Supporting Information for

A Volumetric and Diffusion Study of Solutions of $AlCl_3$ in Two Ionic Liquids - $[C_2TMEDA][Tf_2N]$ and $[C_4mpyr][Tf_2N]$

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Table S1. Densities (ρ /g·cm^{-3}), Apparent Molar Volumes of $AlCl_3$ ($V_{\phi,1}$ /cm^3·mol^{-1}) and Partial Molar Volumes (V_i/cm^3·mol^{-1}) of $AlCl_3$ (1) and [C_2TMEDA][Tf_2N] (0) in their Mixtures as a Function of Temperature, *T,* Mole Fraction *x* and Molality *m*.

		T / K								
$x_1(AlCl_3)$	m_1/mol·kg^{-1}	293.15	298.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
		ρ /g·cm^{-3}								
0[a]	0	1.377 76	1.373 35	1.368 94	1.360 14	1.351 40	1.342 69	1.334 05	1.325 41	1.316 89
0.0786	0.2005	1.390 69	1.386 22	1.381 82	1.373 04	1.364 31	1.355 63	1.346 99	1.338 41	1.329 88
0.1764	0.5034	1.408 82	1.404 25	1.399 70	1.390 84	1.382 13	1.373 47	1.364 84	1.356 25	1.347 69
0.2295	0.7027	1.421 08	1.416 55	1.412 01	1.402 94	1.394 28	1.385 65	1.377 05	1.368 46	1.359 87
0.2993	1.0038	1.436 64	1.432 10	1.427 60	1.418 63	1.409 66	1.401 03	1.392 44	1.383 78	1.375 07
		c /mol·L^{-1}								
0.0786	0.2005	0.2716	0.2708	0.2699	0.2682	0.2665	0.2648	0.2631	0.2614	0.2597
0.1764	0.5034	0.6646	0.6624	0.6603	0.6561	0.6520	0.6479	0.6438	0.6398	0.6357
0.2295	0.7027	0.9130	0.9101	0.9072	0.9014	0.8958	0.8903	0.8848	0.8792	0.8737
0.2993	1.0038	1.2719	1.2679	1.2639	1.2560	1.2480	1.2404	1.2328	1.2251	1.2174
		V_ϕ/cm^3·mol^{-1} (raw values, eq 2)								
0	0	61.67	61.97	62.30	62.66	62.50	62.61	62.75	62.77	62.88
0.0786	0.2005	62.24	62.48	62.54	62.68	62.81	62.93	63.07	63.10	63.29
0.1764	0.5034	62.86	63.12	63.38	63.63	63.79	63.93	64.10	64.23	64.46
0.2295	0.7027	62.35	62.53	62.72	63.12	63.24	63.37	63.51	63.66	63.90
0.2993	1.0038	63.18	63.35	63.50	63.79	64.12	64.28	64.44	64.65	64.96
V_ϕ/cm^3·mol^{-1} (smoothed values, from a binomial fit of density as a function of molarity, *c*)										
0	0	61.7	62.0	62.3	62.7	62.5	62.6	62.8	62.8	62.9
0.0786	0.2005	62.0	62.2	62.5	62.9	62.8	62.9	63.1	63.1	63.3

0.1764	0.5034	62.4	62.6	62.9	63.2	63.3	63.4	63.6	63.7	63.9
0.2295	0.7027	62.7	62.9	63.1	63.4	63.6	63.7	63.9	64.0	64.3
0.2993	1.0038	63.1	63.2	63.4	63.7	64.0	64.2	64.3	64.6	64.9
$u(V_\phi)$ /cm^3·mol^{-1}		1.2								
		V_1 /cm^3·mol^{-1} (smoothed values)								
0	0	61.7	62.0	62.3	62.7	62.5	62.6	62.8	62.8	62.9
0.0786	0.2005	62.3	62.5	62.8	63.1	63.1	63.3	63.4	63.5	63.7
0.1764	0.5034	63.1	63.3	63.4	63.8	64.1	64.2	64.4	64.6	64.9
0.2295	0.7027	63.6	63.7	63.8	64.2	64.6	64.8	65.0	65.3	65.6
0.2993	1.0038	64.3	64.4	64.4	64.7	65.4	65.6	65.8	66.2	66.7
$u(V_1)$ /cm^3·mol^{-1}		1.2								
		V_0 /cm^3·mol^{-1} (smoothed values)								
0	0	308.8	309.8	310.8	312.8	314.8	316.8	318.9	321.0	323.0
0.0786	0.2005	308.7	309.7	310.7	312.8	314.8	316.8	318.9	320.9	323.0
0.1764	0.5034	308.6	309.6	310.6	312.7	314.6	316.7	318.7	320.8	322.8
0.2295	0.7027	308.5	309.5	310.5	312.6	314.5	316.5	318.6	320.6	322.6
0.2993	1.0038	308.2	309.3	310.3	312.4	314.2	316.2	318.3	320.3	322.3
$u(V_0)$ /cm^3·mol^{-1}		1.2								

Table S2. Densities (ρ /g·cm^{-3}), Apparent Molar Volumes of $AlCl_3$ ($V_{\phi,1}$ /cm^3·mol^{-1}) and Partial Molar Volumes (V_i/cm^3·mol^{-1}) of $AlCl_3$ (1) and [C_4mpyr][Tf_2N] (0) in their Mixtures as a Function of Temperature, *T,* Mole Fraction *x* and Molality *m*.

