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Effect of the environmental humidity on the bulk, interfacial and nanoconfined properties of an ionic liquid

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Water uptake by [HMIM] $EtSO_4$ estimated by Fourier transform infrared (FTIR) spectroscopy

Table S1: Detected IR modes, and corresponding peak positions in dry and 45% equilibrated [HMIM] $EtSO_4$. We have compared our peak positions with respect to peaks previously assigned to [EMIM] $EtSO_4$ in ref.[1]. The d-values [cm^{-1}] show differences in 45% equilibrated [HMIM] $EtSO_4$ relative to dry [HMIM] $EtSO_4$.

IR mode	[EMIM] $EtSO_4$ from ref. [1]		Dry [HMIM] $EtSO_4$		45% [HMIM] $EtSO_4$		d [cm^{-1}]	
O-S-O wag	577	565	576.5	565	578	566	1.5	1
N-C stretch	617	600	618	-	619	-	1	-
CN oscillation	648		653.5	-	653	-	-0.5	-
S-O stretch	731		729	-	737	-	8	-
C-C-H wag	756	708	758	-	765	-	7	-
N-C-H wag	808		-	-	-	-	-	-
C-C stretch + C-C-H wag	849		-	-	-	-	-	-
O-S-O symm. stretch	960	912	-	913	-	914.5	1.5	-
C-N-C stretch	1014		1016	-	1014.5	-	-1.5	-
O-C stretch	1061		1061	-	1061	-	0	-
H-C-H twist	1109		1109.5	-	1109.5	-	0	-
N-C-H + O-S-O symm. stretch	1169		1167	-	1166	-	-1	-
S-O stretch	1215		1215	-	1212	-	-3	-
N-C-H rock + S-O stretch	1242		1244	-	1246.5	-	2.5	-
N-C-H rock	1328	1302	-	-	-	-	-	-
H-C-H, H-C-H rock	1387		1385.5	-	1387.5	-	2	-
H-C-H rock	1435		1431.5	-	1431.5	-	0	-
H-C-H, H-C-H scissor	1460		1458.5	-	1458	-	-0.5	-
H-C-H scissor	1470		1468	-	1468	-	0	-
N-C-H rock	1574		1573.5	-	1573.5	-	0	-
C-H stretch	3151	3103	3148	3102	3151	3107	3	5

Long-term chemical stability of [HMIM] $EtSO_4$ equilibrated at 45% RH studied by NMR

