Electronic Supplementary Information

Spectroscopic Determination of Relative Brønsted Acidity as a Predictor of Reactivity in Aprotic Ionic Liquids

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Experimental Methods

Materials

Pyridine (ACS reagent grade, 99%), formic acid (98%), nitric acid (Fluka, ≥69%), and TMOS (deposition grade, 98%) were purchased from Sigma Aldrich. 110 copper foil (99.9%) was purchased from McMaster-Carr. Synthesis-grade ionic liquids were purchased from EMD Merck. All chemicals were used as received.

FTIR-enabled Acid Titration of Pyridine-in-IL Solutions

Solutions containing pyridine in the IL with a 1:5 volume ratio were prepared. Pyridine is highly miscible with all of the ILs used in this study. To prepare each titration sample for FTIR spectroscopy, a measured amount of acid was added to 175 µL of the pyridine-in-IL solution, thoroughly mixed, and allowed to sit for several hours to ensure equilibration between the acid and pyridine. In total, 29 microliters (approximately 360 micromoles) of pyridine were added to each sample. Samples were first prepared with increasing acid contents in 10 µL increments, with between 0 – 100 µL of the acid added. FTIR spectra of these samples were then measured to determine the approximate acid concentration range in which the free pyridine peak visually disappeared. Next, samples were prepared with increasing acid contents in 5 µL increments within a 20 – 25 µL range centered on the approximate transitional acid concentration, followed by samples with acid contents differing by 1 µL in a further reduced 5 – 7 µL range to more precisely determine the threshold molarity. Samples were tested on either side of the identified ranges to ensure that the peak transition occurred reproducibly within this range. FTIR spectra were measured on a JASCO Corporation FT/IR-6200 by conducting 100 scans. The spectra shown in Fig. 1a were baseline-corrected using a multi-point linear correction for display purposes. Numerical derivatives were performed on unprocessed spectra; these were performed in MATLAB® using the simple difference-based differential function.

Ionogel Preparation and Determination of Gel Times

Ionogels were prepared as previously described.[1] Two precursor formulations were investigated, one containing a large excess of formic acid (FA), the other containing a lower amount of FA. The high FA formulation used in this study had a 13.8:1 molar ratio of FA:TMOS while the low FA formulation had a 4.8:1 FA:TMOS molar ratio. Both formulations initially contained 66% IL by volume, which was held constant for the different ILs to ensure that the gel times could be reasonably compared. To determine the gel time, samples were gently tilted every five minutes until no flow behavior was observed. Samples were allowed to dry uncovered for at least one week before being photographed or undergoing SEM sample preparation. The IL was removed from the silica scaffold for SEM imaging by heating the sample under nitrogen to ~700 °C until no further mass loss was observed.

Copper Etching

Nitric acid-in-IL solutions were prepared by adding HNO_3 stock solution to pure ILs to make solutions with 0.3 mL total volume. Samples were sealed, thoroughly mixed, and allowed to equilibrate. As water is both less dense than and immiscible with the hydrophobic ILs utilized in this study, the small amount of water introduced by the acid stock solution first formed a thin layer on top of the IL and then slowly evaporated into the headspace of the sealed vial; no final aqueous phase was observed after this step.

Pieces of copper foil (5 mm x 5 mm x 0.05 mm thick) were weighed before being submerged in the acid-in-IL solutions and allowed to react undisturbed overnight. After 24 hours, the copper pieces were removed, thoroughly rinsed with deionized water, dried under flowing nitrogen, and weighed again. The fraction of copper etched was calculated from the measured mass difference. Copper was present in molar excess to ensure that availability of the acid would be the limiting factor in the etching rate. The photos shown in Fig. 3b were color-balanced to ensure comparability.

Supplementary Discussion Regarding Acids in Nonaqueous Media

There is a substantial body of knowledge in the literature that concerns Brønsted acidity in nonaqueous media, dating from early in the twentieth century.[2,3] A number of techniques ranging from the spectroscopic[4] to the potentiometric[5] have been used to explore concepts such as the proton affinity,[6] tendency to donate or accept a hydrogen bond,[7] polarizability,[8] and solvent-related shifts in pK_a.[9]

However, these concepts have been very difficult to apply in a rigorous and useful way to IL media. Although they belong to the same class of materials, individual ILs are chemically distinct from one another and the polarizability, proton affinity, and so forth of one IL says little about that of another IL, nor is it straightforward to compare ILs using these parameters in a way that has predictive value for reactions of interest. As discussed by Mihichuk *et al*:[10]

> "…for many cases, a change of [conventional] solvent results in a change of pK_a that is independent of the protic molecule. This change reflects the modification of the proton's local environment. In the case of ionic liquids the situation is more complex: the acidic species is likely to be a hetero-conjugate anion derived from the protic molecule and the solvent anion, so the change in proton environment is difficult, if not impossible, to separate out."

