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ESI

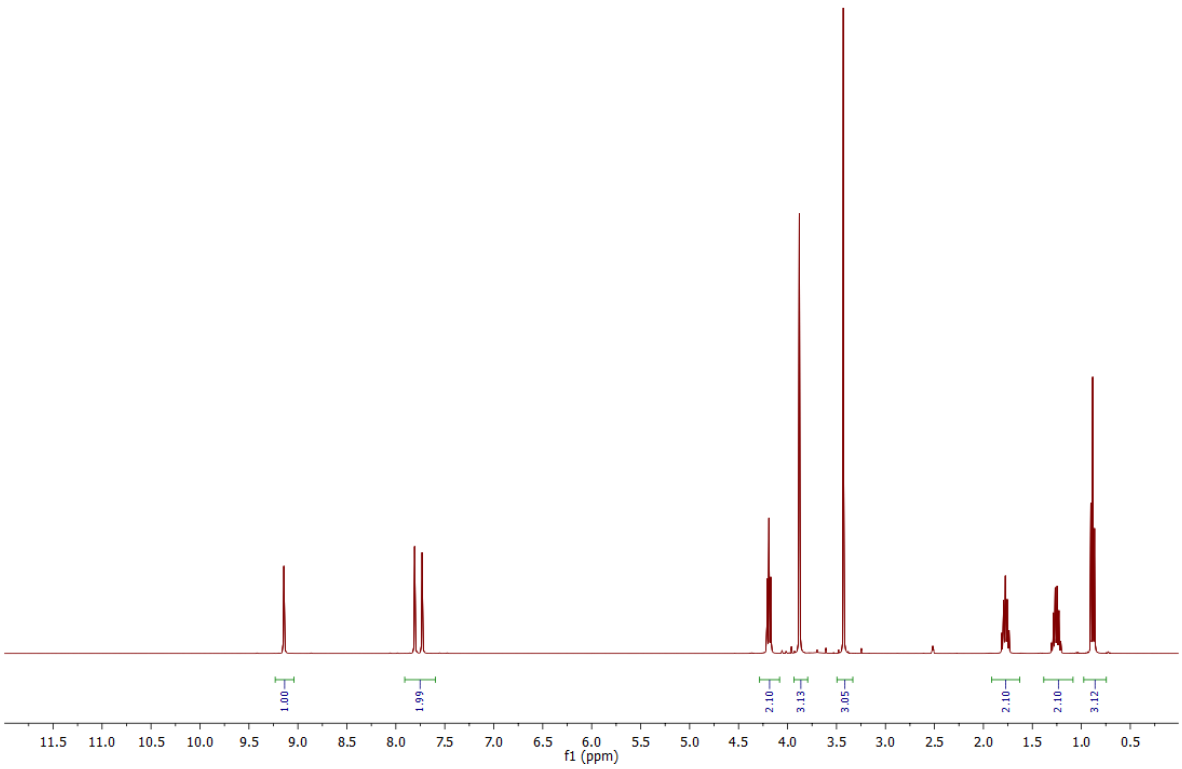
1 - Synthesis and sample preparation

Purification of starting materials

1-Butylimidazole and dimethylsulfate were distilled under vacuum from potassium hydroxide and calcium oxide respectively. Mesityl oxide was distilled from calcium oxide and toluene was retrieved from departmental solvent drying towers. H_2SO_4 (95-98 wt%) was used as received from Sigma-Aldrich. All starting materials were used within a day of preparation. Reactions were carried out in dry glassware, with dried chemicals and under an inert atmosphere of dry nitrogen, unless water or diluted aqueous H_2SO_4 (see separate section for acid preparation) was used as part of the experiment.

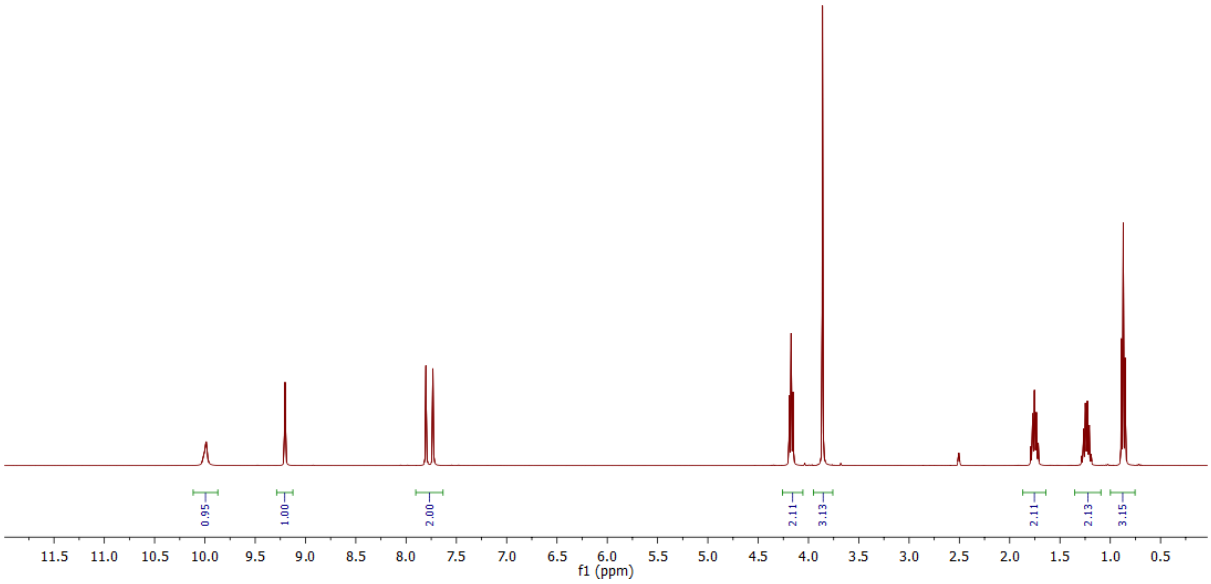
$[C_4C_1im][MeSO_4]$

1-Butylimidazole (143 ml, 1.09 mol) was diluted in 150 ml toluene and cooled in an ice bath. Dimethyl sulfate (103 ml 1.09 mol) was then added drop wise (flow rate *ca*. 0,5 drops / sec) with stirring. After the addition was complete, the reaction mixture was stirred for another hour at room temperature before the upper toluene layer was removed using Schlenk techniques. The lower IL layer was subsequently washed three times with 3x100 ml of toluene before it was dried overnight at 65 °C under vacuum and with vigorous stirring, resulting in 242.44g (89%) of a clear viscous liquid.