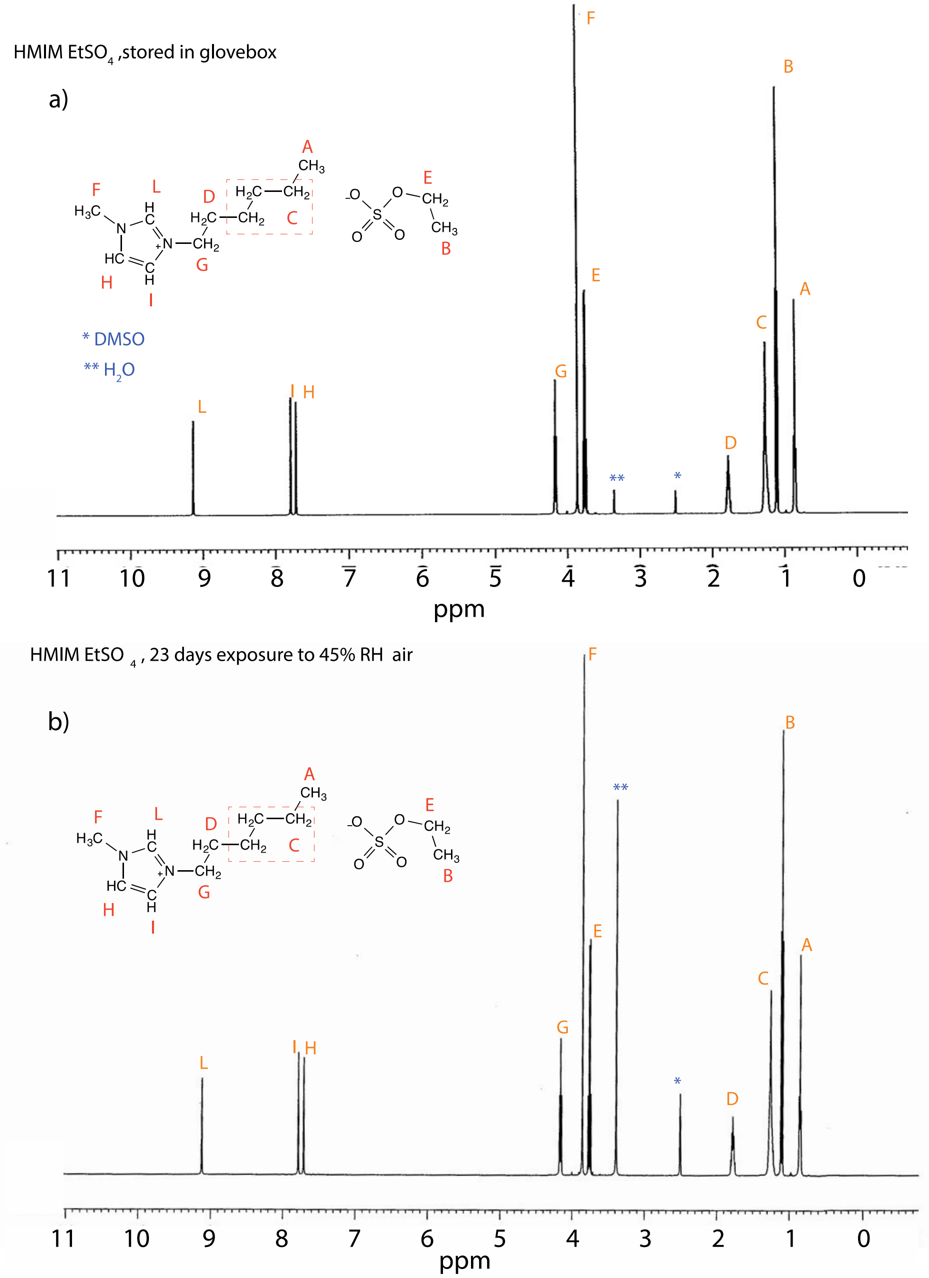


Figure S1: *^{1}H NMR* of [HMIM] $EtSO_4$ (a) as received from Iolitec and stored in a glovebox and (b) after exposure to 45% RH for 23 days at room temperature. The ^{1}H NMR spectra were recorded in *dimethyl sulfoxide-d6* (99.5+ atom % D) at 296 K using a Bruker Avance 500 NMR spectrometer operating at 500.1 MHz.

Table S2 shows the intensity of the *^{1}H NMR* data. According to these results, there is no significant change in composition since the cation to anion ratio is approximately the same.

Further, hydrolysis of the IL with water is not detected since the H-signals attributed to the anion as a function of storage time with water remain constant. The water /IL ratio is ~ 0.68. In a previous work [2] it was shown that the anion $EtSO_4$ can hydrolyse in sealed vessels with large amounts of water, but only at high temperature conditions.

Table S2: Intensity of the NMR signals measured from the spectra presented in Figure S2. The area are normalized with respect to the C(2)H signal.

	A	B	C	D	E	F	G	H	I	L
As received	3.02	2.98	5.98	2.01	1.98	2.95	1.98	0.99	1.01	1.00
Stored at 45% RH for 23 days	3.04	3.05	6.02	2.02	2.02	3.01	2.02	1.00	1.01	1.00