These authors also assert that: "the question of acidity then is the matter of how readily the proton is available to be transferred from the base to which it is the least tightly bound." The subject of exactly what species are present in solutions of Brønsted acids in aprotic IL media is one of present debate and active investigation.[11] The possible basic species available for a proton to interact with in such a solution vary widely depending on the IL and acid in question, leading to a huge number of possible equilibria.

The work of Robert *et al.*, which discusses a method for determining the Hammett acidities of acids dissolved in ILs, demonstrates the complexity inherent in attempting to apply the theories discussed above to ILs.[12] This work explains that the calculation of Hammett acidity for a particular combination of an acid dissolved in an IL was found to be dependent on the indicator used. The requirement of correcting the Hammett acidity based on the indicator used strongly suggests that the theory behind the Hammett acidity is insufficient to describe acidity in ILs, as it assumes that the solvent is completely inert vis-à-vis the dissociation of the indicator.

The contribution of our manuscript, then, is to offer a way to observe the behavior of Brønsted acids dissolved in ILs *as participants in a reaction of interest*. Notably, the shift in acidity observed for different acids in different ILs is not consistent or easily predictable (as evidenced by the fact that the ordering of relative acidity is reversed for formic vs. nitric acid). This strongly suggests that a single set of IL-specific solvent parameters is insufficient to describe the behavior of different acids in an IL, more generally. In addition, our method can be easily used to compare *the same acid* in *different ionic liquids* whereas previous studies are mainly concerned either with inherent IL properties or with *different acids* in the *same ionic liquid*. We present this technique with the intention that it may be used both by experimentalists as a straightforward and facile screening tool, as well as by theorists as a way to further investigate crucial questions of the behavior of acids in IL-based solutions.

Table S1. Room temperature density, viscosity, and water content values of the ILs used in this investigation.[13]

Cation	Anion	Density (g/mL)	Viscosity (mPa·s)	Water Content (ppm)
EMI	TFSI	1.53	28	740
BMP	TFSI	1.4	73	306
EMI	FAP	1.71	60	249