$[C_4C_1im][HSO_4]$

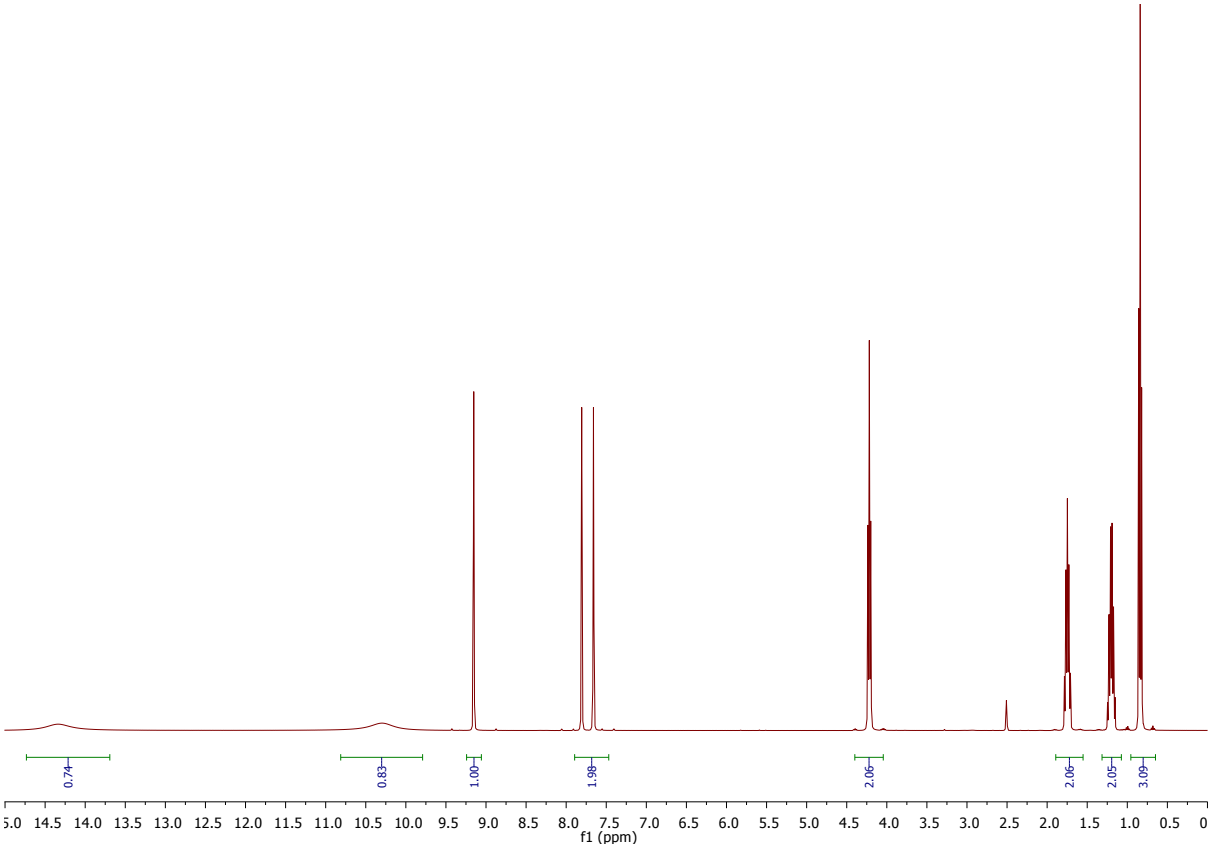
$[C_4Him][MeSO_4]$ (100g) was diluted in 20 ml deionized water and was placed on a heating block at 215 °C. The temperature of the mixture was monitored and kept between 170 to 180 °C for 4 hours by the slow addition of deionized water. Afterwards the reaction mixture was dried overnight under vacuum at 65 °C and with vigorous stirring, resulting in 92.51g (98%) of a clear highly viscous liquid.



$[C_4Him][HSO_4]$

The amount of starting material that was used differed depending on what Mol% acid was desired but a typical preparation was as follows. Because of the importance of control of the Mol% acid, a four figure analytical balance was used for these reactions.

1-Butylimidazole (35.8609g, 0.28878 mol) was added to a pre-weighed round bottom flask and cooled in and ice bath. Approximately 36.5g of diluted H_2SO_4 (see separate section for acid preparation) was added drop wise with stirring. When the addition was completed the flask was weighed again to confirm the precise amount of diluted H_2SO_4 that had been added (36.5886g, 0.28886 mol). The reaction mixture was then dried overnight under vacuum at 65 °C with vigorous stirring. The resulting IL – acid mixture made was $[C_4Him][HSO_4]$ with 0.027 Mol % H_2SO_4. The result was a light pink viscous liquid. The colour was removed by diluting the IL in water (1:3 IL:water) and passing it through a pre-packed Isolute™ C-18 Flash column. The resulting IL was a clear viscous liquid



Preparation of diluted H_2SO_4 (60 wt% -70 wt%)

H_2SO_4 (95-98 wt%) received from Sigma-Aldrich was titrated a minimum of five times against a 0.1 M NaOH solution so that the exact concentration was known. The acid was then diluted with deionized water to reach a concentration between 60 wt% -70 wt%. Both the acid and water added was weighed so that an exact concentration of the diluted sulfuric could be calculated.

Preparation of concentrated H_2SO_4 (99.8 wt% - 100 wt%)

99.8% - 100% sulfuric acid was prepared from fuming sulfuric acid (H_2SO_4 + 60% SO_3) and an aqueous sulfuric acid solution (95-98%). Fuming sulfuric acid was added to the aqueous sulfuric acid in a dry two necked round bottom flask until the solution contained a slight excess of SO_3. This was indicated by continued fuming of the solution even after a few minutes of stirring. The solution was then heated to 60 °C overnight under stirring and a flow of dry nitrogen. The nitrogen stream from the round bottom flask was bubbled out through a water trap that was fuming due to the SO_3 present in the nitrogen stream. After the fuming inside the water trap had ceased the acidity of the solution was tested using a UV-probe (4-nitroanaline). If needed, the acidity was fine-tuned by the addition of small amounts of deionized water or fuming sulfuric acid until a satisfactory sulfuric acid concentration was reached.

Preparation of IL – H_2SO_4 systems.

The IL – H_2SO_4 systems were prepared differently depending on the acid concentration. The IL water content was monitored using Karl-Fisher and never exceeded 650 ppm.

At lower acid concentrations (H_2SO_4 < 30 Mol%) [C_4Him][HSO_4] - H_2SO_4 was prepared directly from 1-butylimidazole and diluted H_2SO_4 (See separate section above for acid preparation and [C_4Him][HSO_4] synthesis). [C_4C_1im][HSO_4] - H_2SO_4 was prepared by mixing [C_4C_1im][HSO_4] with diluted H_2SO_4 (See separate section for acid preparation). A typical preparation is as follows:

[C_4C_1im][HSO_4] (25.0905g, 0.1062 Mol) was added to a pre-weighed round bottom flask. Roughly 3g of diluted H_2SO_4 was added to the flask and the two components were thoroughly mixed. The flask was weighed again to confirm the exact amount of diluted H_2SO_4 added (3.0544g, 0.0311 Mol). The resulting IL – acid mixture was [C_4C_1im][HSO_4] – 22.68 Mol % H_2SO_4. All reaction mixtures were made in this way and dried overnight under vacuum at 65 °C with vigorous stirring. Afterwards the water content was measured using Karl-Fisher titration and never exceeded 650 ppm.

At higher acid concentrations (H_2SO_4 > 30 Mol%) all the IL - H_2SO_4 mixtures were prepared in the same way. A typical preparation is as follows:

[C_4C_1im][HSO_4] (5.0872g, 0.0229 Mol) was added to a pre-weighed round bottom flask equipped with a rubber septum and magnetic stirrer. The flask was kept under an overpressure of nitrogen during the whole procedure. Approximately 9 g of concentrated H_2SO_4 (see separate section for acid preparation) was added to the flask and the two components were thoroughly mixed. The flask was weighed again to confirm the exact amount of concentrated H_2SO_4 added (8.9256, 0.0910 Mol). The resulting IL – acid mixture was [C_4C_1im][HSO_4] – 79.90 Mol % H_2SO_4.

