

# Electroviscous Retardation of the Squeeze-Out of Nanoconfined Ionic Liquids

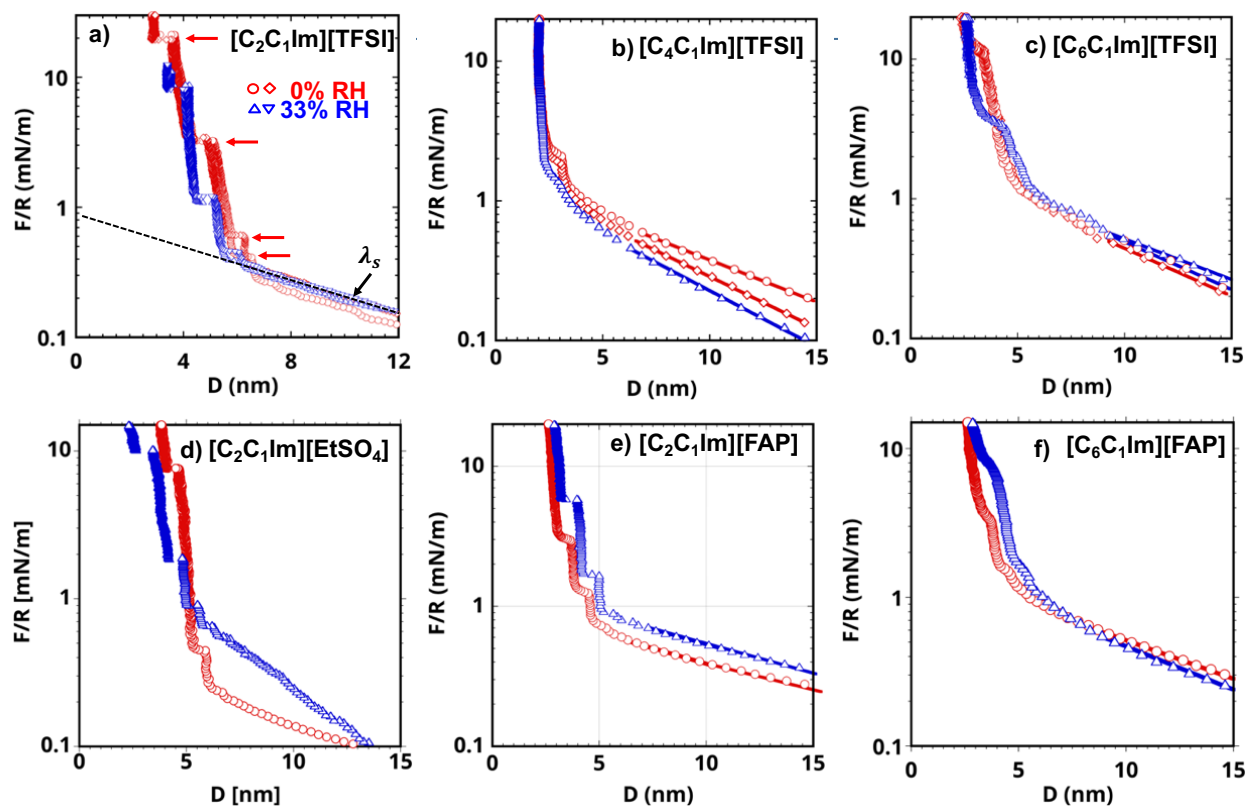
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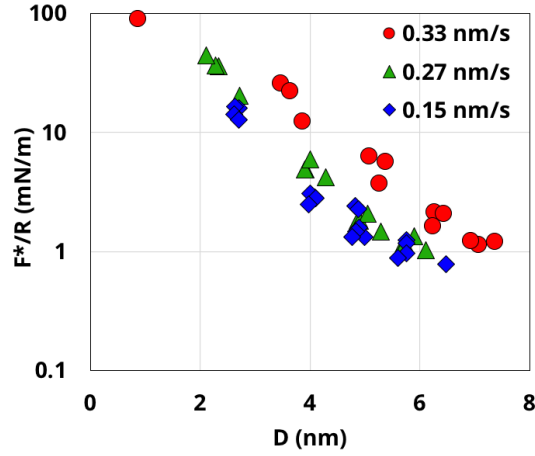
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**Table S1.** Provider and purity of the IL, molar mass, viscosities (at a given temperature) and densities of the bulk ILs (given by the provider), and measured water uptakes at 44% RH after 7 days of equilibration. The reference for the viscosity of the dry ILs is given as well. Since a viscosity range has been reported for some ILs, the numbers in cursive show the values used in this work for the calculation of Figure 7.

