbance due to the carboxylate anion[8,67,68] species in the region 1540 - 1570 cm^{-1} depending on the shift in frequency due to the corresponding change in liquid composition (Figure 5). For the amine rich mixtures there is only a small absorbance due to neutral carboxylic species, with the mixtures with 0.1 and 0.2 mole fraction HOAc show negligible absorbance for carboxylic species. This correlates exceptionally well with the observed values for β as discussed above.

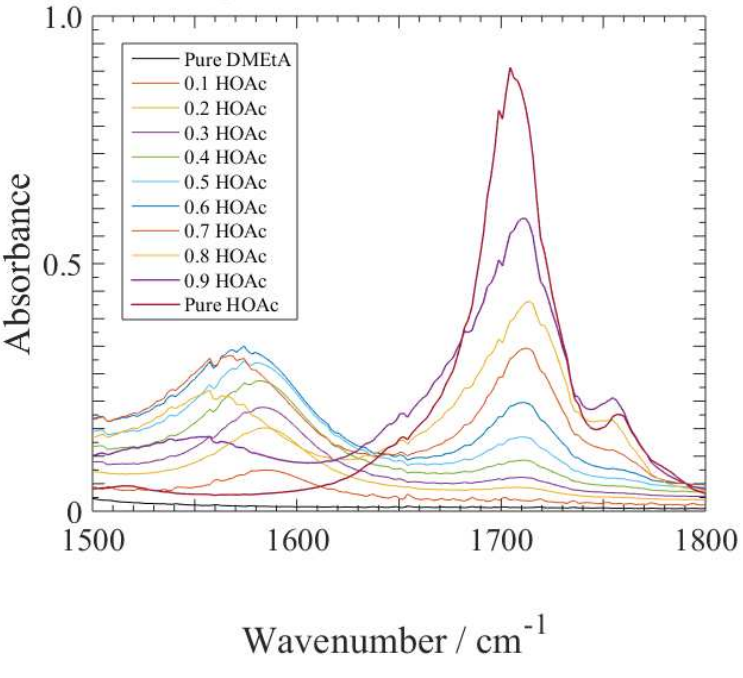

Figure 5. ATR–IR spectra of the HOAc-DMEtA binary system over the entire composition range in the region of 1500–1800 cm^{-1}. The peak for the acetate species occurs at ~1570 cm^{-1} and the peak corresponding to HOAc species is at ~1710 cm^{-1}.[8,67]

The compositions which exhibit the largest absorbances from the carboxylate anion species are 0.5, 0.6 and 0.7 mole fraction acetic acid. Considering that the absorbance due to the carboxylic acid species increases systematically with the increasing mole fraction of acetic acid, it is likely the composition with the greatest ionic character is either the 0.5 mole fraction acetic acid, or some composition between 0.5 and 0.6 mole fraction acetic acid. This correlates very well with the values of π* found for these systems, with the maximum value found for the mixture of 0.6 mole fraction acetic acid, and the 0.5 and 0.7 mole fractions acetic acid all having large values of π*. It also supports our observations for the hydrogen bond donor capability of the solvent, where even in the 0.1 acid mole fraction mixture, there is only evidence of acetate species and no neutral acetic acid, which supports our observation of preferential hydrogen bond donor interactions from the PIL in the amine-rich mixtures.

4. Conclusion

We have shown that solvent-solute interactions in the acetic acid-*N,N*-dimethylethanolamine binary system, of which the equimolar composition is also known as the PIL *N,N*-dimethylethanolammonium acetate, are highly composition dependent. To characterize the hydrogen bond acidity of a system, the Kamlet-Taft parameter α and the Gutmann Acceptor Number (AN) values were determined, both showing complementary changes in the hydrogen bond donor capability of the solvent with composition. The amine-rich compositions exhibit a preferential solvation by the PIL species, while in acid rich mixtures there is a systematic change in hydrogen bond donor capacity as the PIL concentration degreases with increasing acid concentration. The difference in solvent-solute interactions as a function of composition is particularly evident with the apparent hydrogen bond basicity (β) of the binary mixtures; some compositions exhibited larger values of β than the pure amine, while others exhibited lower values of β than the pure acid. The dipolarity-polarizability (π*) of all binary mixtures are greater than their corresponding precursors, with acid-rich compositions exhibiting the greatest dipolarity-polarizability. This is rationalized by the proton transfer reaction between acid and amine species as inferred from infrared spectroscopy. The absorbance of acetate species relative to neutral species correlates well with the observed trends in dipolarity-polarizability. The sensitivity of solvent-solute interactions in these binary systems can be exploited as a potential strategy to further expand the tunability of the solvation properties of PILs.