2 - Data for Figure 1,3 and 4

Table S1: All the data used in figures 1, 3 and 4. The only data excluded are found in reference 8 for figure 1 and reference 13 for figure 4.

Figure 1				**Figure 3**		**Figure 4**	
$[C_4Him][HSO_4]$		$[C_4C_1im][HSO_4]$		$[C_4Him][HSO_4]$			
Mol % Acid	H_0	Mol % Acid	H_0	Mol% acid	Δδ	Δδ	H_0
0.00	1.73	0.00	1.96	33.00	49.44	49.44	-3.50
-6.03	2.14	33.00	-2.66	-24.00	29.89	29.89	2.93
-24.77	2.93	50.00	-4.81	19.00	36.10	36.10	-2.19
-2.00	1.94	66.00	-7.01	14.00	34.21	34.21	-1.43
2.00	0.39	80.00	-8.58	7.50	32.69	32.69	-0.72
3.19	0.10	1.83	1.77	36.00	53.38	53.38	-3.63
75.00	-8.10	92.30	-11.30	46.00	66.13	66.13	-4.99
33.31	-3.50	36.15	-2.56	56.00	72.79	72.18	-6.31
19.17	-2.19	53.12	-5.72	25.00	39.80	39.80	-2.39
14.30	-1.43	98.36	-11.32	67.00	74.89	74.89	-7.17
7.49	-0.72	96.80	-11.04	80.00	77.87	42.25	-2.56
35.91	-3.63	95.35	-10.81	90.00	79.88	68.51	-5.72
45.53	-4.99	99.06	-11.48	61.00	73.59	31.40	2.14
55.52	-6.31	97.63	-11.15	51.00	70.64	31.29	0.38
24.72	-2.39	100.00	-11.92	3.20	32.04	32.04	0.10
67.10	-7.17	8.81	0.38	42.00	63.33	31.08	1.96
98.07	-11.29	22.68	-0.98	-100.00	29.28	39.08	-2.66
97.17	-11.11			-49.00	29.48	64.51	-4.81
96.03	-10.94			-25.00	29.82	74.21	-7.01
99.32	-11.60			-1.01	31.52	77.33	-8.58
94.71	-10.81			0.99	31.54	80.07	-11.30
100.00	-11.93					80.90	-11.74
						32.15	1.73
						80.90	-11.74

3 – Using molecular solvent solution Vs neat solution

In our initial experiments we directly measured the Hammett acidity (H_0) of various $[C_4C_1im][HSO_4]$ – H_2SO_4 solutions (Figure S1). To measure H_0 for any given IL-acid solution it has been a common practise to dissolve it in a molecular solvent at different concentrations and then to extrapolate the H_0 for the neat solution from this data. The argument has been made that a molecular solvent solution is easier to handle and less viscous than the IL itself, and in the case of water being used then the acidity of the aqueous solutions can be measured using a pH meter, so simplifying the procedure even further. It is also claimed that the Hammett probes are used in such low concentration in these measurements that they are hypersensitive to impurities in the ionic liquids and that this problem can be alleviated by the use of molecular solvents in this way. Hence, we have included this method (Figure S1) to compare the results that this gave to direct measurements of the acidity of our IL-acid solutions, using water and acetonitrile. The water systems are measured both with a pH meter and a Hammett dye.

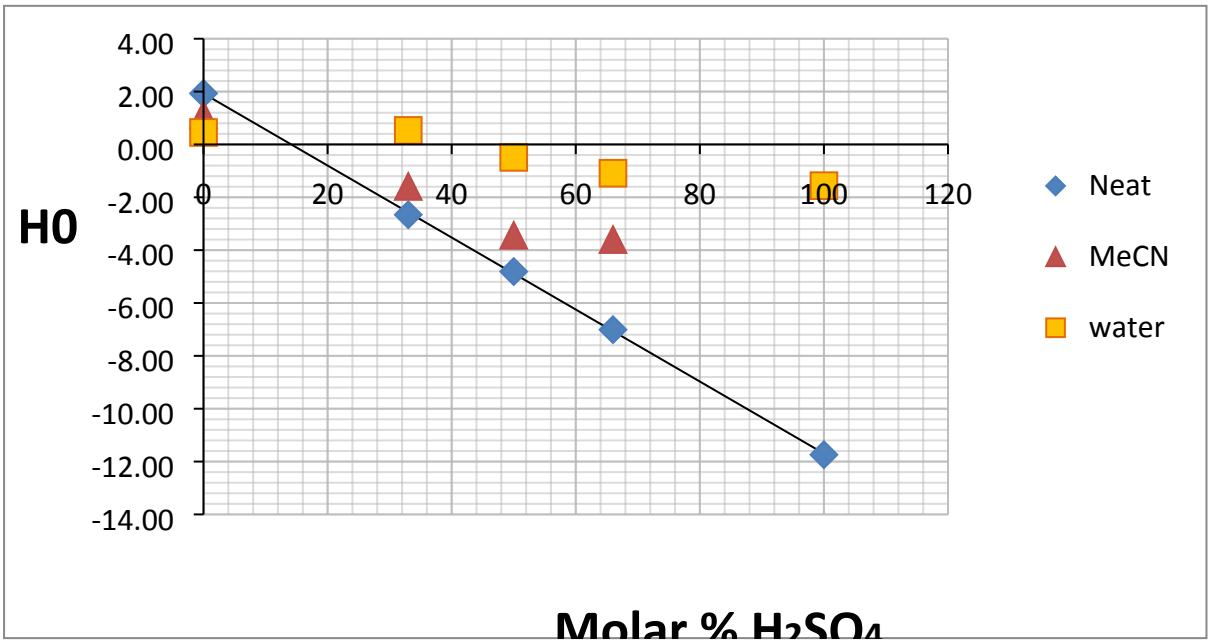


Figure S1. The Hammett acidities of various $[C_4C_1im][HSO_4]$ – H_2SO_4 solutions

The IL-acid system shows a linear relationship between acid concentration and the Hammett acidity culminating in a H_0 value of -11.74 for concentrated sulphuric acid, which is consistent with results from the literature [IREF 004]. For the aqueous solution samples however we see a much lower acidity and a non-linear trend for both pH and H_0, especially at higher acid concentrations. The acid species actually present in these aqueous solutions are H_3O^+ and higher order clusters, the concentrations of which are dependent on the amount of H_2SO_4 added to the original ionic liquid solution, but not necessarily linearly so. Even when using acetonitrile, which does not have this problem, we can still see the effect of the basicity of the solvent, where it is observed that the acidity starts to level, even at lower acid concentrations (Figure S1). Additionally, it is worth mentioning that at high concentration of strong acid acetonitrile will undergo an acid catalysed polymerisation reaction and that was the reason for the limited range of the data for the acetonitrile

molecular solvent system. Clearly, the use of solutions of IL-acid in molecular solvents does not give a good representation of the effect of adding acid to an ionic liquid. The molecular solvent inevitably affects the result, so the acidity of solution will depend on the concentration of the acid used but also on the solvent in which it is dissolved.