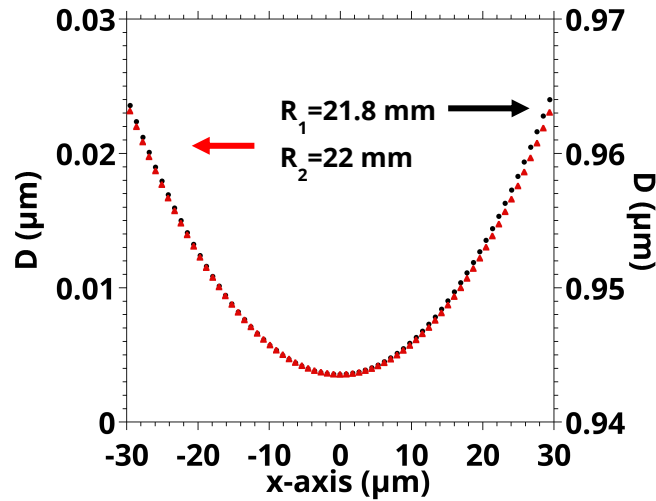
IL	Provider/purity	Mole mass (g/mol)	density (g/cm <sup>3</sup> )	Viscosity (Temp) (mPa.s)	viscosity reference	water uptake at 44%RH (wt. %)
[C <sub>2</sub> C <sub>1</sub> Im][TFSI]	Iolitec (Heilbronn, Germany) /99%	391.31	1.52	32-34 (25°C) <i>33</i>	Tariq et al. <sup>1</sup>	0.46
[C <sub>4</sub> C <sub>1</sub> Im][TFSI]	Iolitec (Heilbronn, Germany) /99%	419.36	1.43	51-69 (25°C) <i>61</i>	Tariq et al.	0.37
[C <sub>6</sub> C <sub>1</sub> Im][TFSI]	Iolitec (Heilbronn, Germany) /99%	447.42	1.37	68-81 (25°C) <i>81</i>	Tariq et al.	0.18
[C <sub>2</sub> C <sub>1</sub> Im][FAP]	Merck kGaA (Darmstadt, Germany) $\geq$ 98%	556.17	1.71	71 (22°C)	Nazet et al. <sup>2</sup>	0.07
[C <sub>6</sub> C <sub>1</sub> Im][FAP]	Merck kGaA (Darmstadt, Germany) $\geq$ 99%	612.29	1.56	116 (20°C)	Merck	0.08
[C <sub>2</sub> C <sub>1</sub> Im][EtSO <sub>4</sub> ]	Merck kGaA (Darmstadt, Germany) $\geq$ 99%	236.29	1.24 1.21 <sup>a</sup>	- 116 (22°C) - 17.5 <sup>a</sup>	Fröba et al. <sup>3</sup>	11.7



**Figure S1.** Representative force-separation curves in  $[\text{C}_2\text{C}_1\text{Im}][\text{TFSI}]$ ,  $[\text{C}_4\text{C}_1\text{Im}][\text{TFSI}]$ , and  $[\text{C}_6\text{C}_1\text{Im}][\text{TFSI}]$  at 25 °C in  $[\text{C}_2\text{C}_1\text{Im}][\text{FAP}]$ ,  $[\text{C}_6\text{C}_1\text{Im}][\text{FAP}]$  and  $[\text{C}_2\text{C}_1\text{Im}][\text{EtSO}_4]$  at 22 °C. The force measurements were conducted in a dynamic fashion during approach of the mica surfaces at constant velocity of a-c)  $\sim 0.5$  nm/s and d-f)  $\sim 0.3$  nm/s. The measurements were conducted in vacuum-dry ILs in an atmosphere of dry  $\text{N}_2$  (red) and with ILs equilibrated at  $\sim 33(6)\%$  RH (blue).



**Figure S2.** Force normalized by the radius of the surfaces required to squeeze-out a layer of ions ( $F^*/R$ ) as a function of the film thickness ( $D$ ) in vacuum-dry  $[\text{C}_2\text{C}_1\text{Im}][\text{FAP}]$  at 0% RH. The approach velocity was varied between 0.33 nm/s and 0.15 nm/s in this experiment with the same pair of mica surfaces.



