Supporting Information: Impact of Anion Mixing on Li^+ Coordination and Transport Properties in Pyrrolidinium-Based Ionic Liquid Electrolytes

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Table S1 Viscosity and density values, collected at different temperatures, for all ionic liquid electrolytes. The viscosity values have an uncertainty of $\pm 0.5\%$ and the density values have an uncertainty of ± 0.0001 g/cm^3.

Sample	T (K)	Viscosity (mPa·s)	Density (g/cm^3)
$Pyr_{14}FSI$	293	61.11	1.31
	303	42.57	1.30
	313	31.13	1.29
	323	23.44	1.29
	333	18.27	1.28
	343	14.82	1.27
	353	12.05	1.26
$(LiFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	293	108.60	1.37
	303	70.64	1.36
	313	49.49	1.35
	323	35.85	1.35
	333	26.99	1.34
	343	21.02	1.33
	353	16.87	1.32
$(LiTFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	293	138.44	1.39
	303	88.97	1.38
	313	60.45	1.37
	323	43.60	1.36
	333	32.32	1.35
	343	24.83	1.35
	353	19.54	1.33
$Pyr_{14}TFSI$	293	96.17	1.40
	303	60.32	1.39
	313	40.71	1.38
	323	28.82	1.37
	333	21.26	1.36
	343	16.09	1.35
	353	12.35	1.35
$(LiTFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	293	369.75	1.46
	303	195.66	1.45
	313	113.85	1.44
	323	71.27	1.43
	333	47.62	1.42
	343	33.94	1.41
	353	24.90	1.40
$(LiFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	293	279.18	1.44
	303	155.76	1.43
	313	94.20	1.43
	323	61.16	1.42
	333	41.98	1.41
	343	31.42	1.40
	353	22.93	1.39

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Table S2 Ionic conductivity values in S/cm, for all ionic liquid electrolytes.

T (K)	$Pyr_{14}FSI$	$(LiFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	$(LiTFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	$Pyr_{14}TFSI$	$(LiTFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	$(LiFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$
193	–	6.59e-09	–	–	–	–
203	–	1.65e-07	–	–	–	3.39e-10
213	–	1.71e-06	–	–	–	1.44e-08
223	–	9.50e-06	3.64e-06	–	–	2.95e-07
233	–	3.82e-05	1.61e-05	–	–	5.44e-07
243	–	1.15e-04	5.49e-05	–	1.22e-08	7.84e-06
253	–	2.78e-04	1.48e-04	–	1.57e-07	2.45e-05
263	1.23e-03	5.80e-04	3.29e-04	–	5.17e-05	6.99e-05
273	2.04e-03	1.06e-03	6.38e-04	7.67e-04	9.90e-05	1.71e-04
283	3.09e-03	1.76e-03	1.10e-03	1.39e-03	2.20e-04	3.84e-04
293	4.48e-03	2.72e-03	1.77e-03	2.29e-03	5.93e-04	7.01e-04
298	5.36e-03	3.32e-03	2.20e-03	2.88e-03	–	–
303	6.26e-03	3.98e-03	2.66e-03	3.53e-04	1.05e-03	1.17e-03
313	8.23e-03	5.47e-03	3.75e-03	4.99e-03	1.70e-03	1.81e-03
323	1.04e-03	7.30e-03	5.10e-03	6.84e-03	2.56e-03	2.64e-03
328	1.18e-03	8.35e-03	5.89e-03	7.95e-03	–	–
333	1.31e-03	9.45e-03	6.71e-03	9.07e-03	3.63e-03	3.66e-03
343	1.58e-02	1.18e-02	8.45e-03	1.14e-02	4.93e-03	4.88e-03
353	1.89e-02	1.45e-02	1.05e-02	1.42e-02	6.45e-03	6.31e-03
363	2.19e-02	1.73e-02	1.27e-02	1.72e-02	8.12e-03	7.94e-03
373	2.53e-02	2.05e-02	1.15e-02	2.02e-02	1.01e-02	9.74e-03

Table S3 Parameters from the linear fit of the Walden plots: the slope α and the intersection point log (C).