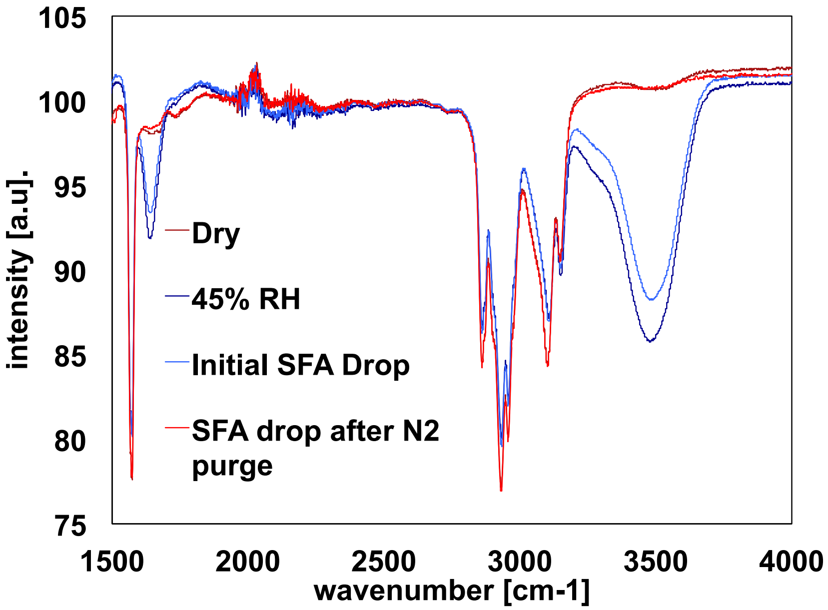


Figure S2: FTIR spectra of a droplet of [HMIM] $EtSO_4$ used in an eSFA experiment, before and after the SFA experiment where it was subjected to 0% RH. The IR spectra are compared to the spectra of the dry [HMIM] $EtSO_4$ and equilibrated at 45% RH. Reversible drying of the [HMIM] $EtSO_4$ droplet is achieved by purging with dry N_2 for three days in the eSFA cell.

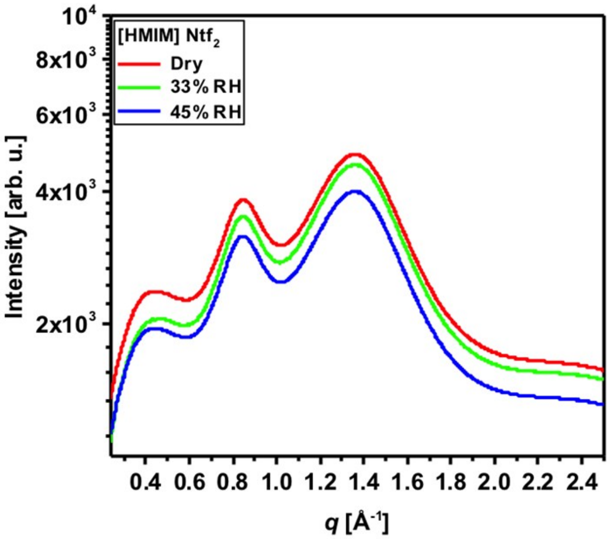


Figure S3: WAXS spectra obtained for dry [HMIM] Ntf2 (red line), and equilibrated at 33% relative humidity (green line), and 45% RH (blue line). Three reflections at the *q* ranges of 0.3 to 1.8 Å^{-1} correspond to nanostructure of the ILs as: the average lateral separation between IL filaments (first peak), distance between alkyl tails along a IL filament (second peak), and average anion-cation distance within the IL filament (third peak). No peak shift is detected in the presence of water.