		T / K								
$x_1(AlCl_3)$	m_1/mol·kg^{-1}	293.15	298.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
		ρ /g·cm^{-3}								
0	0	1.398 94	1.39451	1.39009	1.38129	1.37256	1.36388	1.35525	1.34669	1.33818
0.0777	0.1995	1.404 49	1.40006	1.39564	1.38681	1.37799	1.36920	1.36060	1.35180	1.34301
0.1745	0.5003	1.414 14	1.40950	1.40488	1.39572	1.38662	1.37758	1.36887	1.35979	1.35072
0.2281	0.6997	1.420 14	1.41554	1.41094	1.40175	1.39256	1.38337	1.37437	1.36522	1.35593
0.2970	1.0001	1.430 00	1.42523	1.42052	1.41108	1.40163	1.39219	1.38282	1.37343	1.36396
		c /mol·L^{-1}								
0.0777	0.1995	0.2730	0.2721	0.2713	0.2695	0.2678	0.2661	0.2644	0.2627	0.2610
0.1745	0.5003	0.6632	0.6610	0.6589	0.6546	0.6503	0.6461	0.6420	0.6377	0.6335
0.2281	0.6997	0.9089	0.9059	0.9030	0.8971	0.8912	0.8853	0.8796	0.8737	0.8678
0.2970	1.0001	1.2618	1.2576	1.2535	1.2451	1.2368	1.2285	1.2202	1.2119	1.2036
		V_ϕ/cm^3·mol^{-1} (raw values, eq 2 ; V_ϕ^0 eq. 7)								
0	0	80.96	81.18	81.43	81.99	82.74	83.42	84.30	85.30	86.41
0.0777	0.1995	80.26	80.51	80.78	81.39	82.18	82.87	83.75	84.73	85.81
0.1745	0.5003	79.25	79.54	79.85	80.53	81.38	82.07	82.96	83.91	84.95
0.2281	0.6997	78.61	78.93	79.27	79.98	80.87	81.58	82.46	83.40	84.41
0.2970	1.0001	77.70	78.06	78.43	79.21	80.15	80.86	81.74	82.67	83.63
$u(V_\phi)$ /cm^3·mol^{-1}		1.2 (20 °C) to 0.2 (90 °C) cm^3·mol^{-1}								

		V_1 /cm^3·mol^{-1} (smoothed values, from a binomial fit of density as a function of molarity, c)								
0	0	80.96	81.18	81.43	81.99	82.74	83.42	84.30	85.30	86.41
0.0777	0.1995	80.44	80.56	80.71	81.11	81.65	82.38	83.37	84.36	85.53
0.1745	0.5003	77.62	77.96	78.29	79.02	79.79	80.68	81.88	82.77	83.71
0.2281	0.6997	76.54	76.92	77.27	78.04	78.82	79.73	81.01	81.81	82.64
0.2970	1.0001	74.76	75.20	75.59	76.44	77.27	78.25	79.71	80.47	81.22
$u(V_1)$ /cm^3·mol^{-1}		1.2 (20 °C) to 0.2 (90 °C)								
		V_0 /cm^3·mol^{-1}								
0	0	301.94	302.90	303.86	305.79	307.74	309.70	311.67	313.65	315.64
0.0777	0.1995	301.98	302.94	303.90	305.83	307.78	309.73	311.70	313.68	315.68
0.1745	0.5003	302.18	303.14	304.10	306.03	307.97	309.92	311.84	313.84	315.85
0.2281	0.6997	302.42	303.37	304.33	306.25	308.19	310.13	312.01	314.02	316.06
0.2970	1.0001	302.92	303.86	304.81	306.72	308.66	310.58	312.36	314.41	316.49
$u(V_0)$ /cm^3·mol^{-1}		0.3								

Table S3a. Coefficients for the Fit to Eq (4) for $AlCl_3$ Solutions, Molality, m, together with Mean Expansivities α [= $-(\partial\rho/\partial T)_p/\rho$].[a]

Solvent	[C_2TMEDA][Tf_2N], 293.15-363.15 K					[C_4mpyr][Tf_2N], 293.15-363.15 K				
m / mol·kg^{-1}	0.0 [b]	0.2005	0.5034	0.7027	1.0038	0.0 [c]	0.1995	0.5003	0.6997	1.0001
a_0 / g·cm^{-3}	1.657 48 ± 0.0012	1.672 79 ± 0.0012	1.705 22 ± 0.0058	1.725 16 ± 0.0082	1.736 54 ± 0.0073	1.680 73 ± 0.0006	1.672 88 ± 0.0043	1.704 24 ± 0.0091	1.692 71 ± 0.0052	1.711 38 ± 0.0022
10^3 a_1/ g·cm^{-3}·K^{-1}	-1.0221 ± 0.0076	- 1.0383 ± 0.0073	- 1.1245 ± 0.036	- 1.1708 ± 0.050	- 1.1404 ± 0.045	- 1.0365 ± 0.0037	- 0.9465 ± 0.026	- 1.0593 ± 0.056	- 0.9410 ± 0.032	- 0.9739 ± 0.013
10^6 a_2/ g·cm^{-3}·K^{-2}	0.2319 ± 0.012	0.2589 ± 0.011	0.3859 ± 0.054	0.4548 ± 0.077	0.4002 ± 0.068	0.2565 ± 0.0057	0.1052 ± 0.040	0.2372 ± 0.085	0.0380 ± 0.049	0.0475 ± 0.020
10^6 σ/ g·cm^{-3} [d]	15	15	72	100	91	8	54	110	65	27
10^3 α/ K^{-1} [e]	0.647 ± 0.001	0.638 ± 0.004	0.617 ± 0.004	0.629 ± 0.006	0.625 ± 0.004	0.634 ± 0.001	0.638 ± 0.006	0.654 ± 0.002	0.658 ± 0.009	0.673 ± 0.008

[a] More than the minimum number of significant figures are retained in the fitted coefficients in this and subsequent Tables to minimize the accumulation of errors in calculations employing these coefficients. [b] Data from ref. 1. [c] Data from ref. 2. [d] σ is the standard deviation of the fit, (k =1). [e] average deviations for the temperature range are included.

Table S3b. Coefficients for the Fit to Eq (5) for $AlCl_3$ Solutions.