Sample	α	log (C)
$Pyr_{14}FSI$	0.90±0.005	-0.149±0.003
$(LiFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	0.92±0.003	-0.202±0.001
$(LiTFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	0.93±0.003	-0.266±0.001
$Pyr_{14}TFSI$	0.91±0.007	-0.172±0.004
$(LiTFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	0.90±0.002	-0.282±0.001
$(LiFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	0.90±0.006	-0.343±0.002

The apparent Li^+ transference number was calculated as follow:

$$t_{\mathrm{Li^+}} = \frac{D_{\mathrm{Li^+}} \cdot x_{\mathrm{Li^+}}}{D_{\mathrm{Li^+}} \cdot x_{\mathrm{Li^+}} + D_{\mathrm{Pyr_{14}}} \cdot x_{\mathrm{Pyr_{14}}} + D_{\mathrm{FSI}} \cdot x_{\mathrm{FSI}} + D_{\mathrm{TFSI}} \cdot x_{\mathrm{TFSI}}} \tag{1}$$

D_i being the apparent self-diffusion coefficient and x_i being the molar fraction of the *i*-th component.

The propagated errors were estimated using the propagation formulas below:

$$\sigma_{\Lambda} = \Lambda \cdot \sqrt{\left(\frac{\sigma_{\sigma_{\mathrm{dc}}}}{\sigma_{\mathrm{dc}}}\right)^2 + \left(\frac{\sigma_{\rho}}{\rho}\right)^2} \tag{2}$$

$$\sigma_{\Lambda_{\mathrm{NE}}} = \frac{F^2}{R \cdot T} \sqrt{\sum_i (x_i \cdot \sigma_{D_i})^2} \tag{3}$$

$$\sigma_{\mathrm{ionicity}} = ionicity \cdot \sqrt{\left(\frac{\sigma_{\sigma_{\mathrm{dc}}}}{\sigma_{\mathrm{dc}}}\right)^2 + \left(\frac{\sigma_{\rho}}{\rho}\right)^2 + \left(\frac{\sqrt{\sum_i (x_i \cdot \sigma_{D_i})^2}}{\sum_i (x_i \cdot D_i)}\right)^2} \tag{4}$$

Table S4 ^{1}H, ^{19}F and ^{7}Li self-diffusion coefficient values for all electrolyte samples in the temperature range 298 K - 353 K. The errors are estimated from the fitting.

Sample	T (K)	D_{Pyr14} (10^{-11} m^2/s)	D_{FSI} (10^{-11} m^2/s)	D_{TFSI} (10^{-11} m^2/s)	D_{Li^+} (10^{-11} m^2/s)
$Pyr_{14}FSI$	298	2.39±0.005	3.02±0.007	n/a	n/a
	313	4.11±0.011	4.89±0.006	n/a	n/a
	328	6.45±0.006	7.51±0.073	n/a	n/a
	343	9.61±0.020	11.10±0.039	n/a	n/a
	353	12.10±0.033	14.00±0.032	n/a	n/a
$(LiFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	298	1.47±0.002	1.68±0.004	n/a	1.24±0.011
	313	2.69±0.004	2.91±0.010	n/a	2.16±0.013
	328	4.49±0.003	4.75±0.015	n/a	3.57±0.008
	343	6.93±0.009	7.26±0.025	n/a	5.52±0.019
	353	9.07±0.022	9.23±0.054	n/a	7.20±0.049
$(LiTFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	298	1.29±0.008	1.37±0.004	0.99±0.002	0.96±0.009
	313	2.40±0.009	2.47±0.004	1.83±0.003	1.76±0.009
	328	4.13±0.011	4.18±0.006	3.17±0.008	3.00±0.008
	343	6.56±0.022	6.58±0.021	5.07±0.017	4.71±0.005
	353	8.54±0.021	8.55±0.023	6.66±0.017	6.18±0.009
$Pyr_{14}TFSI$	298	1.75±.009	n/a	1.47±0.004	n/a
	313	3.28±0.007	n/a	2.80±0.007	n/a
	328	5.52±0.020	n/a	4.78±0.009	n/a
	343	8.58±0.061	n/a	7.46±0.013	n/a
	353	11.10±0.104	n/a	9.70±0.024	n/a
$(LiTFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	298	0.59±0.005	n/a	0.38±0.001	0.36±0.028
	313	1.29±0.008	n/a	0.88±0.003	0.68±0.038
	328	2.67±0.010	n/a	1.75±0.002	1.28±
	343	4.79±0.043	n/a	3.08±0.004	2.18±0.014
	353	6.72±0.014	n/a	4.28±0.010	3.10±0.027
$(LiFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	298	0.68±0.002	0.66±0.001	0.49±0.002	0.47±0.040
	313	1.43±0.004	1.40±0.004	1.07±0.003	0.81±0.016
	328	2.84±0.008	2.60±0.007	2.06±0.004	1.51±0.026
	343	5.01±0.012	4.38±0.005	3.52±0.006	2.52±0.075
	353	6.91±0.021	5.94±0.012	4.80±0.021	4.14±0.148