X-Ray photoelectron spectroscopy (XPS) analysis

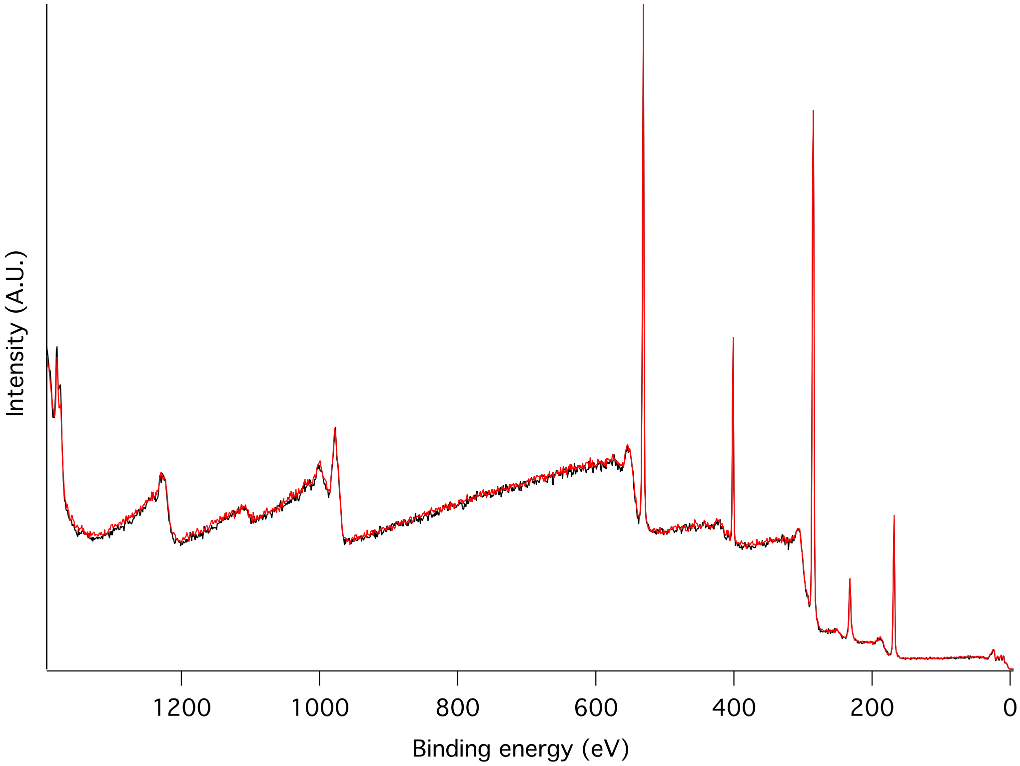


Figure S4: Survey spectra obtained on the dry [HMIM] $EtSO_4$ (black) and on [HMIM] $EtSO_4$ equilibrated at 45% RH (red), both of them used in the WAXS experiments and stored in the capillaries until the XPS measurements were conducted. The survey spectra were acquired between 0 and 1250 eV. Only S2p, C1s, O1s and N1s signals are detected together with the CKLL and OKLL, thus reflecting the composition of the IL under investigation.