Acknowledgements

J. E. S. J. Reid gratefully acknowledges financial support from the Engineering and Physical Sciences Research Council (EPSRC), through an industrial CASE award, supervised by S.S. and A.J.W.

Conflicts of Interest

The authors report of no known conflict of interest.

References

1 R. A. Sheldon, *Chem. - A Eur. J.*, 2016, **22**, 12984–12999.

2 J. H. Clark, A. Hunt, C. Topi, G. Paggiola and J. Sherwood, *Sustainable Solvents*, Royal Society of Chemistry, Cambridge, 1st edn., 2017.

3 C. J. Clarke, W.-C. Tu, O. Levers, A. Bröhl and J. P. Hallett, *Chem. Rev.*, 2018, **118**, 747–800.

4 T. Welton, *Proc. R. Soc. A*, 2015, **471**, 1–26.

5 EP1805131, *Eur. Pat. 1 805 131*, 2004.

6 C. Austen Angell, Y. Ansari and Z. Zhao, *Faraday Discuss.*, 2012, **154**, 9–27.

7 T. L. Greaves and C. J. Drummond, *Chem. Rev.*, 2015, **115**, 11379–11448.

8 J. E. S. J. E. S. J. Reid, C. E. S. C. E. S. S. Bernardes, F. Agapito, F. Martins, S. Shimizu, M. E. M. E. Minas Da Piedade and A. J. A. J. Walker, *Phys. Chem. Chem. Phys.*, 2017, **19**, 28133–

28138.

9 J. E. S. J. Reid, F. Agapito, C. E. S. Bernardes, F. Martins, A. J. Walker, S. Shimizu, M. E. M. da Piedade and M. E. Minas da Piedade, *Phys. Chem. Chem. Phys.*, 2017, **19**, 19928–19936.

10 M. V. S. Oliveira, B. T. Vidal, C. M. Melo, R. de C. M. de Miranda, C. M. F. Soares, J. A. P. Coutinho, S. P. M. Ventura, S. Mattedi and Á. S. Lima, *Chemosphere*, 2016, **147**, 460–466.

11 J. E. S. J. Reid, H. Prydderch, M. Spulak, S. Shimizu, A. J. Walker and N. Gathergood, *Sustain. Chem. Pharmacol.*, 2018, **7**, 17–26.

12 J. E. S. J. Reid, N. Sullivan, L. Swift, G. A. Hembury, S. Shimizu and A. J. Walker, *Sustain. Chem. Process.*, 2015, **3**, 17.

13 A. Tzani, M. Elmaloglou, C. Kyriazis, D. Aravopoulou, I. Kleidas, A. Papadopoulos, E. Ioannou, A. Kyritsis, E. Voutsas and A. Detsi, *J. Mol. Liq.*, 2016, **224**, 366–376.

14 C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon and M. Poliakoff, *Science*, 2012, **337**, 695–699.

15 C. S. K. Lin, L. A. Pfaltzgraff, L. Herrero-Davila, E. B. Mubofu, S. Abderrahim, J. H. Clark, A. A. Koutinas, N. Kopsahelis, K. Stamatelatou, F. Dickson, S. Thankappan, Z. Mohamed, R. Brocklesby and R. Luque, *Energy Environ. Sci.*, 2013, **6**, 426–464.