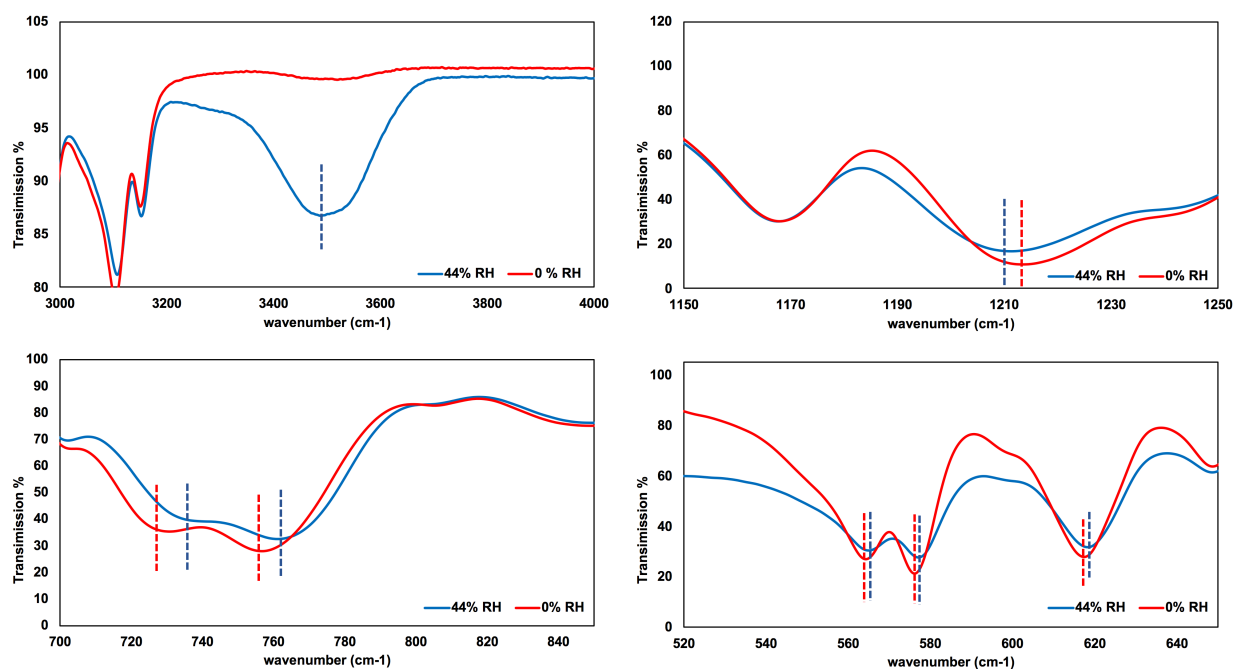
**Figure S3.** Surface separation between mica surfaces in  $[\text{C}_2\text{C}_1\text{Im}][\text{TFSI}]$  along the x-axis at two different separations  $D_1 = 1 \mu\text{m}$  ( $F/R \sim 0 \text{ mN/m}$ , right Y-axis, black circles) and  $D_2 = 3 \text{ nm}$  ( $F/R \sim 40 \text{ mN/m}$ , left axis, red). SFA measurements typically provide  $D$  at the point of closest approach, i.e. at the center of the confining geometry ( $x = 0 \mu\text{m}$ ). However,  $D$  can also be measured over a larger region along the x and y axis to determine the curvature of the mica surfaces. The estimated radii are  $\sim 21.8 \text{ mm}$  and  $\sim 22 \text{ mm}$ , respectively, for this particular experiment.

**Table S2.** Parameters used for the calculation of the X-axis in the inset of Figure 4 ( $c_{ion}$ ,  $a$  and  $\epsilon_r$ ) and the experimentally determined screening length ( $\lambda_s$ ) with the standard deviation in parenthesis (see manuscript).  $c_{ion}$  =ion concentration,  $a$ =ion diameter (estimated from the cube root of the volume per ion pair halved) and  $\epsilon_r$ =relative dielectric constant. The dielectric constant of [C<sub>2</sub>C<sub>1</sub>Im][FAP] and [C<sub>6</sub>C<sub>1</sub>Im][FAP] have not been reported yet, to the best of our knowledge, and therefore, calculations were not possible for these two ILs. The values in the presence of water were estimated using effective medium theory<sup>4</sup>. The ion concentration at 33% RH was estimated assuming that the density of all ILs, except [C<sub>2</sub>C<sub>1</sub>Im][EtSO<sub>4</sub>] (see Table S1), remain constant.

