The structure of protic ionic liquids based on sulfuric acid, doped with excess of sulfuric acid or with water

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Materials

Pyridine, *conc* sulfuric acid and D_2O were purchased from Sigma Aldrich. Pyridine-d_5 and *conc* sulfuric acid-d_2 (D >99%) were purchased from Goss Scientific Instruments Inc. (Cambridge Isotope Laboratories Inc.) and deionised water collected from a Barnsted deionisation system, polished to 18.2 MΩ cm^{-1}. All materials were used as received, the two sulfuric acids were estimated to be 98% sulfuric acid, that is, containing 0.2 M of either H_2O or D_2O respectively, which is consistent with the measured neutron scattering levels.

Synthesis of ionic liquids

In a typical experiment, sulfuric acid or sulfuric acid-d_2 (0.02 mol) was weighed (± x10^{-4} g) into a round bottomed flask (50 cm^3), equipped with a magnetic stirrer. The flask was then transferred to an ice bath. Pyridine or pyridine-d_5 (in 0.02 or 0.04 mol quantities) was added dropwise using a syringe pump (2 cm^3 h^{-1}) with stirring, which was continued for 30 min at 0 °C after the addition was complete. Where samples required water addition (0.04 mol), the round-bottomed flask was again placed on a four-figure balance, and the required quantity of deionised water was added accurately (± x10^{-4} g) *via* a pipette. The round bottomed flask was secured with a stopper and the mixture was homogenised (40 °C, 10 min, 500 rpm) then transferred to 22 cm^3 screw cap vials and stored until use. All samples (Table 1, main text) were homogeneous liquids at ambient temperature.

The experimental design included sulfuric acid (χ_{H2SO4} = 1.00), sulfuric acid:pyridine mixtures (χ_{H2SO4} = 0.67) and sulfuric acid:pyridine:water (χ_{H2SO4} = 0.25). For each composition, isotopologues containing protiated (H), deuteriated (D) or equimolar mixture of protiated and deuteriated components (H/D) were prepared. Throughout the paper, samples are denoted through relative molar ratios of the three components: sulfuric acid:pyridine:water.

Neutron scattering experiments

Neutron scattering data from the seventeen samples were recorded using the SANDALS spectrometer at the ISIS Pulsed Neutron and Muon Source at Rutherford Appleton Laboratory, Oxfordshire, UK. The instrument uses neutrons over a wavelength range 0.05-4.5 Å, giving an accessible Q range of 0.05-50 Å^{-1}. All samples were measured in quartz cells (Figure S1).
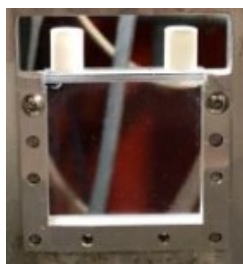
Figure S1. Corrosion-resistant quartz cell sample holder with 2 mm internal cavity, filled with sample 6 in place on the beam line autosampler and held in place with brackets.

Reference potential parameters and constraints used in the EPSR simulation model are shown in **Table S1** and **Table S2**, respectively. Charges were scaled to ± 0.8 e, in line with results from neutron diffraction and MD simulations of ILs,[54] here reduced charges have been shown to reproduce experimental data more effectively. This better simulates effects of electronic polarisability captured when using more expensive polarisable force fields.[55]

The total number of pyridine, hydrogen sulfate, protons and/or sulfuric acid and water and size of each simulation box, corresponding to the experimentally determined molecular densities of the fully protiated mixtures are detailed in **Table S3**. Centre of mass radial distribution functions, RDFs, were calculated using the SHARM routines within EPSR.

Selected interatomic distances (taken from the first peak maximum in the site-site radial distribution functions) and relative coordination numbers (N_{coord}, calculated to the minimum after the first peak in the radial distribution functions) between different atom types are shown in **Table S4** for *conc* sulfuric acid (H_2SO_4:H_2O 1:0.2), **Table S5** for 2:1:0.4 'anhydrous' acidic PIL, and in **Table S6** for the 1:1:2 sulfuric acid:pyridine:water system.
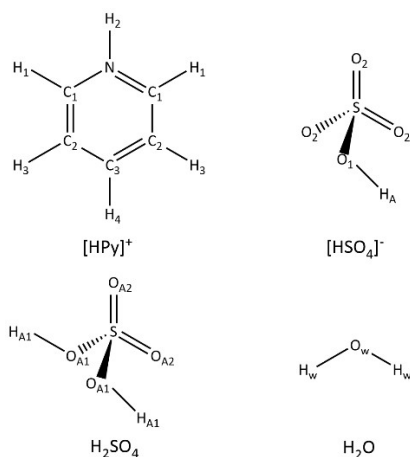

Figure S3. Atom types used in the EPSR simulation models for the pyridinium cation, hydrogen sulfate anion, molecular sulfuric acid and water.