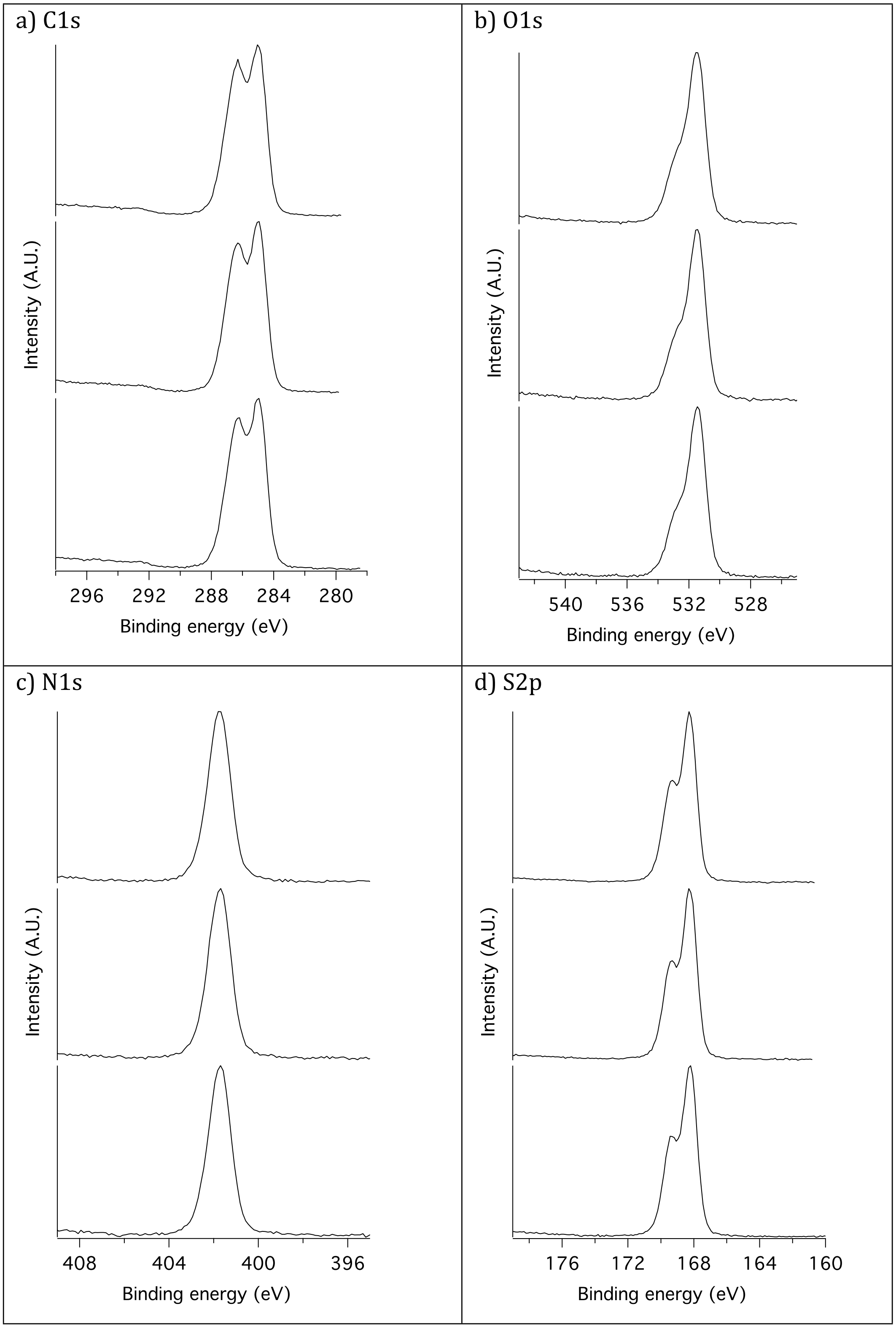


Figure S5: High-resolution spectra at 69 eV for a) C1s, b) O1s, c) N1s, and d) S2p for (going from top to bottom for the following samples) dry [HMIM] $EtSO_4$ stored in a WAXS (quartz) capillary, 45% equilibrated [HMIM] $EtSO_4$ stored in a WAXS capillary, and reference [HMIM] $EtSO_4$ stored at 45% RH.