$[C_2TMEDA][Tf_2N]$, 0 –1.0 mol·kg^{-1}									
T / K	293.15	298.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
b_0 / g·cm^{-3}	1.377 70 ± 0.000 39	1.373 29 ± 0.000 41	1.368 91 ± 0.000 42	1.36 015 ± 0.000 35	1.351 38 ± 0.000 40	1.342 67 ± 0.000 41	1.334 03 ± 0.000 41	1.325 39 ± 0.000 42	1.316 87 ± 0.000 43
10^{-3} b_1/ g^2·cm^{-3}·mol^{-1}	0.066 31 ± 0.0019	0.065 90 ± 0.0020	0.065 48 ± 0.0020	0.065 10 ± 0.0017	0.065 66 ± 0.0019	0.065 81 ± 0.0020	0.065 84 ± 0.0020	0.066 09 ± 0.0020	0.066 15 ± 0.0021
10^{-6} b_2/ g^3·cm^{-3}·mol^{-2}	- 0.00744 ± 0.0018	- 0.007 16 ± 0.0019	- 0.006 86 ± 0.0020	- 0.006 73 ± 0.0016	- 0.007 46 ± 0.0019	- 0.007 53 ± 0.0019	- 0.007 49 ± 0.0019	- 0.007 77 ± 0.0020	-0.008 01 ± 0.0020
10^6 σ/ g·cm^{-3} [c]	430	460	470	380	440	450	460	470	470
$[C_4mpyr][Tf_2N]$, 0 –1.0 mol·kg^{-1}									
T / K	293.15	298.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
b_0 / g·cm^{-3}	1.398 83 ± 0.000 23	1.394 42 ± 0.000 17	1.390 02 ± 0.000 12	1.381 25 ± 0.000 06	1.372 53 ± 0.000 05	1.363 86 ± 0.000 04	1.355 24 ± 0.000 02	1.346 67 ± 0.000 04	1.338 15 ± 0.000 04
10^{-3} b_1/ g^2·cm^{-3}·mol^{-1}	0.029 14 ± 0.001 1	0.028 86 ± 0.000 82	0.028 51 ± 0.000 59	0.027 89 ± 0.000 31	0.027 25 ± 0.000 24	0.026 58 ± 0.000 22	0.026 82 ± 0.000 11	0.025 71 ± 0.000 19	0.024 35 ± 0.000 22
10^{-6} b_2/ g^3·cm^{-3}·mol^{-2}	0.002 02 ± 0.001 1	0.001 96 ± 0.000 79	0.002 00 ± 0.000 57	0.001 95 ± 0.000 30	0.001 87 ± 0.000 23	0.001 77 ± 0.000 21	0.000 76 ± 0.000 11	0.001 06 ± 0.000 19	0.001 48 ± 0.000 21
10^6 σ/ g·cm^{-3} [c]	250	190	130	71	54	49	26	44	49

Table S3c. Coefficients for the Fit to Eq (6) for $AlCl_3$ Solutions.

[a] A linear fit yields a composition independent V_ϕ, but as the values are somewhat higher than those calculated directly from eq 4 the binomial fit has been preferred.

$[C_2TMEDA][Tf_2N]$, 0 –1.27 mol·L^{-1}									
T / K	293.15	298.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
B_0 / g·cm^{-3}	1.377 69 ± 0.000 40	1.373 28 ± 0.000 42	1.368 91 ± 0.000 43	1.360 14 ± 0.000 35	1.335 36 ± 0.000 35	1.342 66 ± 0.000 41	1.334 01 ± 0.000 42	1.325 38 ± 0.000 43	1.31686 ± 0.000 43
B_1/ kg·mol^{-1}	0.048 37 ± 0.001 5	0.048 22 ± 0.001 6	0.048 06 ± 0.001 6	0.048 11 ± 0.001 4	0.048 87 ± 0.001 6	0.049 28 ± 0.001 6	0.049 62 ± 0.001 6	0.050 14 ± 0.001 7	0.05053 ± 0.001 7
B_2/ kg·dm^3·mol^{-2} [a]	- 0.001 5 ± 0.001 2	- 0.001 4 ± 0.001 2	- 0.001 2 ± 0.001 3	- 0.001 2 ± 0.001 0	- 0.001 7 ± 0.001 2	- 0.001 7 ± 0.001 3	- 0.001 7 ± 0.001 3	- 0.001 9 ± 0.001 3	- 0.002 1 ± 0.001 4
$10^6\,\sigma$/ g·cm^{-3} [c]	440	460	470	380	440	450	460	470	470
$[C_4mpyr][Tf_2N]$, 0 –1.26 mol·L^{-1}									
T / K	293.15	298.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
B_0 / g·cm^{-3}	1.398 85 ± 0.000 22	1.394 44 ± 0.000 16	1.390 04 ± 0.000 11	1.381 26 ± 0.000 05	1.372 55 ± 0.000 03	1.363 87 ± 0.000 03	1.355 25 ± 0.000 02	1.346 68 ± 0.000 02	1.338 16 ± 0.000 03
B_1/ kg·mol^{-1}	0.020 54 ± 0.000 84	0.020 41 ± 0.000 61	0.020 22 ± 0.000 42	0.019 91 ± 0.000 17	0.019 58 ± 0.000 11	0.019 22 ± 0.000 11	0.019 62 ± 0.000 09	0.018 89 ± 0.000 09	0.017 95 ± 0.000 12
B_2/ kg·dm^3·mol^{-2}	0.003 29 ± 0.000 64	0.003 25 ± 0.000 47	0.003 27 ± 0.000 33	0.003 25 ± 0.000 14	0.00319 ± 0.000 08	0.003 12 ± 0.000 08	0.002 44 ± 0.000 07	0.002 64 ± 0.000 08	0.002 90 ± 0.000 09
$10^6\,\sigma$/ g·cm^{-3} [c]	240	170	120	49	30	30	26	26	32

Table S4a. Intra-diffusion Coefficient Data for {$AlCl_3$ + $[C_2TMEDA][Tf_2N]$}, Steady Gradient Technique (UNSW, Canberra)