4 - Mass spectrometric data

Mass spectrometry using fast atom bombardment (FAB-MS) was carried out for the $[C_4C_1im][HSO_4]/H_2SO_4$ system. Fast atom bombardment can be considered a mild ionization technique and will primarily form the protonated $[M+H]^+$ or deprotonated $[M-H]^-$ form of the molecules present in the liquid matrix. For ionic liquids, FAB-MS shows signals due the ions present and their singly charged clusters. The presence of these clusters in FAB-MS spectra can only be considered as indicative of their presence in the ionic liquids and should not be considered to be quantitative.

Table S2: Up to 33 mol% sulphuric acid, only signals corresponding to the anion could be detected. At 50 mol% and above higher order clusters of $[HSO_4]^-$ / H_2SO_4 start to be detected; at 80% and above $[H_3S_2O_8]^-$ can be seen as the most dominant form of $[HSO_4]^-$ / H_2SO_4 cluster. In pure sulphuric acid, fragments as high as $[H_{17}S_9O_{36}]^-$ were detected.

H_2SO_4 Mol%	**$[HSO_4]^-$/ H_2SO_4 Ion clusters in negative mass spectra of $[C_4C_1Im][HSO_4]$**			
	$[HSO_4]^-$	$[H_3S_2O_8]^-$	$[H_5S_3O_{12}]^-$	$[H_7S_4O_{16}]^-$ to $[H_{17}S_9O_{36}]^-$
0	100%			
33	100%			
50	100%	50%		
60	100%	75%		
66	100%	80%		
71	100%	90%		
80	80%	100%		
92	60%	100%	10%	
100	35%	100%	55%	0%, 35%, 20%, 15%, 10%,5%

In the positive ion spectra no higher order of sulphuric acid containing clusters could be detected even at an acid content of 92 mol%. Only in pure sulphuric acid could these fragments be detected. In the negative ion spectra however fragments corresponding to higher order clusters of sulphuric acid could be detected (Table S2). An example of a negative mass spectrum is shown in Figure S2.

The $[H_3S_2O_8]^-$ ion can be considered to arise from an small cluster in which a proton is solvated by two anions $\{[HSO_4]_2H]^-\}$ or as arising from the solvation of undissociated sulfuric acid by a single anion of the ionic liquid $\{[[H_2SO_4][HSO_4]]^-\}$. We have deliberately chosen the $[C_4Him][HSO_4]/H_2SO_4$ and $[C_4C_1im][HSO_4]/H_2SO_4$ so as these two possibilities are indistinguishable and the overall acidity of the solution should result only from the acidities of these clusters and their concentrations in the solution. Therefore, the acidities of the IL/acid systems should depend linearly upon the concentration of the acid added, thus supporting the data we see in Figure 1 in the main text. It is only at high concentrations of acid and the appearance of higher order clusters that deviation from linearity is seen.

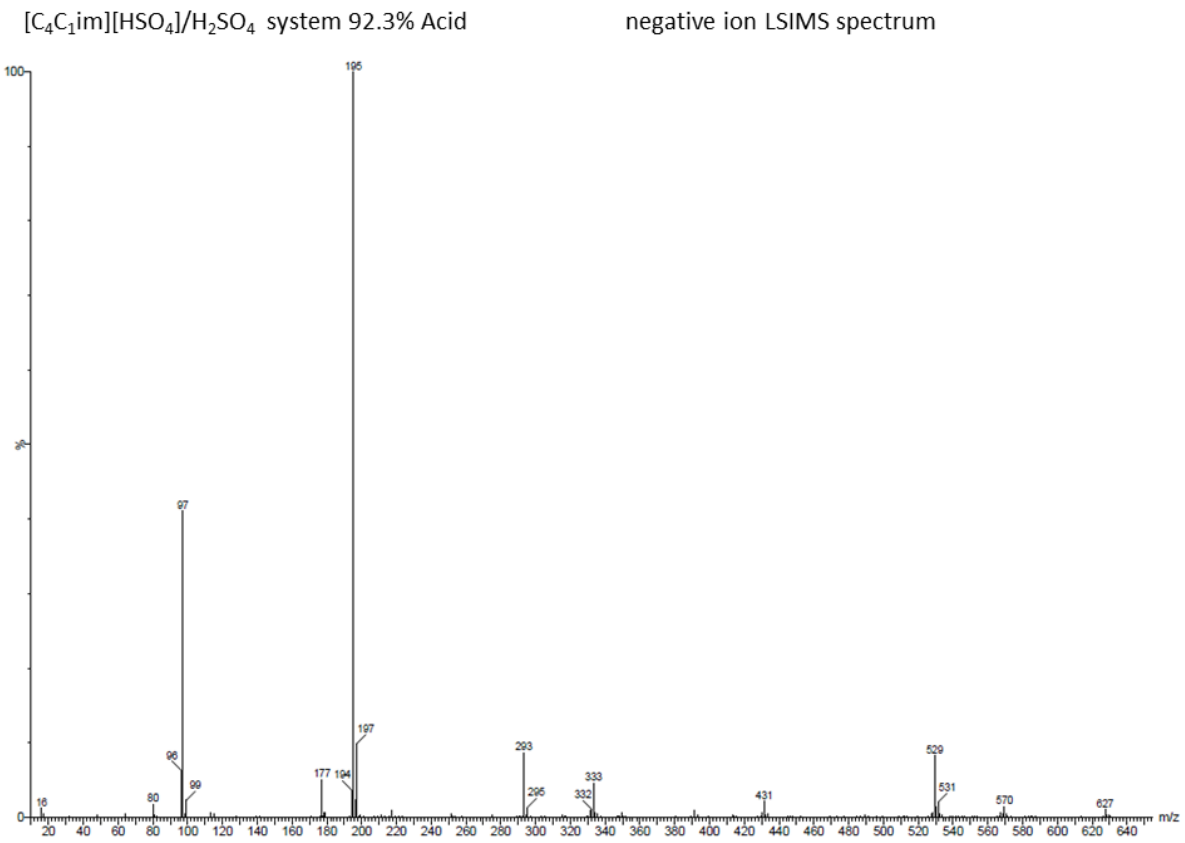


Figure S2: A negative ion FAB-MS for $[C_4C_1im][HSO_4]/H_2SO_4$ containing 92 mol% H_2SO_4 with peaks at 97, 195 and 293 corresponding to $[HSO_4]^-$, $[H_3S_2O_8]^-$, $[H_5S_3O_{12}]^-$ clusters respectively.

5 – Measuring acidity with UV-probe

Measurement of H_0 of pure ionic liquid mixtures using Hammett bases

Several Hammett bases, used as UV-probes, were employed to cover the range of H_0 values of our mixtures of ionic liquid and H_2SO_4. They were 3-nitroaniline, 4-nitroaniline, 4-chloro-2-nitroaniline, 2,4-dichloro-6-nitroaniline, 2,6-dichloro-4-nitroaniline, 2,4-dinitroaniline, 2-bromo-4,6-dinitroaniline, 3-methyl-2,4,6-trinitroaniline, 4-nitrotoluene, 2,6-dinitroaniline and 2-nitroaniline. The use of Hammett bases is based on the premise that the base will be partly protonated and therefore the acidity of the system can be calculated by the Hammett equation (equation 1).

$$H_0 = pK_{BH^+} - \log\left(\frac{[BH^+]}{[B]}\right)$$

Equation S1: H_0 can be calculated through the Hammett equation by knowing the pK_{BH+} of the Hammett base and the concentration difference between the protonated and un-protonated species of the base ($[BH^+]/[B]$).