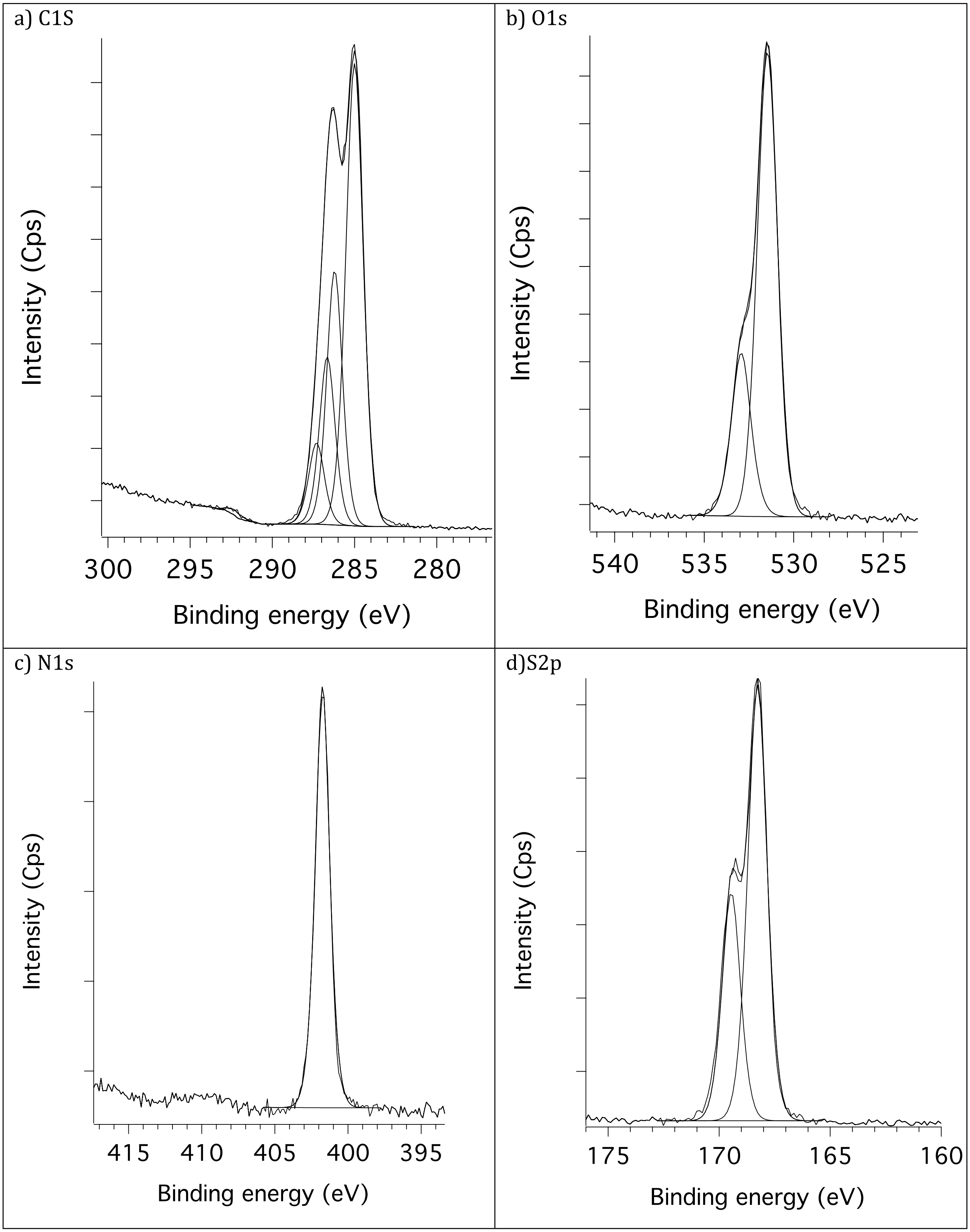
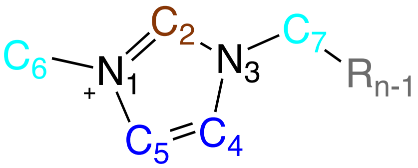
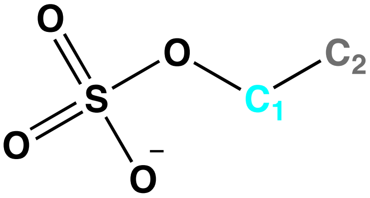


Figure S6: Fits to the high-resolution spectra of the reference dry [HMIM] $EtSO_4$.

The C1s photoelectron signal was fitted using 4 model functions: each of them is the product of a Gaussian/Lorentzian function with a G/L ratio equal to 45. The binding energy value of the first component is set at 285.0 and assigned to the aliphatic carbon atoms following the assignment of the scheme reported in the scheme provided as insert of Figure S7. The other signals have the peak maxima at 286.2, 286.7, and 287.3 eV and are assigned referring to the scheme to C_6 –C_7 and C_1, to C_5 and C_4 and to C_2 respectively (see the schematics below).



C6
N1
+
C2
N3
C7
Rn-1
C5
C4



O
O
S
O
−
O
C1
C2

Schematics: [HMIM] cation (left) and $EtSO_4$ anion (right).

The area ratio of the second component was constrained to 0.5 of the first one according to the chemical formula and the third and the fourth were constrained to be 2/6 and 1/6 of the first peak. The contribution of the shake-up satellite at 292.2 eV was summed to the areas of the other components when calculating the atomic percentages. Shake-off signals were not revealed under these experimental conditions and thus they were not considered in fitting the data. The binding energy values resulting from this fitting procedure are in agreement with the chemical formula of the IL and with the literature[3,4], and references quoted herein.