{$AlCl_3$ + $[C_2TMEDA][Tf_2N]$}											
0.2005 mol·kg^{-1}				**0.5034 mol·kg^{-1}**				**0.7027 mol·kg^{-1}**			
T/K	10^{12} D_{S+}/m^2·s^{-1}	T/K	10^{12} D_{S-}/m^2·s^{-1}	T/K	10^{12} D_{S+}/m^2·s^{-1}	T/K	10^{12} D_{S-}/m^2·s^{-1}	T/K	10^{12} D_{S+}/m^2·s^{-1}	T/K	10^{12} D_{S-}/m^2·s^{-1}
303.11	11.20	318.14	18.86	323.02	17.57	328.02	19.54	328.10	14.17	328.10	14.80
303.14	10.53	318.14	18.75	323.03	16.90	328.04	19.39	328.12	14.71	328.10	14.76
303.16	10.58	318.14	19.24	323.04	17.62	328.04	19.86	328.16	14.22	328.10	14.82
303.16	11.51	318.15	20.33	328.06	21.81	328.04	18.87	333.02	17.45	332.82	18.20
308.12	13.82	322.93	24.12	328.06	21.85	333.25	25.15	333.03	18.06	338.33	23.18
308.16	14.11	322.98	23.68	328.07	20.86	333.27	24.47	333.04	17.73	338.33	23.30
308.17	13.65	322.98	24.29	328.08	21.27	333.28	24.81	338.21	21.69	338.33	22.71
308.18	13.11	322.98	23.47	333.12	27.19	333.29	25.66	338.25	22.31	343.03	29.59
313.14	17.98	323.03	24.19	333.13	27.19	338.27	31.53	338.25	22.13	343.18	28.75
313.15	17.00	323.03	23.56	333.22	26.32	343.23	37.24	338.28	21.54	343.19	28.18
313.15	18.17	323.03	22.62	338.22	31.36	343.24	36.20	342.91	27.18	343.22	28.39
313.15	17.43	323.07	23.29	338.22	30.96	343.33	34.98	342.91	28.13	347.98	36.76
318.00	21.59	328.09	29.93	338.22	32.06	348.16	37.83	342.92	27.23	347.99	36.25
318.00	22.03	328.10	27.86	338.22	31.91	348.19	38.48	342.93	29.09	348.01	34.06
318.00	22.69	328.10	28.20	343.04	39.37	348.24	46.56	347.76	32.14	348.01	33.00
318.02	21.52	328.10	31.22	343.07	39.22	352.91	46.16	347.76	31.11	348.02	35.00

322.98	26.31	328.10	29.78	348.01	43.55	352.92	45.32	347.79	32.49	348.02	33.45
323.00	26.17	328.11	28.40	348.02	44.10	352.94	53.32	347.81	32.70	348.08	33.78
323.00	26.82	328.13	30.20	348.02	44.10	358.36	53.89	352.43	39.69	352.87	41.56
323.01	25.83	328.14	29.54	348.05	42.85	358.40	51.72	352.73	40.79	352.88	39.80
328.09	32.02	333.12	37.98	357.63	58.31	358.40	63.47	352.73	41.08	358.22	49.95
328.11	31.69	333.16	35.54	357.65	60.25	363.90	64.54	352.74	39.37	358.24	50.44
328.11	32.56	333.16	37.73	357.69	58.64	363.91	59.69	357.72	46.83	358.24	52.08
328.13	33.28	333.18	35.32	363.41	73.32	363.91	74.68	357.77	46.51	363.59	55.62
332.84	38.40	338.28	44.11	363.42	73.85	328.02	75.77	357.80	45.37	363.62	60.54
333.02	38.41	338.28	43.71	363.42	72.94	328.04	76.55	357.94	47.44	363.68	56.33
333.05	38.63	338.30	44.46					363.09	56.11		
333.28	38.88	338.33	41.68					363.10	55.31		
338.22	45.74	342.99	49.82					363.11	54.93		
338.23	45.93	343.00	50.74					363.12	56.84		
338.25	45.98	343.01	50.86					**1.0038 mol·kg^{-1}**			
338.26	46.26	343.02	51.47					328.08	9.34	328.22	9.83
343.04	55.48	347.72	59.10					333.07	11.51	328.30	9.68
343.05	52.91	347.95	58.76					333.07	11.34	333.29	12.74
343.08	52.24	347.98	59.89					333.08	11.99	333.30	12.25
343.08	53.82	352.83	68.60					338.12	14.56	333.30	12.38
347.99	63.51	352.86	70.85					338.13	14.53	338.43	16.17
348.01	63.61	352.90	69.53					338.13	14.65	338.43	15.91

348.03	60.73	352.90	67.48					338.14	14.75	338.43	16.65
348.05	61.04	358.21	79.29					342.67	17.43	338.44	15.93
352.51	70.71	358.21	78.36					342.96	17.85	342.61	18.77
352.77	70.15	358.22	77.48					342.98	18.42	342.62	19.36
352.78	71.40	363.52	90.12					343.00	18.21	342.64	20.28
352.79	72.54	363.53	91.42					347.96	21.63	342.64	20.51
357.83	81.26	363.57	90.52					348.30	22.22	343.03	19.10
357.85	86.64							352.61	26.81	343.03	19.50
357.85	80.92							352.62	25.56	348.35	25.03
357.86	84.23							352.65	27.02	348.35	25.58
363.21	91.31							352.68	26.28	348.35	26.06
363.21	94.17							358.00	32.83	348.51	25.91
363.21	93.43							358.01	32.80	353.20	29.73
363.23	92.89							358.02	33.09	353.23	30.38
								358.03	32.05	353.23	30.78
								363.37	40.92	358.42	37.04
								363.37	41.47	358.42	37.45
								363.37	40.06	358.46	35.66
								363.39	41.48	363.84	45.56
										363.86	45.16

Table S4b. Intra-diffusion Coefficient Data for {$AlCl_3$ + $[C_4mpyr_]$[Tf_2N]}, Steady Gradient Technique (UNSW, Canberra