Table S1. Lennard-Jones parameters, including the charges and masses used for reference potential of the EPSR refinement model.

Atom type	ε / kJ mole^{-1}	s / Å	q / e
Pyridinium			
N	0.5	3.2	0.1500
H_2	0.0	0.0	0.2820
H_1	0.2	2.4	0.0800
C_1	0.5	3.5	0.0736
H_3	0.2	2.4	0.0512
C_2	0.5	3.5	-0.024
C_3	0.5	3.5	-0.0448
H_4	0.2	2.4	0.0512
Hydrogen sulfate[a]			
S_1	1.046	3.55	0.944
O_1	0.837	3.15	-0.544
O_2	0.837	3.15	-0.544
H_A	0.0	0.0	0.432
Water			
O_w	0.65	3.1	-0.667
H_w	0.0	0.0	0.336

[a] The parameters for hydrogen sulfate and sulfuric acid are the same, except that both hydrogens in sulfuric acid have q = 0.616 e.

Table S2. Constraints used to define EPSR simulation model.

Intramolecular bond distance	Å		Bond angle/°
Pyridinium			
N-C1	1.432	C1-N-C1	121.37
C1-C2	1.469	N-C1-C2	120.09
C1-H1	1.082	N-C1-H1	120.08
C2-C3	1.467	C2-C1-H1	119.83
C2-H3	1.082	C1-C2-C3	119.34
C3-H4	1.082	C1-C2-H3	120.35
N-H2	1.044	C3-C2-H2	119.73
		C2-C3-C2	119.74
		C2-C3-H3	120.15
Hydrogen sulfate[a]			
S-O1	1.490	O1-S-O2	109.79
S-O2	1.490	O2-S-O2	109.79
O1-HA	0.970	S1-O1-H1	114.98
Water			
Ow-Hw	0.960	Hw-Ow-Hw	103.47

[a]Sulfuric acid and hydrogen sulfate bond distances and angles are the same.

Table S3. Simulation box size parameters.

Acid:pyridine:H$_2$O	$N_i{}^a$	Box size, n / Å	Number density / atoms Å^{-3}
1:0:0.2	600 (500:0:100)	36.41	0.0787
2:1:0.4	1700 (1000:500:200)	53.43	0.0859
1:1:2.2	2100 (500:500:1100)	50.61	0.0949

Table S4. Interatomic distances (taken from the first peak maximum in the site-site radial distribution functions) and relative coordination numbers (N$_{coord}$, calculated to the minimum after the first peak in the radial distribution functions) between different atom types in *conc* sulfuric acid (H$_2$SO$_4$:H$_2$O 1:0.2).

Interaction	Peak (minima)	N$_{coord}$
S⋯S	4.6 (6.4)	11.0±1.3
OA2⋯OA2	3.1 (4.0)	4.2±1.3
OA2⋯OA1	2.6 (3.0)	5.7±1.3
OA1⋯OA1	3.1 (3.8)	4.0±1.3
OA1⋯Ow	2.6 (4.0)	0.5±0.7
OA2⋯Ow	2.9 (4.0)	0.5±0.7
Ow⋯Ow	2.8 (4.0)	0.6±0.7
Hw⋯Ow	3.2 (4.8)	0.4±0.5
Hw⋯OA1	3.2 (4.6)	8.3±1.6
Hw⋯OA2	1.9 (2.3)	0.4±0.5
HA⋯OA2	1.6 (2.3)	0.8±0.5
HA⋯OA1	3.8 (4.6)	8.0±1.6
HA⋯Ow	1.6 (2.3)	0.1±0.3
Ow⋯HA	1.6 (2.3)	0.9±0.6
OA2⋯HA	1.6 (2.3)	0.8±0.6
OA1⋯HA	3.8 (4.6)	8.1±1.5

Table S5. Interatomic distances (taken from the first peak maximum in the site-site radial distribution functions) and relative coordination numbers (N_{coord}, calculated to the minimum after the first peak in the radial distribution functions between different {SO$_4$} oxygen sites in the 2:1:0.4 'anhydrous' acidic PIL. Half the {SO$_4$} units in the system were described as H_2SO_4 and half as [HSO$_4$]$^-$ giving rise to the apparent duplication of correlations.