Unfortunately most ILs tend to absorb UV light in the region where the protonated peak can be found. Thus a modified version of the Hammett equation is needed (equation S2).

$$H_0 = pK_{BH^+} - \log\left(\frac{\varepsilon_0 - \varepsilon}{\varepsilon}\right)$$

Equation S2: A modification of that Hammett equation that does not require the protonated peak to be visible (for proof of the equation see separate section below).

To establish the extinction coefficient (ε_0) for the non-protonated Hammett bases dichloromethane was used as the non-acidic solvent. For each base, eight to ten data points of absorbance at λ_{max} versus concentration were gathered. A plot of absorbance against concentration multiplied by pathlength (Figure S3) gave a straight line with a gradient equal to the extinction coefficient (ε_0) of the base, according to the Beer-Lambert law ($A = \varepsilon_0 cl$).

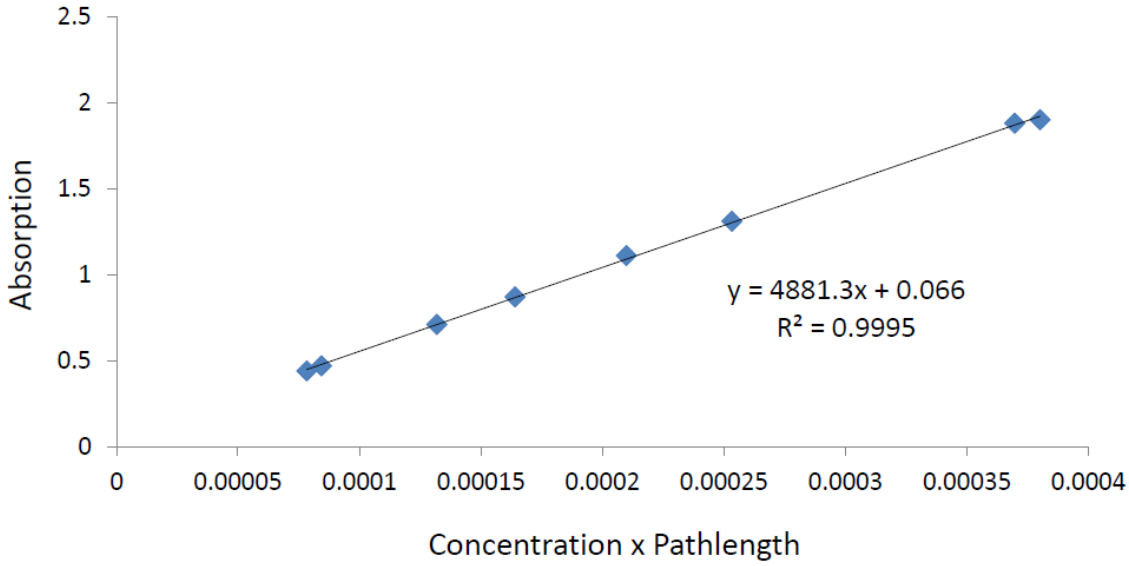


Figure S3: A plot of absorbance against concentration x pathlength for the Hammett base 2-nitroaniline in dichloromethane. The equation for the trend line shows an extinction coefficient (ε_0) of 4881.

The extinction coefficient values for the non-protonated Hammett bases used in this paper are shown in table S3.

Table S3: Extinction coefficient (ε_0) for Hammett bases in dichloromethane.

Hammett base	**pK_{BH+}**	**ε_0 (Mol^{-1} Lcm^{-1})**
3-nitroaniline	2.47	1395
4-nitroaniline	1.00	15447
2-nitroaniline	-0.26	4881
4-chloro-2-nitroaniline	-0.97	5289
2,4-dichloro-6-nitroaniline	-3.01	5573
2,6-dichloro-4-nitroaniline	-3.27	13418
2,4-dinitroaniline	-4.27	14439
2,6-dinitroaniline	-5.37	9065
2-bromo-4,6-dinitroaniline	-6.46	12893
3-methyl-2,4,6-trinitroaniline	-8.22	5324
4-nitrotoluene	-11.35	10018

The same protocol was followed for solutions of the bases in the ionic liquid mixtures. For each pair of base and ionic liquid, six to ten data points of absorbance at λ_{max} versus concentration were gathered. A plot of absorbance against concentration x pathlength gave a straight line with gradient equal to the effective extinction coefficient (ε) (figure S4). Once ε_0 and ε were obtained, the acidity function H_0 was calculated according to the modified Hammett equation (equation S2).

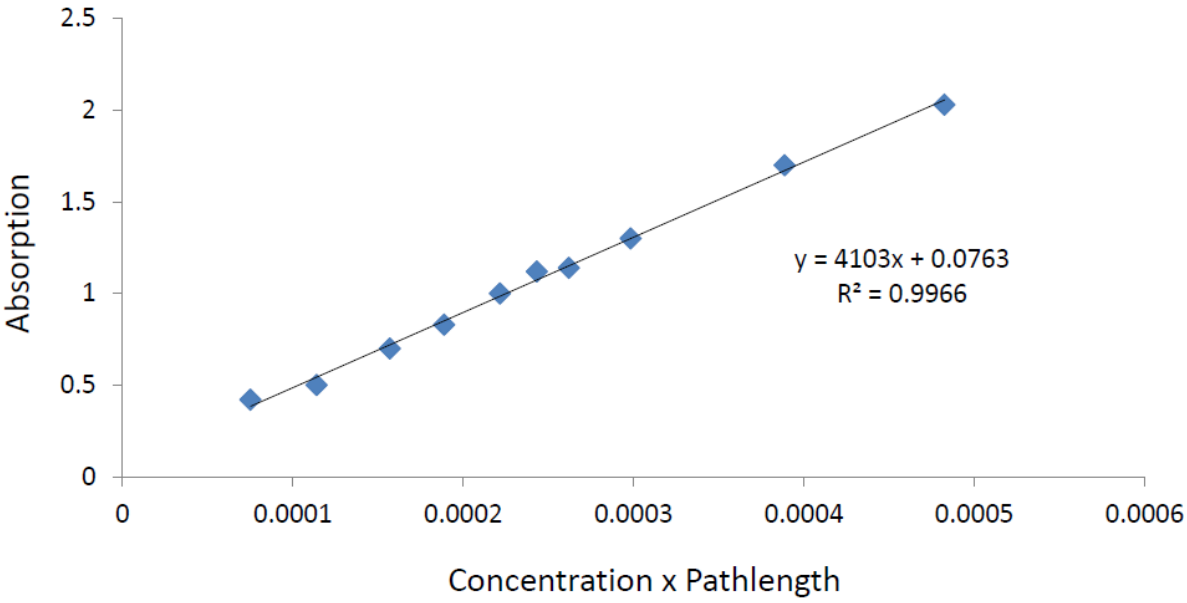


Figure S4: A plot of absorbance against concentration x pathlength for the Hammett base 2,4-dichloro-6-nitroaniline in a $[C_4C_1im][HSO_4]/H_2SO_4$ system containing 36 mol% H_2SO_4. The equation for the trend line shows an effective extinction coefficient (ε) of 4103.

5.1 – Proof for Equation 2

First a few things needs to be established. Absorption will remain linear to the concentration according to Beer-Lambert law ($A= \varepsilon_0[B]l$) and we need to assume that the extinction coefficient (ε_0) will remain the same for the unprotonated peak across different solutions.