{$AlCl_3$ + $[C_4mpyr_]$[Tf_2N]}											
0.1995 mol·kg^{-1}				**0.5003 mol·kg^{-1}**				**0.6997 mol·kg^{-1}**			
T/K	10^{12} D_{S+}/m^2·s^{-1}	*T*/K	10^{12} D_{S-} /m^2·s^{-1}	*T*/K	10^{12} D_{S+}/m^2·s^{-1}	*T*/K	10^{12} D_{S-} /m^2·s^{-1}	*T*/K	10^{12} D_{S+}/m^2·s^{-1}	*T*/K	10^{12} D_{S-} /m^2·s^{-1}
298.24	14.09	298.17	11.71	302.97	16.13	312.94	19.93	308.13	17.46	308.14	15.84
303.33	17.98	303.02	14.73	308.15	21.31	318.13	25.46	313.03	21.80	313.00	19.86
308.20	22.70	303.06	14.87	313.00	26.64	323.13	30.00	318.06	27.79	318.10	22.75
313.04	27.04	308.05	18.16	318.25	32.44	323.31	31.33	323.20	33.62	323.14	28.22
317.90	33.31	313.05	23.34	322.71	36.73	328.15	36.03	323.23	34.91	323.06	29.03
317.94	34.98	318.11	28.01	323.07	37.63	333.19	44.14	323.24	33.30	327.66	34.96
323.10	42.39	323.26	34.78	323.49	39.43	338.22	50.32	328.14	39.81	333.26	43.21
323.24	42.21	328.21	41.77	328.12	45.62	343.21	59.81	333.08	47.39	338.28	50.51
323.25	39.85	333.13	50.28	333.08	54.45	348.17	65.43	338.11	57.92	343.08	57.91
328.01	47.89	333.15	48.03	337.97	62.62	352.72	77.41	343.15	67.74	348.26	69.88
333.05	57.35	338.16	57.28	342.97	71.89	353.68	77.82	348.11	78.71	353.17	81.69
337.96	66.71	343.16	65.72	343.04	73.26	357.93	93.08	352.96	90.79	358.18	86.03
343.08	78.36	348.18	77.06	343.28	74.47	358.09	86.52	358.08	102.6	363.54	98.74
348.00	90.31	352.99	87.48	347.89	85.03	363.15	102.3	363.50	117.9		
348.07	89.68	357.94	100.1	352.93	95.76	363.57	105.2	**1.000$_1$ mol·kg^{-1}**			
353.05	100.8	358.19	98.35	353.17	97.31			313.12	19.66	323.15	24.37

353.05	104.0	363.49	109.4	357.93	112.8			318.17	24.41	323.17	24.04
358.04	111.7	363.52	115.8	358.05	113.2			323.20	29.62	323.20	23.58
358.06	118.4			363.22	128.9			323.12	30.95	328.03	28.01
363.29	132.6			363.33	129.0			323.24	29.77	328.18	27.93
363.39	126.7			363.46	131.2			328.15	35.56	333.12	33.96
363.48	137.4							333.18	44.23	333.12	35.49
0 mol·kg^{-1}								338.03	54.24	338.02	338.03
298.89	17.06	303.27	17.44					338.06	53.69	343.02	47.64
303.30	20.70	312.94	25.58					343.02	62.68	343.34	49.94
313.04	31.49	323.39	38.69					348.19	73.20	347.98	53.73
322.76	44.81	333.18	52.64					352.99	81.35	347.98	55.72
333.08	63.35	343.18	70.45					353.15	85.74	353.00	65.02
343.17	84.61	353.64	93.08					358.11	94.22	353.27	66.25
353.49	109.8	363.54	116.5					363.28	112.4	357.95	77.15
363.49	137.5							363.36	109.1	358.01	74.75
								363.41	109.9	363.27	82.28
										363.31	87.64

Table S5a. Intra-diffusion Coefficient Data for {$AlCl_3$ + [C_2TMEDA][Tf_2N]}, Pulsed Gradient Technique (WSU)

	{$AlCl_3$ + [C_2TMEDA][Tf_2N]}								
	0.1607 mol·kg^{-1}			**0.3994 mol·kg^{-1}**		**0.5587 mol·kg^{-1}**		**0.7950 mol·kg^{-1}**	
T/K	10^{12} D_{S+}/m^2·s^{-1}	10^{12} D_{S-} /m^2·s^{-1}	10^{12} $D_{S,Al}$/m^2·s^{-1}	10^{12} D_{S+}/m^2·s^{-1}	10^{12} D_{S-} /m^2·s^{-1}	10^{12} D_{S+}/m^2·s^{-1}	10^{12} D_{S-} /m^2·s^{-1}	10^{12} D_{S+}/m^2·s^{-1}	10^{12} D_{S-} /m^2·s^{-1}
303.00	12.42	9.92	-	7.40	-	5.63	-	3.28	3.42
303.00	-	-	-	-	-	-	-	3.45	3.57
303.00	-	-	-	-	-	-	-	-	3.65
313.00	19.62	16.10	-	-	-	9.79	-	5.88	6.57
313.00	-	17.73	-	-	-	-	-	6.53	-
313.00	-	-	-	-	-	-	-	6.28	-
323.00	28.00	24.09	-	20.84	-	15.55	15.21	**9.56** [a]	-
323.00	-	26.60	-	-	-	-	15.94	10.14	10.51
323.00	-	-	-	-	-	-	-	11.04	11.29
333.00	-	-	-	-	-	-	-	**15.46**	17.06
333.00	38.60	-	-	29.92	-	22.88	23.70	15.86	18.15
333.00	-	-	-	-	-	24.22	24.65	17.21	-
338.00	-	-	**40.08**	36.00	34.91	27.73	27.78	19.33	20.13
338.00	-	-	-	-	-	28.72	28.51	21.11	21.08
338.56	**46.16**	-	-	**33.76**	-	**28.05**	-	**19.98**	-
343.05	**55.42**	-	-	**40.20**	-	**34.49**	-	**24.71**	-

[a] Bold entries indicate measurements made with the 500 MHz (^{1}H) NMR spectrometer, normal font indicates the 600 MHz spectrometer.