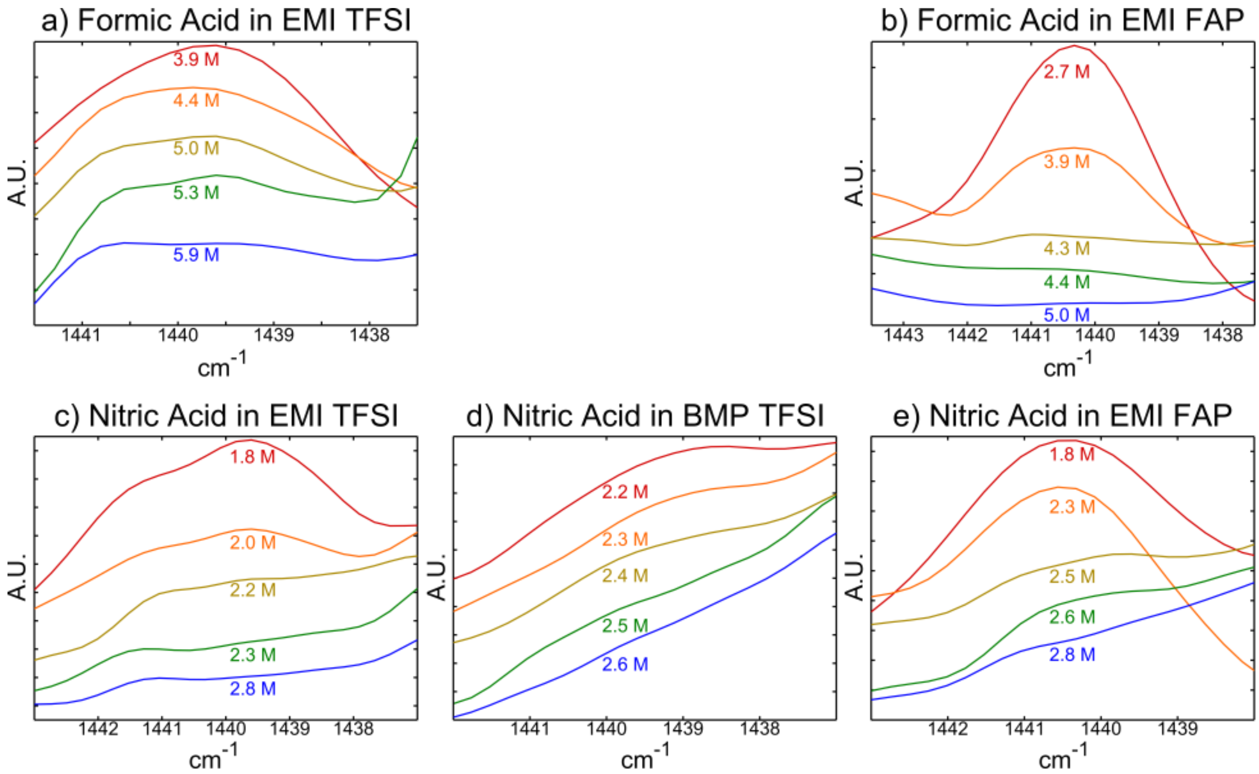

Figure S1. FTIR titration spectra for formic acid and nitric acid in the remaining ILs, showing the disappearance of the free pyridine peak.

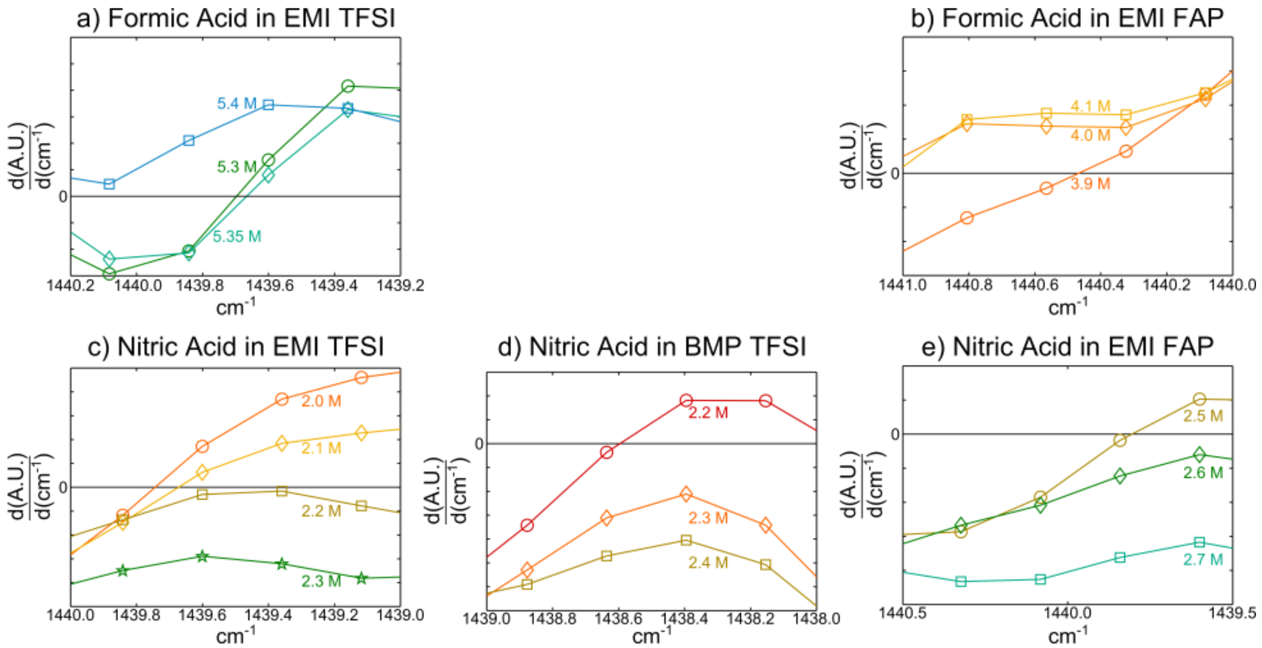

Figure S2. Numerical derivatives of the FTIR titration spectra for formic acid and nitric acid in the remaining ILs, showing the determination of the threshold molarities.