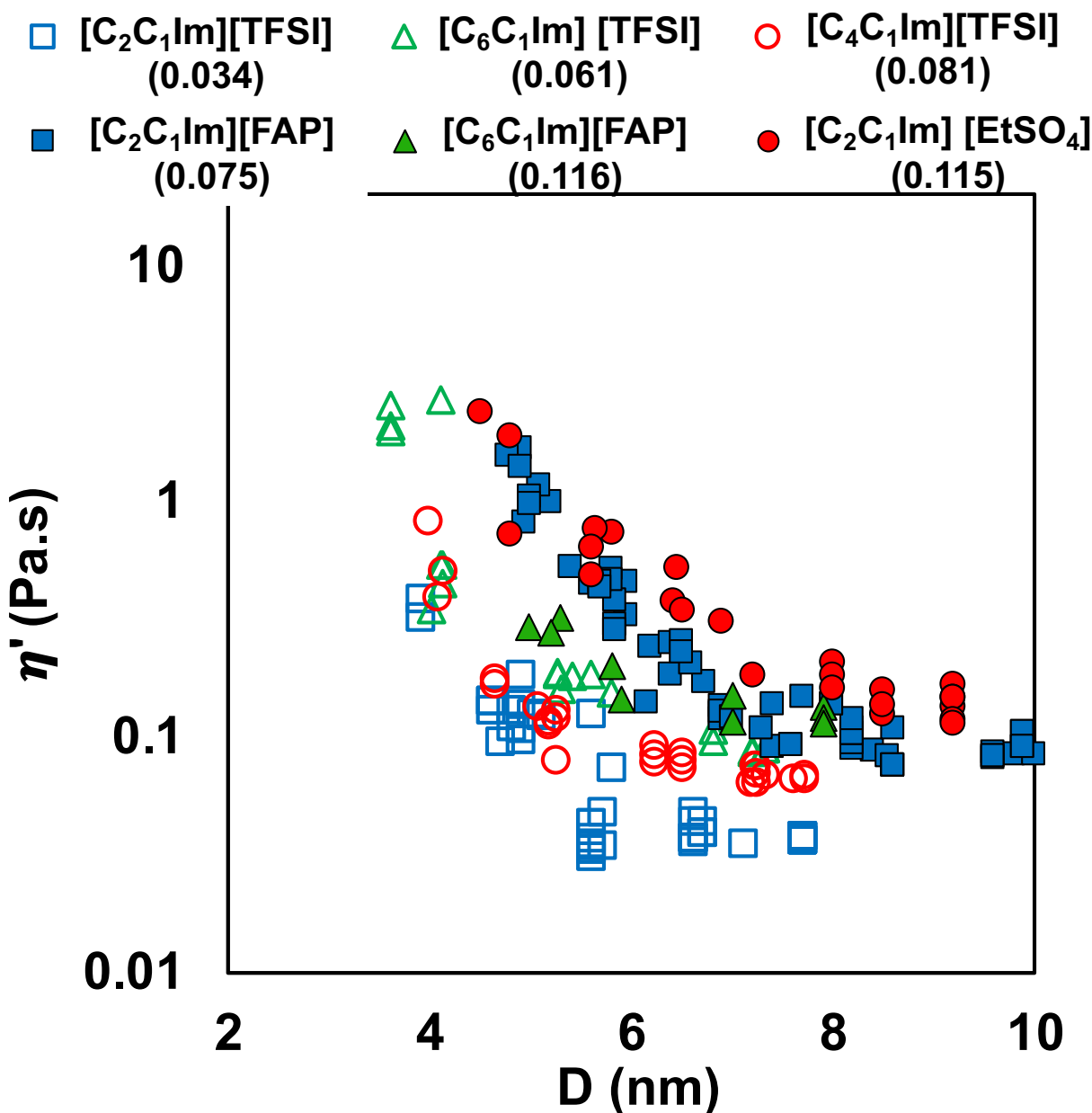
	$c_{ion}$ (M)		$a$ (Å)		$\epsilon_r$ (-)		Ref.	$\lambda_s$ (nm)	
	0%	33%	0%	33%	0%	33%		0%	33%
[C <sub>2</sub> C <sub>1</sub> Im][TFSI]	7.77	7.63	3.77	3.78	12.30	12.64	Ref. <sup>5</sup>	6.9 (0.8)	7.4 (0.5)
[C <sub>4</sub> C <sub>1</sub> Im][TFSI]	6.82	6.74	3.93	3.94	11.60	11.89	Ref. <sup>6</sup>	7.0 (0.8)	
[C <sub>6</sub> C <sub>1</sub> Im][TFSI]	6.12	6.11	4.08	4.08	12.7	12.83	Ref. <sup>5</sup>	6.6 (0.9)	7.0 (0.3)
[C <sub>2</sub> C <sub>1</sub> Im][FAP]	6.15	6.15	4.07	4.07				8.6 (0.9)	8.7 (1.8)
[C <sub>6</sub> C <sub>1</sub> Im][FAP]	5.10	5.09	4.33	4.33				7.6 (0.7)	7.5 (1.0)
[C <sub>2</sub> C <sub>1</sub> Im][EtSO <sub>4</sub> ]	10.5	9.07	3.41	3.43	27.90	34.01	Ref. <sup>6</sup>	9.2 (0.7)	4.5 (0.6)