Table S5 Apparent transference number of the Li^+ (calculated using eq. 1) as a function of temperature for all electrolytes.

Sample	T (K)	t_{Li^+}
$(LiFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	298	0.0799
	313	0.0786
	328	0.0788
	343	0.0794
	353	0.0803
$(LiTFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	298	0.0763
	313	0.0689
	328	0.0688
	343	0.0683
	353	0.0689
$(LiTFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	298	0.0777
	313	0.0664
	328	0.0618
	343	0.0593
	353	0.0603
$(LiFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	298	0.0808
	313	0.0663
	328	0.0637
	343	0.0614
	353	0.0727

Table S6 Molar conductivities (Λ estimated from impedance measurements and Λ_{NE} calculated from the NMR diffusometry data) and the corresponding ionicity values at different temperatures. The errors were calculated using the propagation formulas described above (eq. 3-5).

Sample	T (K)	Λ (S·cm^2/mol)	Λ_{NE} (S·cm^2/mol)	ionicity
$Pyr_{14}FSI$	293	1.10±0.16		
	298		2.033±0.003	0.64
	303	1.55±0.23		
	313	2.05±0.31	3.219±0.005	0.64±0.09
	323	2.61±0.39		
	328		4.765±0.025	0.62
	333	3.30±0.49		
	343	4.01±0.60	6.760±0.014	0.59±0.09
	353	4.81±0.72	8.278±0.014	0.58±0.09
$(LiFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	293	0.58±0.09		
	298		1.166±0.002	0.61
	303	0.86±0.13		
	313	1.19±0.18	1.965±0.004	0.61±0.09
	323	1.60±0.24		
	328		3.091±0.005	0.59
	333	2.09±0.31		
	343	2.62±0.39	4.540±0.008	0.58±0.09
	353	3.23±0.48	5.686±0.018	0.57±0.08
$(LiTFSI)_{0.2}(Pyr_{14}FSI)_{0.8}$	293	0.40±0.06		
	298		0.946±0.003	0.53
	303	0.61±0.09		
	313	0.86±0.13	1.650±0.003	0.52±0.08
	323	1.18±0.18		
	328		2.691±0.004	0.49
	333	1.56±0.23		
	343	1.98±0.30	4.070±0.008	0.49±0.07
	353	2.47±0.37	5.151±0.008	0.48±0.07
$Pyr_{14}TFSI$	293	0.69±0.10		
	298		1.210±0.004	0.72
	303	1.07±0.16		
	313	1.52±0.23	2.175±0.004	0.70±0.10
	323	2.10±0.32		
	328		3.516±0.007	0.69
	333	2.81±0.42		
	343	3.57±0.53	5.236±0.020	0.68±0.10
	353	4.45±0.67	6.597±0.034	0.67±0.10
$(LiTFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	293	0.16±0.02		
	298		0.348±0.003	0.64
	303	0.29±0.04		
	313	0.47±0.07	0.7322±0.0038	0.63±0.10
	323	0.71±0.11		
	328		1.414±0.003	0.61
	333	1.01±0.15		
	343	1.38±0.21	2.399±0.011	0.58±0.09
	353	1.82±0.27	3.259±0.005	0.56±0.08
$(LiFSI)_{0.2}(Pyr_{14}TFSI)_{0.8}$	293	0.18±0.03		
	298		0.437±0.003	0.47
	303	0.30±0.05		
	313	0.47±0.07	0.873±0.002	0.54±0.08
	323	0.70±0.10		
	328		1.619±0.003	0.48
	333	0.97±0.15		
	343	1.31±0.20	2.678±0.006	0.49±0.07
	353	1.70±0.26	3.611±0.012	0.47±0.07