The N1s signal is characterized by the presence of only one peak at 401.7 eV (G/L = 60 and fwhm = 1.1_6 eV). The O1s has two components: one at 531.5 eV and the second at 532.9 eV; they are assigned to the O in the SO_4 group and to C-O-S in agreement with the above-mentioned literature.

The S2p spectrum exhibits the typical asymmetry due to the spin-orbit coupling: the main signal was found at 168.3 eV in agreement with what was found for other sulfates[5].

Distributions of the layer thicknesses of [HMIM] $EtSO_4$ resolved by AFM

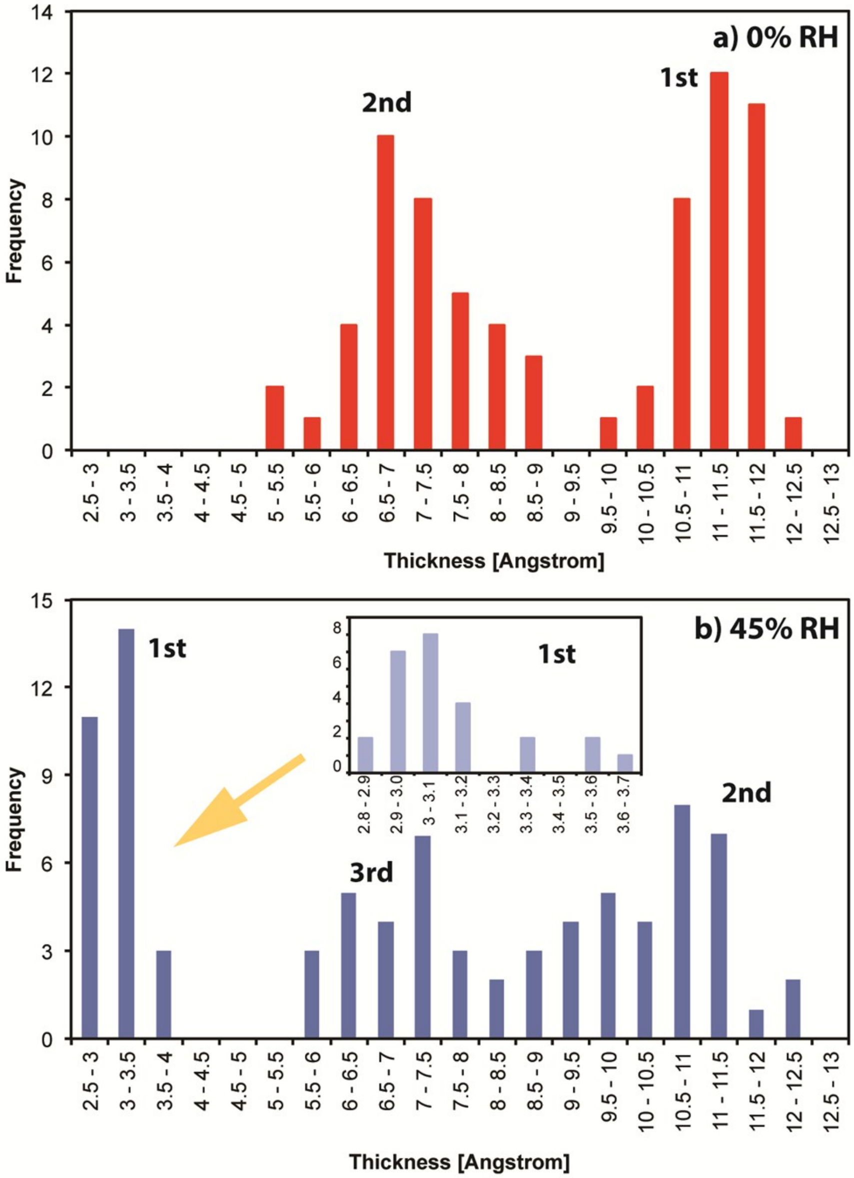


Figure S7: Distribution of the layer thicknesses of [HMIM] $EtSO_4$ on mica resolved with an AFM sharp tip a) for the dry IL at 0% RH and b) for the 45% equilibrated IL at 45% RH. The inset in b) shows a narrower distribution within the range 2.8 Å, and 3.7 Å, with a clear peak between 3 and 3.1 Å. The transition denoted as 1^{st} is the closest to the hard wall; increasing numbers indicate that they are progressively further away from the hard wall. At 0% RH, only two transitions are resolved (1^{st} and 2^{nd}), while at 45%RH, three transitions are resolved. At 0% RH the first layer before the hardwall has an average size of ~1.12 nm and