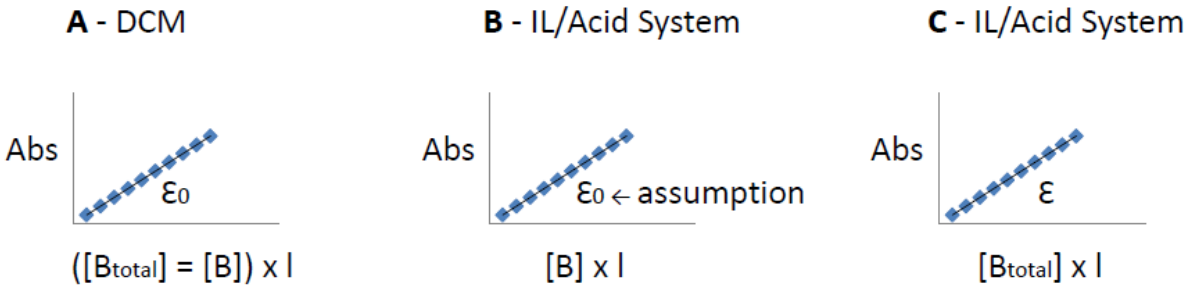


Figure S5: ε can be acquired by plotting absorption against concentration x pathlength according to the Beer-Lambert law (A= εcl).

If that is the case then the extinction coefficient (ε_0) for the unprotonated peak can be calculated by measuring the absorption in a solvent that will not protonate the base (case A in figure S5). In this case the concentration of the base added ($[B_{total}]$) will be the same as the concentration of the unprotonated base ([B]). However, we can't say that for the IL/acid system in which the base added ($[B_{total}]$) is partly protonated and only a fraction of the unprotonated base ([B]) will remain (case b in figure S5). Unfortunately [B] can't be calculated from $[B_{total}]$ since the protonated base ($[BH^+]$) peak is not visible in the IL/acid system. Thus, it is not possible to know the exact concentration of the unprotonated base ([B]) we only know the concentration of the total amount of base added ($[B_{total}]$). Therefore when we plot absorption against concentration of the added base x pathlength ($A= \varepsilon-[B_{total}]l$) we will instead get an effective extinction coefficient (ε) (case C in figure S5). If we accept this we can do as follows:

$K = [BH^+]/[B]$ → $K= ([B_{total}] – [B])/[B]$ → $K[B] = [B_{total}] – [B]$ → $K[B] + [B] = [B_{total}]$ → $(K+1)[B] = [B_{total}]$ → $[B] = [B_{total}]/(K+1)$

$[B] = [B_{total}]/(K+1)$ in $A = \varepsilon_0 l[B]$ gives $A = \varepsilon_0 l[B_{total}]/(K+1)$ → $A/l[B_{total}] = \varepsilon_0/K+1$ ①

$A = \varepsilon l[B_{total}]$ → $\varepsilon = A/ l[B_{total}]$ ②

① and ② gives $\varepsilon = \varepsilon_0/K+1$ → $\varepsilon(K+1) = \varepsilon_0$ → $K \varepsilon + \varepsilon = \varepsilon_0$ → $K = (\varepsilon_0 - \varepsilon)/\varepsilon$

$K = (\varepsilon_0 - \varepsilon)/\varepsilon$ in $K = [BH^+]/[B]$ gives **$[BH+]/[B] = (\varepsilon_0 - \varepsilon)/\varepsilon$**

Thus $H_0 = pK_{BH+} - \log\left(\frac{[BH^+]}{[B]}\right)$ can be written as $H_0 = pK_{BH+} - \log\left(\frac{\varepsilon_0 - \varepsilon}{\varepsilon}\right)$

6 – Measuring acidity with NMR-probe

The acidity of a system can be measured by using mesityl oxide as an NMR-probe. Similarly to the UV-probes this can be done by establishing how much of the probe is protonated in the system. For mesityl oxide this is done by measuring the change in ^{13}C-NMR shift between the α and β carbons. As the system gets more acidic more of the protonated form of mesityl oxide will be formed (figure S6). NMR is a relatively slow form of analytical detection method and will therefore not show separate peaks for the protonated and unprotonated form of mesityl oxide. Instead a population weighted average peak between the two forms will be shown and thus as the system becomes more acidic the chemical shift difference between the α and β carbons (Δδ) will increase. This arises because the chemical shift of the β will increase more than that of the α carbon due to the fact that its partly charged (figure S6).

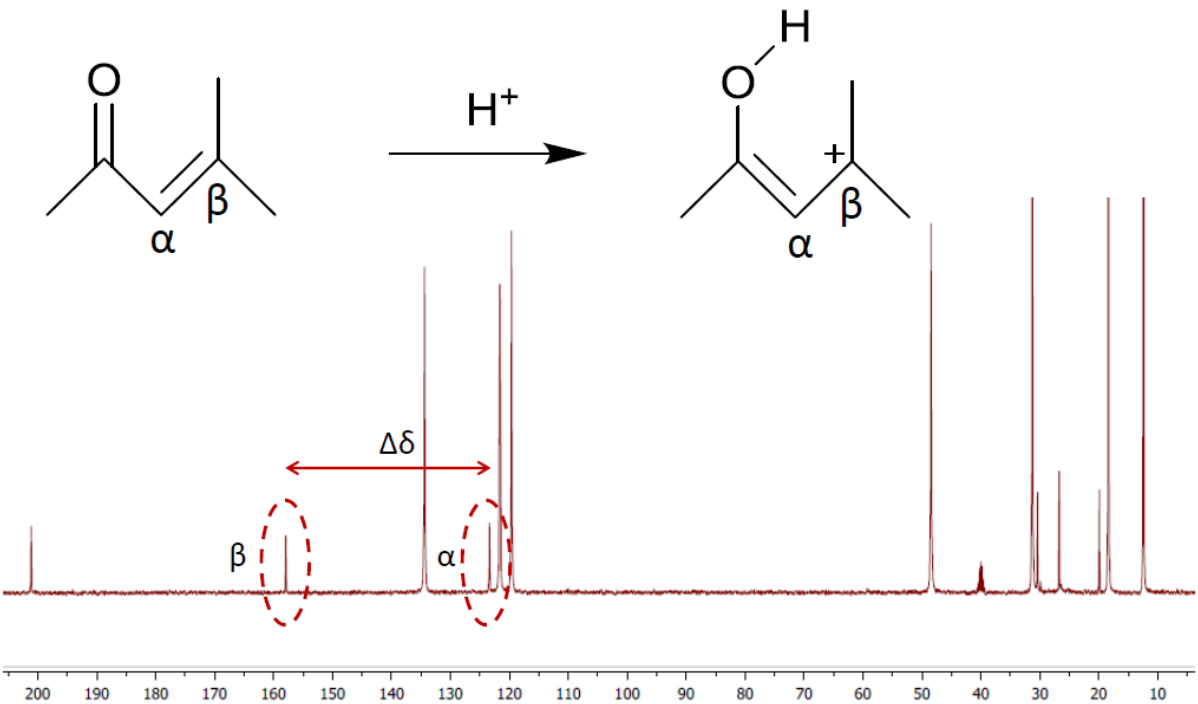
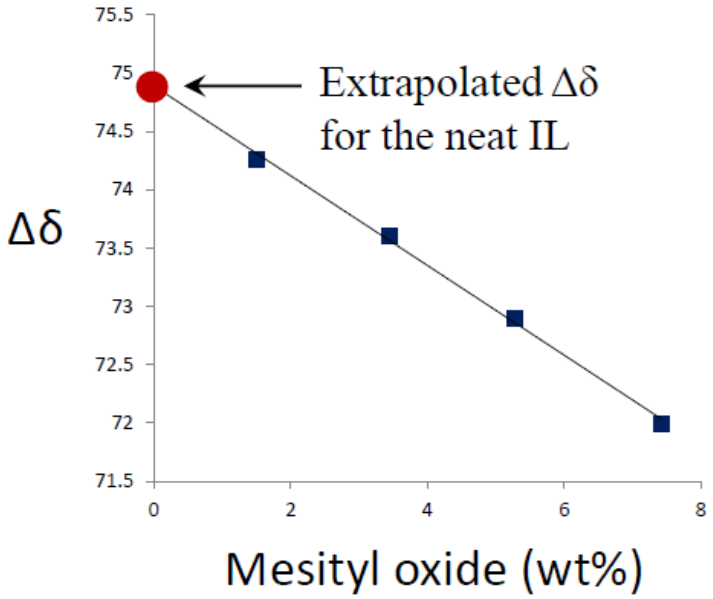