**Table S3.** Refractive index ( $n$ ) of the dry ILs. The refractive index is determined through the analysis of the transmitted interference by fast spectral correlation<sup>7</sup>.

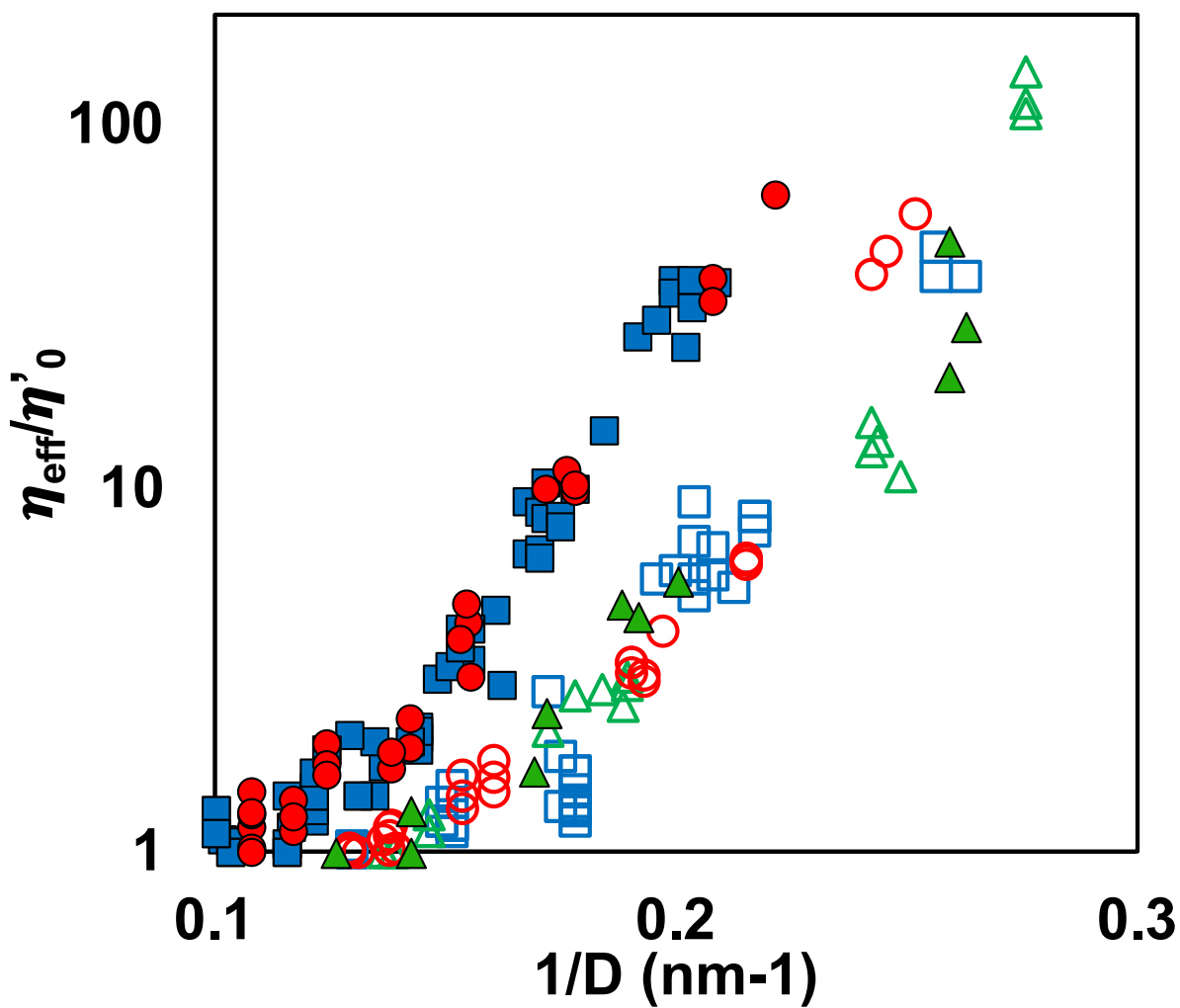
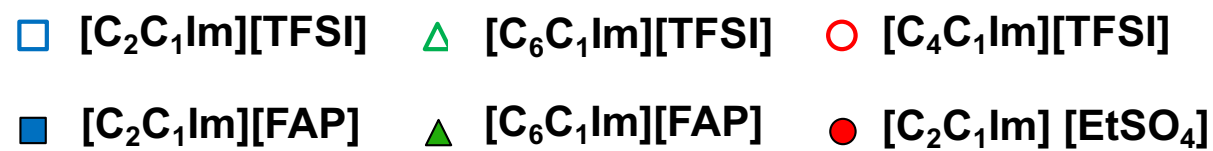
	$n$
[C <sub>2</sub> C <sub>1</sub> Im][TFSI]	1.421
[C <sub>4</sub> C <sub>1</sub> Im][TFSI]	1.428
[C <sub>6</sub> C <sub>1</sub> Im][TFSI]	1.430
[C <sub>2</sub> C <sub>1</sub> Im][FAP]	1.37
[C <sub>6</sub> C <sub>1</sub> Im][FAP]	1.38
[C <sub>2</sub> C <sub>1</sub> Im][EtSO <sub>4</sub> ]	1.48