Table S5b. Intra-diffusion Coefficient Data for {$AlCl_3$ + $[C_4mpyr_]$[Tf_2N]}, Pulsed Gradient Technique (WSU).

{$AlCl_3$ - $[C_4mpyr_]$[Tf_2N]}								
	0.1995 mol·kg^{-1}		**0.5003 mol·kg^{-1}**		**0.6997 mol·kg^{-1}**		**1.000$_1$ mol·kg^{-1}**	
T/K	10^{12} D_{S+}/m^2·s^{-1}	10^{12} $D_{S,Al}$/m^2·s^{-1}	10^{12} D_{S+}/m^2·s^{-1}	10^{12} $D_{S,Al}$/m^2·s^{-1}	10^{12} D_{S+}/m^2·s^{-1}	10^{12} $D_{S,Al}$/m^2·s^{-1}	10^{12} D_{S+}/m^2·s^{-1}	10^{12} $D_{S,Al}$/m^2·s^{-1}
303.00	17.8 [a]	14.9	15.2	13.3	13.6	11.9	11.2	9.72
303.00	17.7	14.8	15.2	13.1	13.5	11.9	11.2	9.23
313.00	27.4	23.5	23.6	20.4	21.7	18.9	18.8	16.4
313.00	27.5	23.4	23.5	20.4	21.7	18.8	18.6	16.1
323.00	41.2	35.1	35.7	31.0	33.4	29.0	28.8	25.1
323.00	41.1	35.4	35.7	30.9	33.5	29.1	29.0	25.2
333.00	57.6	49.8	52.5	45.7	48.0	41.8	43.4	38.1
333.00	57.7	50.5	52.5	45.8	47.9	41.7	43.3	37.5
338.00	65.8	56.9	60.0	52.0	55.3	48.7	49.9	43.6
338.00.	65.9	56.6	59.8	52.1	55.4	48.7	50.0	43.5

[a] Measurements made with the 500 MHz (^{1}H) NMR spectrometer; ^{27}Al-resonance: δ_{Al} = 104.8 ppm at 130.32 MHz.

Table S6. Coefficients for Fits to Eqn (15) [$\ln D_{Si} = \varepsilon + \zeta m$] for Experimental Isotherms Using Smoothed Data from Litovitz Fits at Each Composition.

{$AlCl_3$ + [C_2TMEDA][Tf_2N]}						
20 MHz NMR						
T/K	ε	ζ/kg·mol^{-1}	m range/ mol·kg^{-1}	ε	ζ/kg·mol^{-1}	m range/ mol·kg^{-1}
cation				anion		
303	2.749	-1.807	0 – 0.2	-	-	-
323	3.594	-1.472	0 – 0.5	3.508	-1.6371	0 – 0.2
328	3.826	-1.619	0.2 - 1	3.655	-1.370	0.2 - 1
333	3.969	-1.504	0 - 1	3.935	-1.394	0 - 1
338	4.139	-1.443	0.2 - 1	4.024	-1.239	0.2 - 1
343	4.274	-1.352	0 - 1	4.193	-1.204	0 - 1
348	4.413	-1.283	0 - 1	4.356	-1.126	0 - 1
353	4.537	-1.219	0 - 1	4.459	-1.041	0 - 1
358	4.663	-1.147	0 - 1	4.601	-0.9789	0 - 1
363	4.787	-1.097	0 - 1	4.771	-0.9752	0 - 1
500 & 600 MHz NMR				600 MHz NMR		
	cation			anion		
303	2.858	-2.031	0.16 – 0.8	2.555	-1.622	0.16 – 0.8
313	3.259	-1.794	0.16 – 0.8	3.066	-1.489	0.16 – 0.8
323	3.612	-1.585	0.16 – 0.8	3.454	-1.318	0.16 – 0.8
333	3.924	-1.400	0.16 – 0.8	3.936	-1.344	0.6 – 0.8
338	4.066	-1.316	0.16 – 0.8	4.082	-1.330	0.4 – 0.8
343	4.201	-1.237	0.16 – 0.8	-	-	-
	{$AlCl_3$ + [C_4mpyr][Tf_2N]}					
20 and 600 MHz NMR				20 MHz NMR		
T/K	ε	ζ/kg·mol^{-1}	m range/ mol·kg^{-1}	ε	ζ/kg·mol^{-1}	m range/ mol·kg^{-1}
	cation			anion		
298	2.826	-0.9248	0 – 0.2	2.649	-0.9962	0 – 0.2
303	3.033	-0.5909	0 – 1	2.881	-0.9173	0 – 0.2
308	3.219	-0.4937	0 – 0.7	3.004	-0.3760	0.2 – 0.7
313	3.450	-0.5045	0 – 1	3.271	-0.4715	0 – 0.7
318	3.627	-0.4482	0.2 – 1	3.411	-0.3463	0.2 – 0.7
323	3.817	-0.4285	0 - 1	3.660	-0.4729	0 - 1
328	3.978	-0.3858	0.2 – 1	3.821	-0.4355	0.2 – 1
333	4.141	-0.3613	0 - 1	3.991	-0.4246	0 - 1
338	4.289	-0.3306	0.2 – 1	4.140	-0.3989	0.2 – 1
343	4.428	-0.3018	0 - 1	4.285	-0.3818	0 - 1
348	4.560	-0.2745	0 - 1	4.420	-0.3623	0 - 1
353	4.684	-0.2488	0 - 1	4.547	-0.3438	0 - 1
358	4.812	-0.2378	0.2 – 1	4.675	-0.3375	0.2 – 1
363	4.913	-0.2014	0 - 1	4.781	-0.3098	0 - 1
600 MHz NMR						
	Al species					
303	2.833	-0.5527	0.2 - 1			
313	3.246	-0.4518	0.2 - 1			
323	3.647	-0.4154	0.2 - 1			
333	3.994	-0.3662	0.2 - 1			
338	4.111	-0.3310	0.2 - 1			