Figure S6: As the acidity of the system increase so will Δδ

The NMR probe is used in relatively high concentrations (1 to 7 wt%). This gives a certain robustness to the measurements but it will also reduce the acidity of the system and thus the 'true' acidity must be extrapolated from the gathered data. Therefore, in order to retrieve a true acidity of the system 4 samples were taken each with a different concentration (between 1 and 7 wt%) of mesityl oxide and from these values the true Δδ for the system was acquired (Figure S7).



To keep the samples as dry as possible both the mixing of mesityl oxide with the IL/acid system and the transfer of the solution to the NMR tubes was conducted under an overpressure of dry nitrogen. Since any deuterated solvent would greatly affect the acidity of the system DMSO capillaries were used to lock the NMR on to the samples. It should also be mentioned that even though mesityl oxide was purified before use, a comparison between purified and unpurified mesityl oxide showed a difference of 0.02 ppm. The unpurified mesityl oxide was newly acquired, but water can greatly affect the acidity so purification is still recommended. Once dried, the mesityl oxide can be stored for a long while in an airtight container.

7 – Model for figure 1

The model was derived from the Hammett acidity equation:

$H_0 = pK_{BH+} + \log [B]/[BH^+]$

Where [B] is the concentration of deprotonated mesityl oxide

Where $[BH^+]$ is the concentration of protonated mesityl oxide

and $pK_{BH+} = -4$ for mesityl oxide (from Fărçasiu)

We then asymptotically fit the limits of the mesityl oxide ^{13}C NMR shifts by extrapolating the minimum $\Delta\delta$ and the maximum $\Delta\delta$, which show asymptotic behaviour as the fully deprotonated and fully protonated states are approached.

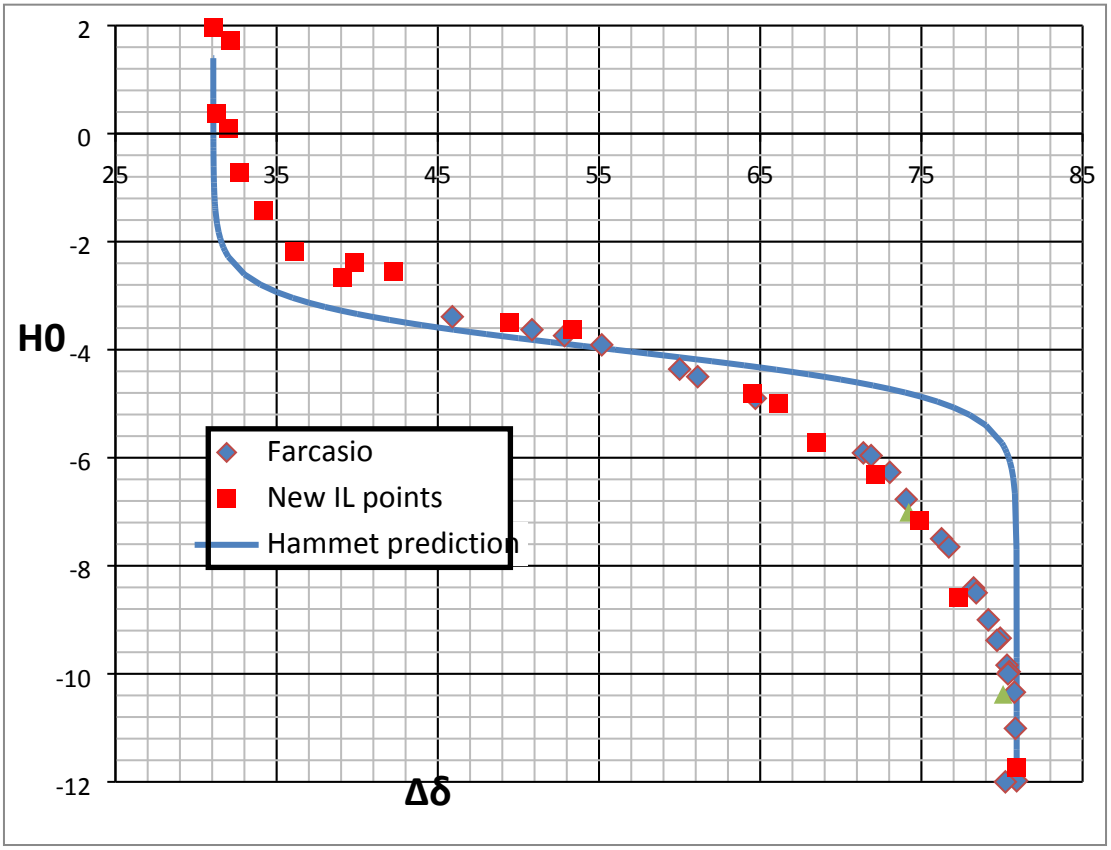
Since the NMR shift is related to the relative amounts of protonated and deprotonated mesityl oxide, we next assumed a linear behaviour between the two extremes, and used this to calculate the ratio $[B]/[BH^+]$:

$H_0 = -4 - \log([\Delta\delta - \Delta\delta_{min}]/[\Delta\delta_{max} - \Delta\delta])$

or

$H_0 = -4 - \log([\Delta\delta - 31.07]/[80.91 - \Delta\delta])$

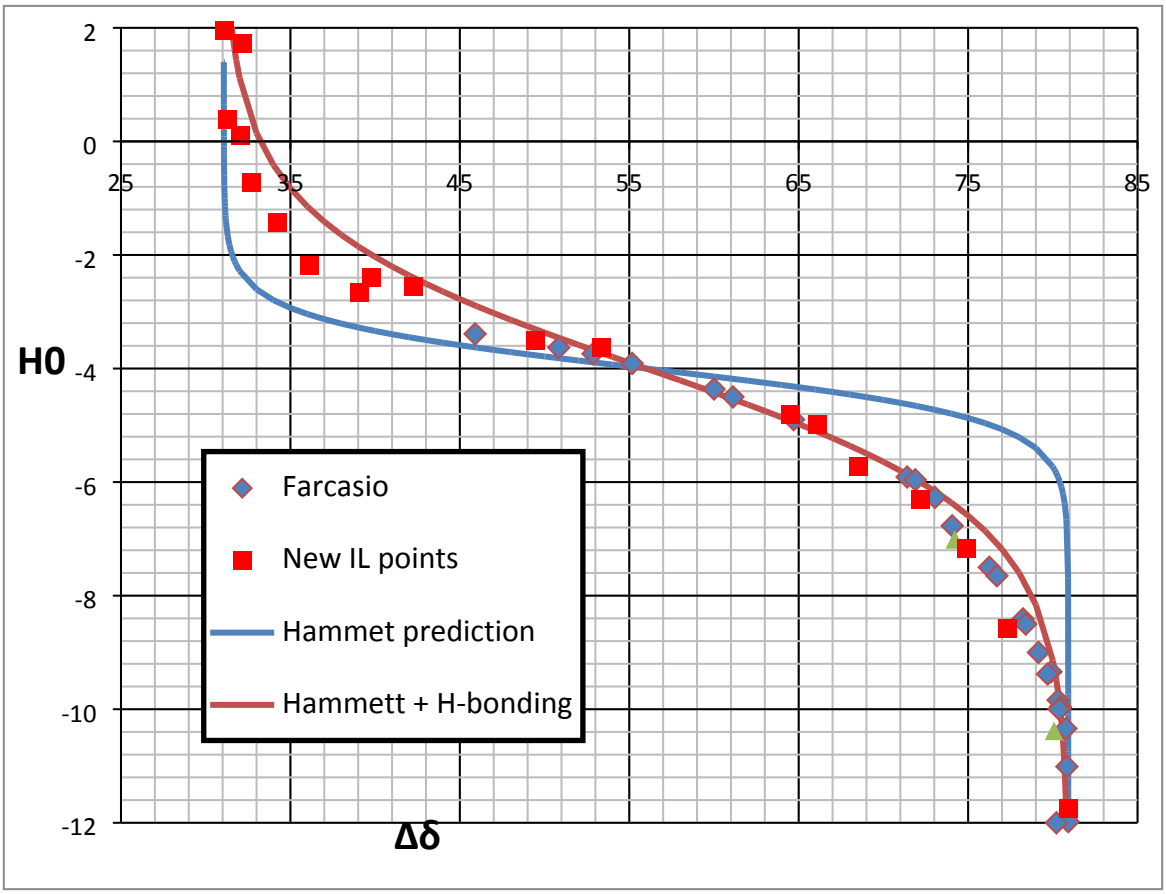
This relationship will naturally leave an equilibration point at $H_0 = -4$



We noticed that while the shape of this model was fairly good, the fit was too steep at very high or very low acidity. We interpreted this as hydrogen bonding effects (between multiple anions and the mesityl oxide) that can mitigate the relative activities of deprotonated and protonated mesityl oxide, which would skew the concentration profile, and so we corrected for this with a slope change:

$H_0 = -4 - s*\log([\Delta\delta - 31.07]/[80.91 - \Delta\delta])$

Where s is an empirically fitted parameter (s = 2.59 for our data).

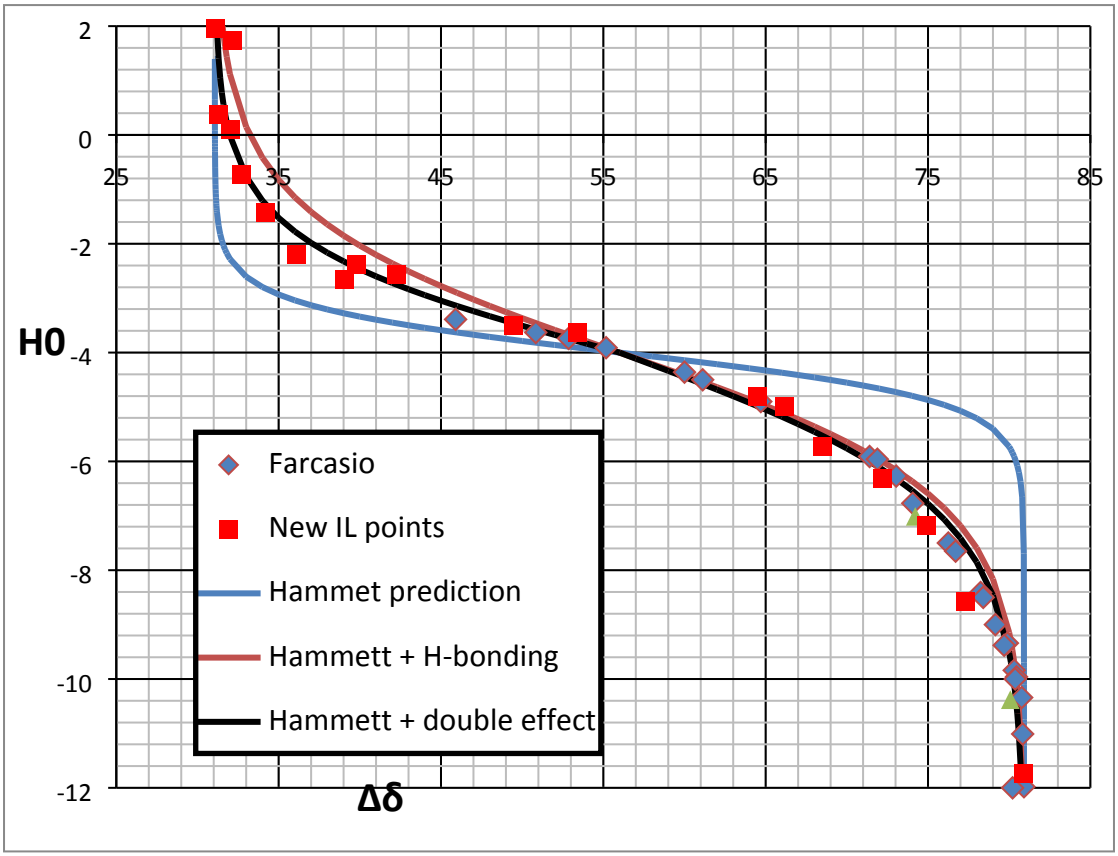


While this provided a highly satisfying fit, we noticed a slight difference between the acidic and basic sides of the Hammett function. We therefore decided to fit *separate* values for the hydrogen-bonding factor, s, for each side of the function:

s = 2.32 below $H_0 = -4$

s = 3.19 above $H_0 = -4$

This gives a highly satisfying fit as shown:



We can interpret the separate hydrogen bonding parameters as two effects: a strong hydrogen bond donation to the deprotonated mesityl oxide (which dominates at higher H_0) coupled with weaker hydrogen bond acceptance. These effects will combine to give weaker mitigation to protonation, therefore giving a smaller s-value. Below H_0 = -4, the reverse is true (the protonated form dominates) and we observe a higher s-value due to stronger hydrogen bond accepting influence from the anion.

Please note that the same analysis could be applied to the alternative (though less familiar) version of the Hammett equation:

$H_0 = \log (a_{BH+} \gamma_{BH+}/\gamma_B]$

by assuming that the NMR shifts are linear with activity rather than concentration, which is a more accurate thermodynamic interpretation of the chemical shift. This version then interprets the slope change as the influence of hydrogen bonding on proton activity. This will give the same relationship once fitted, and is more thermodynamically rigorous.