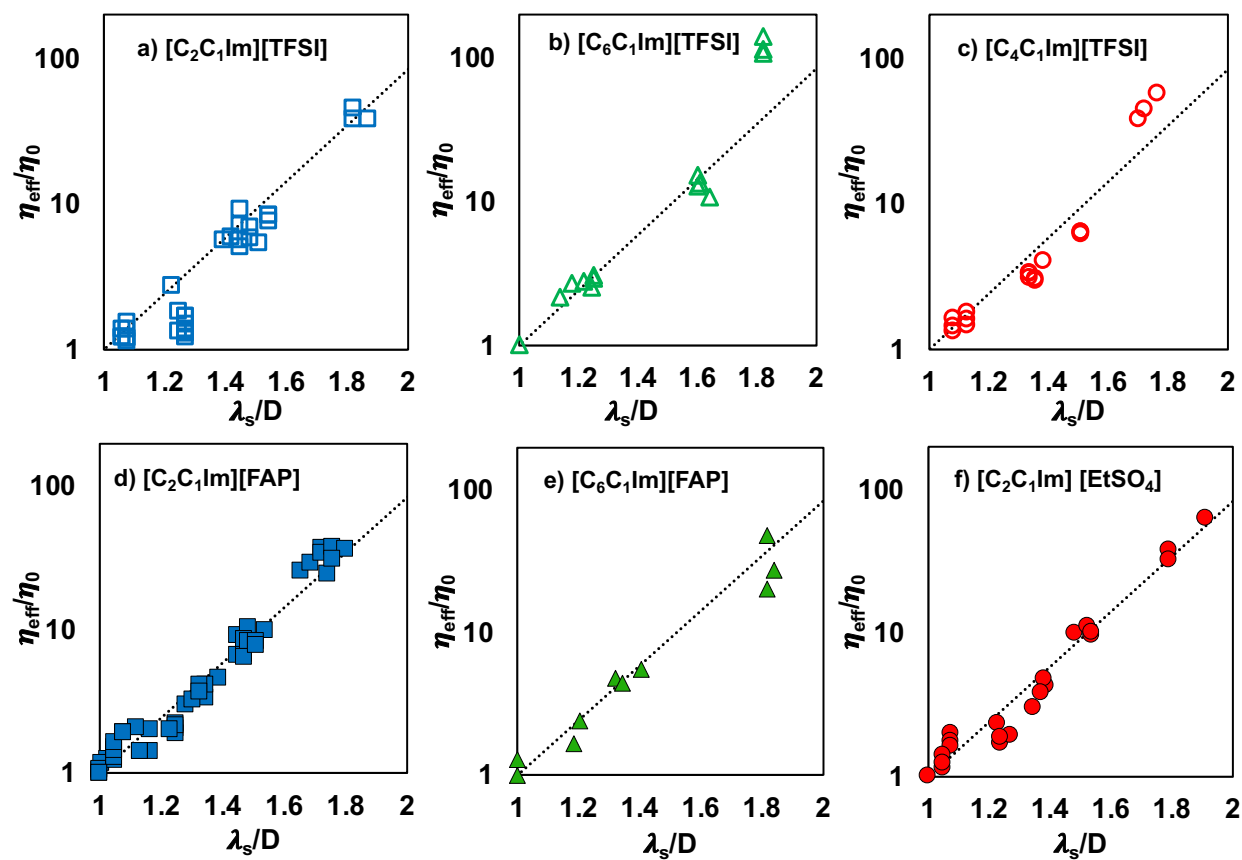
**Figure S4.** FTIR spectra of  $[\text{C}_2\text{C}_1\text{Im}][\text{EtSO}_4]$  equilibrated at 0% RH and 44% RH.  $[\text{C}_2\text{C}_1\text{Im}][\text{EtSO}_4]$  is substantially influenced by the exposure to 44% RH, as suggested by the strong adsorption band at  $3500\text{ cm}^{-1}$ , which is assigned to the O-H stretching in water molecules. As indicated by the dashed lines in the figures, significant shifts in peak positions are found in the bands at  $1213.5\text{ cm}^{-1}$ ,  $729.5\text{ cm}^{-1}$ , and  $757\text{ cm}^{-1}$ ,  $617\text{ cm}^{-1}$ ,  $566\text{ cm}^{-1}$ , and  $576\text{ cm}^{-1}$ . The peaks have been previously assigned to  $-\text{C}-\text{O}-\text{SO}_3$  asymmetrical stretching mode ( $1213.5\text{ cm}^{-1}$ ), symmetrical bending of the imidazolium ring ( $729.5\text{ cm}^{-1}$ ), out-of-plane asymmetric bending of  $-\text{C}-\text{O}-\text{S}-\text{O}$  ( $617\text{ cm}^{-1}$ ), and the in-plane bending of the imidazolium ring ( $566\text{ cm}^{-1}$ , and  $576\text{ cm}^{-1}$ ), respectively.<sup>8</sup> The vibrational modes of the anion are affected by the water uptake, as shown by the small shifts of around  $2\text{ cm}^{-1}$  to  $3\text{ cm}^{-1}$ , which is due to the higher polarity of the anion compared to the cation. However, the vibrational modes on the imidazolium ring are also affected, indicating either the association to free water molecules, or bridging of cations and anions through water.



**Figure S5.** Viscosity of the confined films  $\eta'$  as a function of the film thickness  $D$  for the six selected ILs with the [TFSI] anion (25°C, empty symbols) and with [FAP] and [EtSO<sub>4</sub>] anions (22°C, full symbols) at 0% RH. The viscosity  $\eta'$  was estimated with the slip length  $2D_s$  that results from modeling the drainage of the liquids at large surface separations ( $D > 10$  nm). This is an approximation because the slip length during the squeeze-out of the nanoconfined could differ from  $2D_s$ . As a result,  $\eta'$  can only be estimated if  $D > 2D_s$ . Each data point results from modeling the time-dependent squeeze-out of one IL layer, except in the case of the ILs with the  $[\text{C}_6\text{C}_1\text{Im}]$  cation, which requires an increase in viscosity during the drainage of the bilayer structure.



**Figure S6.** Effective viscosity normalized by the bulk viscosity as a function of the inverse of the film thickness for the six selected ILs.



**Figure S7.** Effective viscosity normalized by the bulk viscosity as a function of the ratio between screening length and film thickness for the six selected ILs, each of them in a separate diagram.

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