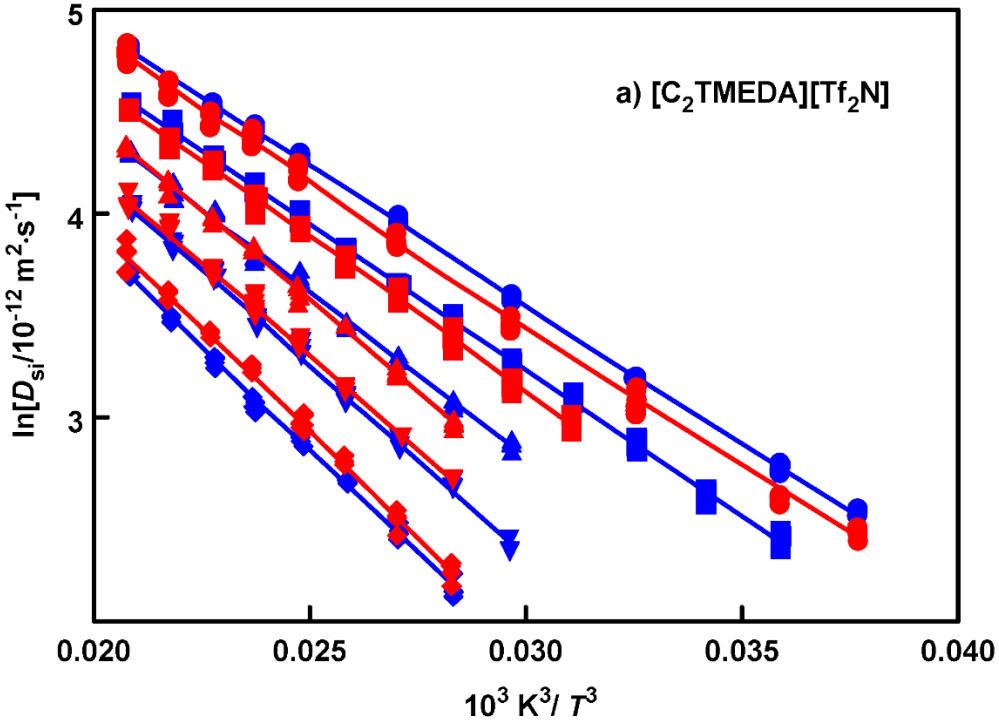
Table S7. Laity Resistance Coefficients, r_{ij}, for [C_4mpyr][Tf_2N], [C_2TMEDA][Tf_2N] and [C_2dmppz][Tf_2N].

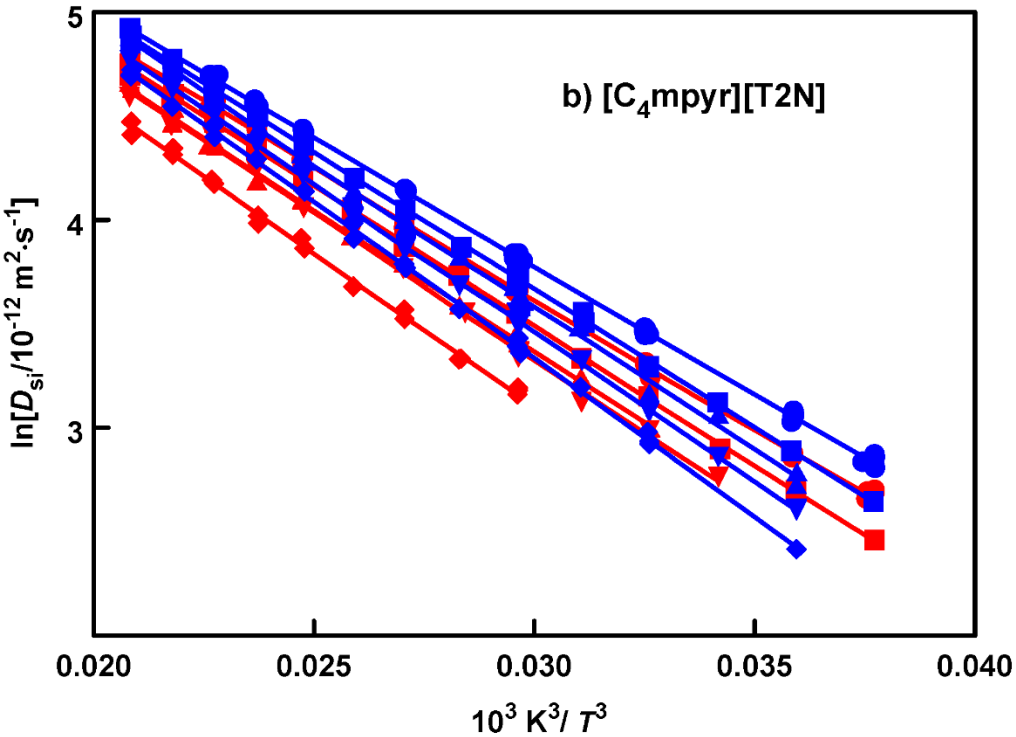
[C_4mpyr][Tf_2N],					
T/K	η/ mPa·s	r_{+-} [a]	r_{++} [a]	r_{--} [a]	$r_{+-}^2/(r_{++}\,r_{--})$ [b]
273.15	317	842			
278.15	228	615			
283.15	169	462			
288.15	128	355			
293.14	98.6	279			
298.15	77.6	223	69.1	122	0.169
303.15	62.1	181	56.0	98.9	0.168
313.15	41.5	125	37.9	66.8	0.162
323.14	29.2	90.7	27.0	46.6	0.153
333.15	21.3	68.4	19.9	33.3	0.142
343.14	16.1	53.3	15.2	24.5	0.131
353.15	12.6	42.6	12.0	18.4	0.121

[a] units: 10^{12} J s m^{-2} mol^{-1} [b] If the quantity $[r_{+-}^2/(r_{++}\,r_{--})]$ =1, the Nernst-Einstein deviation parameter, Δ, is zero.[3,4]