Interaction	Peak (minimum) / Å	N_{coord}	Interaction	Peak (minimum) / Å	N_{coord}
S···S			**S=O···O=S**		
SA1···SA1	4.7 (6.3)	3.4±1.6	OA1···OA1	3.2s (4.0)	2.0±1.0
SA1···S1	4.7 (6.3)	3.5±1.5	OA1···O2	3.2 (4.0)	1.4±1.1
S1···S1	4.7 (6.4)	2.9±1.2	O2···OA1	3.2 (4.0)	0.9±0.9
S-OH···Ow			O2···O2	3.2 (4.0)	3.1±1.0
OA2···Ow	2.8 (4.0)	0.3±0.6	**S=O···HO-S**		
O1···Ow	2.8 (3.9)	0.3±0.5	OA2···OA1	2.6 (3.9)	3.1±1.0
Ow···OA2	2.8 (4.0)	1.7±1.4	OA2···O2	2.6 (2.9)	0.6±0.6
Ow···O1	2.8 (3.9)	0.8±0.8	O1···OA1	2.8 (3.8)	0.8±0.9
S=O···Ow			O1···O2	2.7 (3.7)	4.0±0.9
OA1···Ow	2.8 (3.9)	0.3±0.6	OA1···OA2	2.6 (3.9)	3.2±1.1
O2···Ow	2.8 (4.0)	0.3±0.6	OA1···O1	2.8 (3.8)	0.4±0.6
Ow···OA1	2.8 (3.9)	1.6±1.3	O2···OA2	2.6 (2.9)	0.4±0.6
Ow···O2	2.8 (4.0)	2.5±1.4	O2···O1	2.7 (3.7)	1.3±0.6
{SO$_4$}···Hw			**S-OH···HO-S**		
OA1···Hw	1.8 (2.4)	0.1±0.3	OA2···OA2	3.0 (4.0)^{sh}	1.9±1.0
O2···Hw	1.9 (2.3)	0.1±0.3	O1···O1	2.9 (3.9)	0.4±0.6
O1···Hw	1.8-3.5^{br}	0.4±0.8	OA2···O1	3.0 (4.0)^{sh}	0.4±0.6
OA2···Hw	1.7-3.2^{br}	0.4±0.8	O1···OA2	3.0 (4.0)^{sh}	1.0±1.0
Ow···Ow	2.8 (4.4)	0.5±0.7	HAA···O2	1.7 (2.2)	0.6±0.5
Hw···Ow	1.8 (2.3)	0.4±0.6	HAA···Ow	1.6 (2.2)	0.1±0.2
OA1···HAA	1.6 (2.2)	0.3±0.5	HAA···Hw	2.2 (2.7)	0.2±0.5
OA1···HA	1.8 (2.4)	0.2±0.4	O2···HA	1.8 (2.4)	0.2±0.4

^{sh} shoulder, ^{br} broad

Table S6. Interatomic distances (taken from the first peak maximum in the site-site radial distribution functions) and relative coordination numbers (N_{coord}, calculated to the minimum after the first peak (as indicated in the table) in the radial distribution functions between different $\{SO_4\}$ oxygen sites in the 1:1:2 sulfuric acid:pyridine:water system.

Interaction	RDF distance and minima / Å	N_{coord}
S···S	4.8 (6.0)	2.5±1.1
O1···O1	3.0sh (4.0)	0.5±0.7
O1···O2	2.8 (3.9)	4.5±1.0
O1···Ow	2.7sh (4.0)	1.6±1.5
O1···Hw	3.1sh (4.5)	5.9±4.2
O1···HA	3.1sh (4.5)	1.6±1.1
O2···O1	2.8 (3.9)	1.5±0.6
O2···O2	3.7 (4.0)[sh]	3.0±0.9
O2···Ow	2.7 (3.2)	0.8±0.9
O2···Hw	1.8 (2.4)	0.6±0.7
O2···HA	1.8 (2.5)	0.3±0.5
Ow···O1	2.7 (4.0)[sh]	0.7±0.7
Ow···O2	2.7 (3.2)	1.1±0.9
Ow···Ow	2.7 (4.0)	4.1±2.0
Ow···Hw	1.7 (2.5)	2.2±1.3
Ow···HA	1.8 (2.4)	0.1±0.3
Hw···O1	3.1 (4.5)[sh]	1.3±0.9
Hw···O2	1.8 (2.4)	0.4±0.5
Hw···Ow	1.7 (2.5)	1.1±0.9
HA···O1	3.2sh (4.0)	1.2±0.9
HA···O2	1.8 (2.5)	1.0±0.7
HA···Ow	1.8 (2.4)	0.3±0.5

[sh] shoulder