16 A. J. Walker and N. C. Bruce, *Chem. Commun.*, 2004, **1**, 2570–2571.

17 A. J. Walker and N. C. Bruce, *Tetrahedron*, 2004, **60**, 561–568.

18 R. A. Sheldon, *Green Chem.*, 2005, **7**, 267–278.

19 F. Falcioni, H. R. Housden, Z. Ling, S. Shimizu, A. J. Walker and N. C. Bruce, *Chem. Commun.*, 2010, **46**, 749–751.

20 M. W. Sanders, L. Wright, L. Tate, G. Fairless, L. Crowhurst, N. C. Bruce, A. J. Walker, G. A. Hembury and S. Shimizu, *J. Phys. Chem. A*, 2009, **113**, 10143–10145.

21 C. Yansheng, Z. Zhida, L. Changping, L. Qingshan, Y. Peifang and U. Welz-Biermann, *Green Chem.*, 2011, **13**, 666–670.

22 N. Goujon, X. Wang, R. Rajkowa and N. Byrne, *Chem. Commun.*, 2012, **48**, 1278–1280.

23 A. W. T. King, J. Asikkala, I. Mutikainen, P. Järvi and I. Kilpeläinen, *Angew. Chemie - Int. Ed.*, 2011, **50**, 6301–6305.

24 A. Idris, R. Vijayaraghavan, A. F. Patti and D. R. Macfarlane, *ACS Sustain. Chem. Eng.*, 2014, **2**, 1888–1894.

25 E. C. Achinivu, R. M. Howard, G. Li, H. Gracz and W. A. Henderson, *Green Chem.*, 2014, **16**, 1114–1119.

26 A. George, A. Brandt, K. Tran, S. M. S. N. S. Zahari, D. Klein-Marcuschamer, N. Sun, N. Sathitsuksanoh, J. Shi, V. Stavila, R. Parthasarathi, S. Singh, B. M. Holmes, T. Welton, B. A. Simmons and J. P. Hallett, *Green Chem.*, 2015, **17**, 1728–1734.

27 C. Chiappe, A. Mezzetta, C. S. Pomelli, B. Masciocchi, A. Gentile and G. Iaquaniello, *Green Chem.*, 2016, **18**, 4982–4989.

28 T. Rashid, C. F. Kait, I. Regupathi and T. Murugesan, *Ind. Crops Prod.*, 2016, **84**, 284–293.

29 L. Crowhurst, P. R. Mawdsley, J. M. Perez-arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790–2794.

30 M. a Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N. H. Hassan, J. P. Hallett, P. a Hunt, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton and R. Wilding, *Phys. Chem. Chem. Phys.*, 2011, **13**, 16831–16840.

31 M. Y. Lui, L. Crowhurst, J. P. Hallett, P. A. Hunt, H. Niedermeyer and T. Welton, *Chem. Sci.*, 2011, **2**, 1491.

32 J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.

33 C. A. Angell, N. Byrne and J. P. Belieres, *Acc. Chem. Res.*, 2007, **40**, 1228–1236.

34 K. Fumino, A. Wulf and R. Ludwig, *Phys. Chem. Chem. Phys.*, 2009, **11**, 8790–8794.

35 D. H. Zaitsau, V. N. Emel'yanenko, P. Stange, C. Schick, S. P. Verevkin and R. Ludwig, *Angew. Chemie - Int. Ed.*, 2016, 11682–11686.

36 J. E. S. J. Reid, R. J. Gammons, J. M. Slattery, A. J. Walker and S. Shimizu, *J. Phys. Chem. B*, 2017, **121**, 599–609.

37 I. A. Sedov, T. I. Magsumov, T. M. Salikov and B. N. Solomonov, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25352–25359.