a layering force of ~0.4 nN. The second layer size is ~0.71 nm and has a layering force of ~0.1 nN. The different interfacial structure at 45% RH is clearly demonstrated by the remarkably higher layering force and decreased layer size observed for the last step before the hardwall. This step has an average size of ~0.31 nm and a layering force of ~1.5 nN. The second step has an average size of ~1.06 nm and a layering force of ~0.2 nN. A third, less pronounced step becomes evident in the 45% RH equilibrated sample at ~ 4 nm separation. The average layer size for this transition is ~0.75 nm with an average layering force of ~0.04 nN.

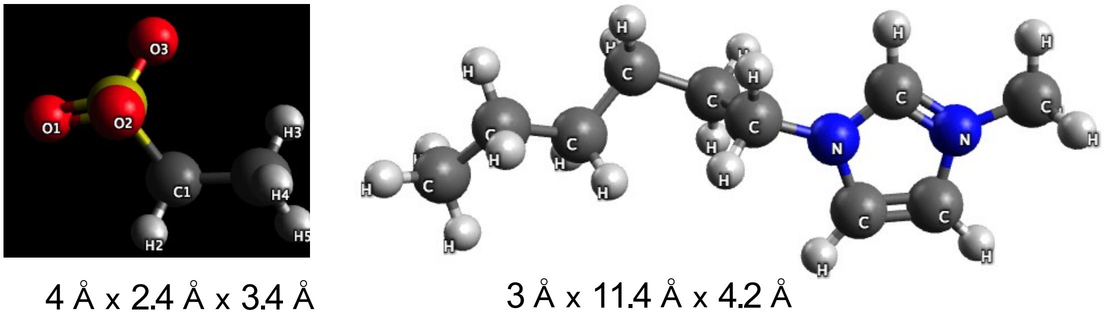


Figure S8: Optimized geometry and size of HMIM+, and EtSO4-, calculated with the software Avogadro by Molecular Mechanics (force field =MMFF94s).

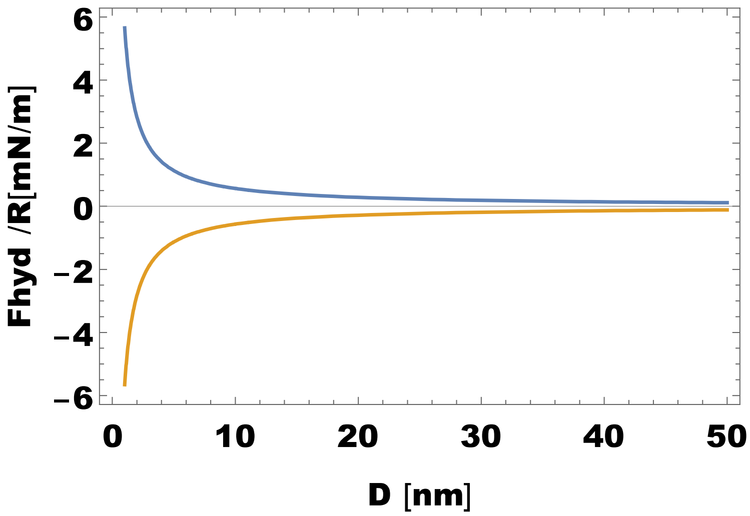


Figure S9: Calculated hydrodynamic force as a function of the surface separation D during approach (blue) and separation (yellow) at constant speed $v = 0.5$ nm/s, assuming no slip, estimated for a viscosity η of 120 mPas and R=20 mm according to:

$$\frac{F_{hyd}}{R} = -6\pi\eta R v/4D$$

References

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