[C_2TMEDA][Tf_2N]					
T/K	η/ mPa·s	r_{+-}	r_{++}	r_{--}	$r_{+-}^2/(r_{++}\,r_{--})$
273.15	583	1715			
278.15	391	1189			
283.15	272	852			
288.15	196	627			
293.15	145	474			
298.15	110	366	42.0	99.6	0.031
303.15	85.3	288	34.4	76.8	0.032
313.15	54.3	189	22.9	46.9	0.030
323.15	36.8	131	15.7	30.1	0.028
333.15	26.3	95.2	10.9	19.9	0.024
343.15	19.5	71.9	8.05	13.9	0.022
353.15	15.0	56.2	6.09	10.0	0.019

[C_2dmppz][Tf_2N]					
T/K	η/ mPa·s	r_{+-}	r_{++}	r_{--}	$r_{+-}^2/(r_{++}r_{--})$
273.15	1757	4410			
278.15	1044	2695			
283.15	656	1734			
288.15	432	1167			
293.14	296	816			
298.15	210	590	82.9	254	0.061
303.15	154	439	68.7	200	0.071
313.15	88.9	262	43.4	124	0.078
323.15	55.8	170	26.6	79.8	0.074
333.15	37.3	117	15.8	52.5	0.060
343.15	26.3	84.9	9.54	36.0	0.048
353.15	19.4	64.2	5.61	25.5	0.035


a) [C2TMEDA][Tf2N]
ln[Dsi/10-12 m2·s-1]
5
4
3
0.020
0.025
0.030
0.035
0.040
10³ K³/ T³


b) [C4mpyr][T2N]
ln[Dsi/10-12 m2·s-1]
5
4
3
0.020
0.025
0.030
0.035
0.040
10³ K³/ T³

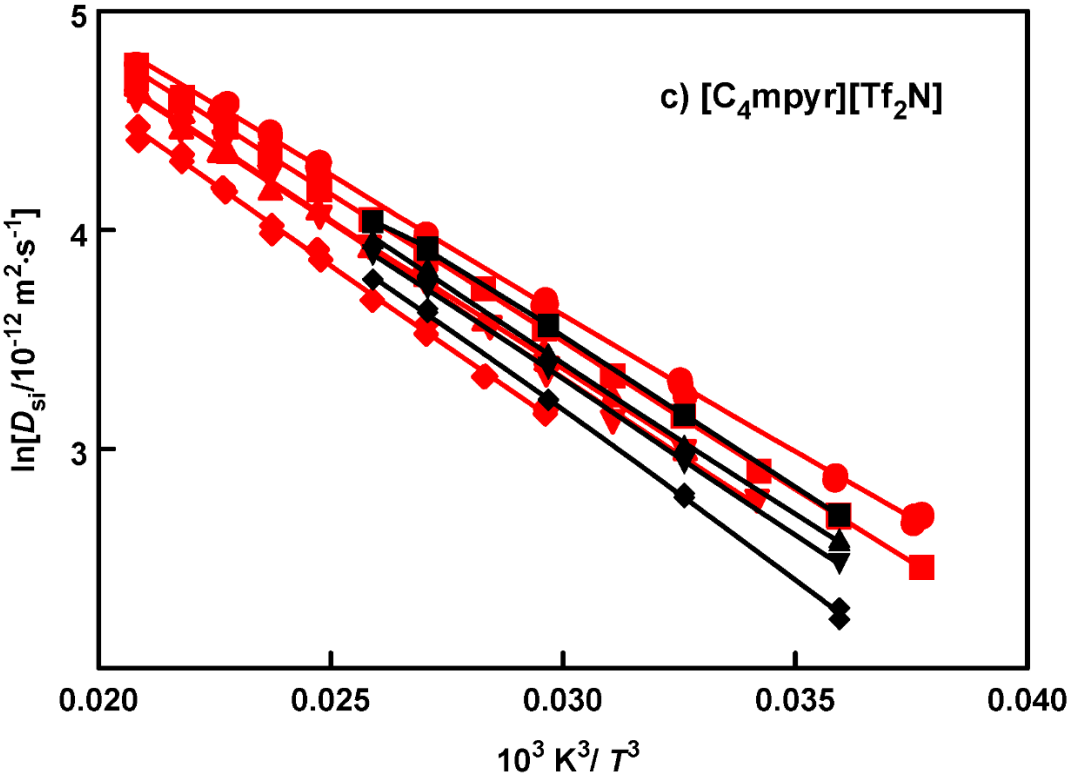


Figure S1. Litovitz plots of the intra-diffusion coefficients (D_{Si}): (a) of $[C_2TMEDA]^+$ (blue symbols) and $[Tf_2N]^-$ (red symbols) ions in $[C_2TMEDA][Tf_2N]$ and its mixtures with $AlCl_3$ (steady gradient measurements only, for clarity); (b) of $[C_4mpyr]^+$ (blue symbols) and $[Tf_2N]^-$ (red symbols) ions in $[C_4mpyr][Tf_2N]$ and its mixtures with $AlCl_3$ (steady gradient measurements only, for clarity); (c) of $[AlCl_3]$ (black symbols, pulsed gradient) and $[Tf_2N]^-$ (red symbols) ions in $[C_4mpyr][Tf_2N]$ and its mixtures with $AlCl_3$. Symbols: circles, $m_1 = 0$ mol/kg; squares, $m_1 = 0.2$ mol/kg; triangles, $m_1 = 0.5$ mol/kg; inverted triangles, $m_1 = 0.7$ mol/kg; diamonds, $m_1 = 1.0$ mol/kg. Note the crossover from the behavior $D_{S+} > D_{S-}$ at low concentrations to $D_{S+} < D_{S-}$ at higher concentrations for $\{AlCl_3 + [C_2TMEDA][Tf_2N]\}$ mixtures, whereas $D_{S+} > D_{S-}$ at all compositions in $\{AlCl_3 + [C_4mpyr][Tf_2N]\}$.

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