38 S. K. Shukla, N. D. Khupse and A. Kumar, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2754–2761.

39 C. Reichardt, *Green Chem.*, 2005, **7**, 339–351.

40 P. G. Jessop, D. Jessop, D. Fu and L. Phan, *Green Chem.*, 2012, **14**, 1245–1259.

41 C. Adam, M. V. Bravo and P. M. E. Mancini, *Tetrahedron Lett.*, 2014, **55**, 148–150.

42 H. Salari, A. Reza, M. R. Elahifard, A. R. Harifi-Mood, M. R. Elahifard and M. R. Gholami, *J. Solution Chem.*, 2010, **39**, 1509–1519.

43 H. Salari, M. Khodadadi-Moghaddam, A. R. Harifi-mood and M. R. Gholami, *J. Phys. Chem. B*, 2010, **114**, 9586–9593.

44 H. Salari, S. Ahmadvand, A. R. Harifi-Mood, M. Padervand and M. R. Gholami, *J. Solution Chem.*, 2013, **42**, 1757–1769.

45 L. Wright, M. W. Sanders, L. Tate, G. Fairless, L. Crowhurst, N. C. Bruce, A. J. Walker, G. A. Hembury and S. Shimizu, *Phys. Chem. Chem. Phys.*, 2010, **12**, 9063–9066.

46 F. Kohler, H. Atrops, H. Kalali, E. Liebermann, E. Wilhelm, F. Ratkovics and T. Salamon, *J. Phys. Chem.*, 1981, **85**, 2520–2524.

47 F. Kohler, R. Gopal, G. Gotze, H. Atrops, M. A. Demiriz, E. Liebermann, E. Wilhelm, F. Ratkovics and B. Palagyl, *J. Phys. Chem.*, 1981, **85**, 2524–2529.

48 K. Orzechowski, M. Pajdowska, K. Fuchs and U. Kaatze, *J. Chem. Phys.*, 2003, **119**, 8558–8566.

49 M. A. B. H. Susan, A. Noda, S. Mitsushima and M. Watanabe, *Chem. Commun.*, 2003, **45**, 938–939.

50 J. A. McCune, A. H. Turner, F. Coleman, C. M. White, S. K. Callear, T. G. A. Youngs, M. Swadźba-Kwaśny and J. D. Holbrey, *Phys. Chem. Chem. Phys.*, 2015, **17**, 6767–6777.

51 P. Berton, S. P. Kelley, H. Wang, A. S. Myerson and R. D. Rogers, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25544–25554.

52 J. E. S. J. Reid, A. J. Walker and S. Shimizu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14710–14718.

53 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877–2887.

54 C. Reichardt, *Solvents and solvent effects in organic chemistry*, 2003.

55 E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253–3260.

56 T. R. Griffiths and D. C. Pugh, *J. Solution Chem.*, 1979, **8**, 247–258.

57 M. A. Kessler and O. S. Wolfbeis, *Chem. Phys. Lipids*, 1989, **50**, 51–56.

58 V. Gutmann, *The donor-acceptor approach to molecular interactions / Viktor Gutmann. - British Library*, Plenum Press, New York, 1978.

59 C. Reichardt and T. Welton, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 4th edn., 2010.

60 N. Nunes, R. Elvas-Leitão and F. Martins, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2014, **124**, 470–479.

61 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319–2358.

62 S. Shimizu and N. Matubayasi, *J. Phys. Chem. B*, 2014, **118**, 3922–3930.

63 S. Shimizu and N. Matubayasi, *Phys. A Stat. Mech. its Appl.*, 2018, **492**, 1988–1996.

64 J. A. McCune, P. He, M. Petkovic, F. Coleman, J. Estager, J. D. Holbrey, K. R. Seddon and M. Swadźba-Kwaśny, *Phys. Chem. Chem. Phys.*, 2014, **16**, 23233–23243.

65 M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377–383.

66 M. J. Kamlet, J. L. Abboud and R. W. Taft, *J. Am. Chem. Soc.*, 1977, **99**, 6027–6038.

67 P. D. A. Pudney, K. J. Mutch and S. Zhu, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5010–5018.

68 M. Shen, Y. Zhang, K. Chen, S. Che, J. Yao and H. Li, *J. Phys. Chem. B*, 2017, **121**, 1372–1376.