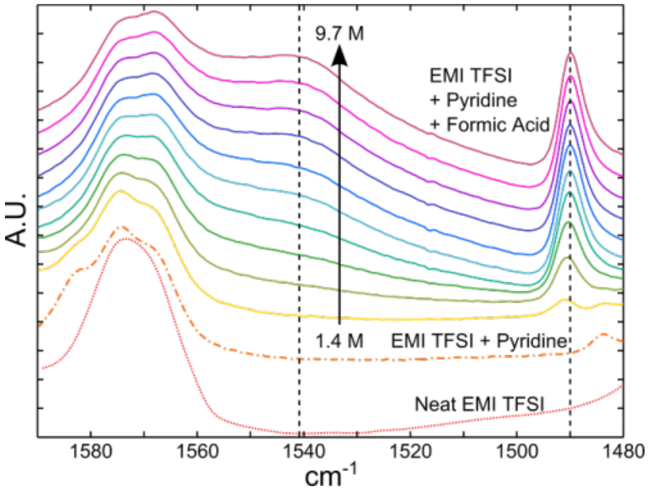

Figure S3. FTIR titration spectra showing the appearance of pyridinium-related peaks with increasing formic acid concentration in EMI TFSI. Spectra for neat EMI TFSI and a 1:5 (v/v) solution of pyridine in EMI TFSI are also shown for reference. The broad peak at 1540 cm^{-1} (pyridinium mode ν_{19b}) appears as a shoulder on the EMI cation peak at ~1570 cm^{-1}, while the narrow peak at 1490 cm^{-1} (pyridinium mode ν_{19a}) appears beginning at very low formic acid concentrations (first detectable at 0.6 M). As such, neither of these peaks were used for quantitative evaluations in this study. However, they do correlate with the disappearance of the free pyridine peak and may potentially be used for titrations when it is obscured by the IL signal.

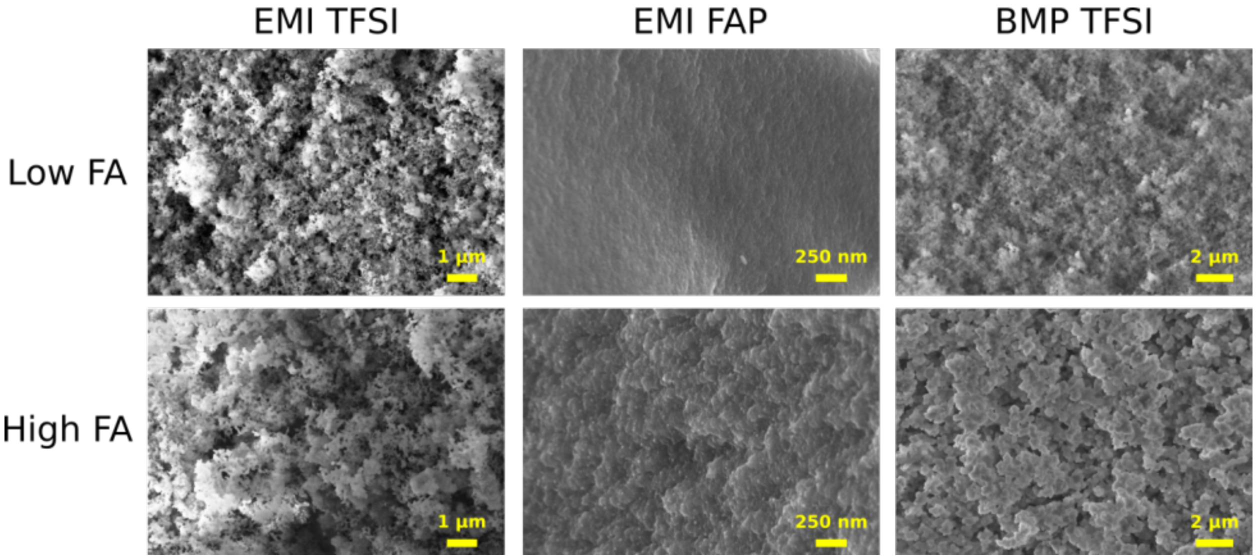

Figure S4. SEM images highlighting the morphologies of the silica scaffolds for ionogels created using EMI TFSI, BMP TFSI, and EMI FAP for both the high and low formic acid (FA) concentration formulations. The morphologies differ based on the identity of the IL, and especially with the identity of the anion. In all cases, the characteristic size scale of the scaffold primary particles appears to increase with increasing FA content in the reaction formulation.

Supplementary References

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