Supporting information for: Ion association of imidazolium ionic liquids in acetonitrile

Marija Bešter-Rogač,[*,†] Alexander Stoppa,[‡] and Richard Buchner[*,‡]

Faculty of Chemistry and Chemical Technology, University of Ljubljana, SI-1000 Ljubljana, Slovenia, and Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

E-mail: Marija.Bester@fkkt.uni-lj.si; Richard.Buchner@chemie.uni-regensburg.de

[*]To whom correspondence should be addressed

[†]Faculty of Chemistry and Chemical Technology, University of Ljubljana, SI-1000 Ljubljana, Slovenia

[‡]Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

Tables

Table S1: Molar Conductivities, Λ, as a Function of IL Molality, m, and Density Gradients, b, for Dilute Solutions of [emim][BF_4], [bmim][BF_4] and [bmim][PF_6] in AN.[a]

$10^3 \cdot m$	Λ								
	T : 273.15	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
[emim][BF_4], $b = 0.0729$									
0.71788	145.686	153.874	162.156	170.551	179.057	187.661	196.371	205.213	214.159
1.14376	143.917	151.971	160.144	168.428	176.801	185.277	193.846	202.550	211.368
1.55318	142.479	150.460	158.547	166.727	175.005	183.376	191.841	200.404	209.114
2.02959	141.050	148.920	157.174	164.837	173.188	181.459	189.824	198.297	206.881
2.66129	139.358	147.127	155.001	162.951	171.034	179.183	187.409	195.779	204.225
3.19133	138.224	145.917	153.717	161.612	169.606	177.672	185.828	194.084	202.443
3.85343	136.828	144.439	152.148	159.952	167.843	175.822	183.875	192.031	200.295
4.65043	135.312	142.830	150.440	158.148	165.942	173.809	181.773	189.811	197.968
5.34223	134.156	141.603	149.139	156.771	164.480	172.280	180.144	188.124	196.168
6.07625	133.031	140.411	147.872	155.429	163.057	170.781	178.568	186.452	194.392
6.77220	132.066	139.398	162.156	154.298	161.867	169.501	177.225	185.035	192.924
[bmim][BF_4], $b = 0.0748$									
0.29421	142.312	150.312	158.421	166.632	174.878	183.406	191.971	200.839	210.000
0.51136	140.910	148.842	156.857	165.014	173.144	181.601	190.003	198.480	207.299
0.79422	139.324	147.196	155.113	163.210	171.388	179.614	188.093	196.489	205.158
1.06541	138.482	146.258	154.098	162.089	170.181	178.377	186.687	195.112	203.677
1.40486	137.329	145.028	152.819	160.708	168.744	176.890	185.114	193.439	201.911
1.78900	136.103	143.727	151.448	159.274	166.743	174.756	182.837	191.072	199.989
2.21506	134.534	142.120	149.731	157.425	165.347	173.459	181.508	189.717	198.076
2.61380	133.987	141.499	149.069	156.739	164.532	172.451	180.445	188.560	196.800
3.05389	133.117	140.543	148.119	155.710	163.420	171.218	179.165	187.196	195.317
3.92843	131.470	138.834	146.260	153.786	161.386	169.077	176.818	184.786	192.793
5.03436	129.692	136.900	144.218	151.637	159.110	166.673	174.383	182.158	190.037
[bmim][PF_6], $b = 0.1074$									
0.23740	139.327	147.162	155.108	163.161	171.310	179.591	187.980	196.436	205.046
0.52184	137.480	145.210	153.044	160.982	169.011	177.159	185.446	193.786	202.279
0.90020	135.735	143.366	151.101	158.931	166.854	174.881	183.058	191.293	199.667
1.23490	134.558	142.109	149.762	157.518	165.363	173.315	181.390	189.554	197.844
1.55442	133.591	141.096	148.690	156.389	164.169	172.070	180.085	188.159	196.401
1.96660	132.486	139.924	147.452	155.078	162.795	170.607	178.544	186.544	194.681
2.43470	131.395	138.762	146.223	153.784	161.424	169.165	177.032	184.952	193.007
2.94352	130.367	137.684	145.072	152.561	160.130	167.805	175.575	183.446	191.416
3.53987	129.274	136.517	143.844	151.267	158.762	166.360	174.073	181.849	189.746
4.24658	128.123	135.316	142.579	149.920	157.352	164.877	172.508	180.208	188.001
4.88901	127.248	134.366	141.557	148.855	156.216	163.684	171.246	178.882	186.596
5.62945	126.308	133.361	140.497	147.736	155.026	162.439	169.928	177.492	185.145
6.43534	125.385	132.392	139.470	146.648	153.892	161.220	168.646	176.146	183.726

[a]Units: m in mol·kg^{-1}; T in K; Λ in Ω^{-1}cm^{2}mol^{-1}; b in kg^{2}L^{-1}mol^{-1}

Table S2: Molar Conductivities, Λ, as a Function of IL Molality, m, and Density Gradients, b, for Dilute Solutions of [hmim][BF_4] and [hmim][NTf_2] in AN.[a]

$10^3 \cdot m$	Λ								
	T : 273.15	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
[hmim][BF_4], $b = 0.0755$									
0.31438	137.001	144.723	152.553	160.502	168.553	176.712	184.969	193.352	201.844
0.61708	135.150	142.763	150.485	158.294	166.226	174.270	182.404	190.650	199.017
1.01888	133.338	140.847	148.457	156.179	163.995	171.910	179.943	188.054	196.301
1.39290	132.049	139.479	147.015	154.654	162.389	170.210	178.149	186.168	194.325
1.83520	130.707	138.058	145.508	153.057	160.699	168.433	176.290	184.214	192.251
2.26754	129.592	136.875	144.258	151.740	159.306	166.953	174.731	182.562	190.522
2.74420	128.513	135.734	143.042	150.458	157.950	165.533	173.227	180.986	188.855
3.20327	127.633	134.807	142.056	149.409	156.842	164.370	171.991	179.679	187.486
3.73862	126.677	133.780	140.972	148.263	155.632	163.086	170.634	178.269	186.003
4.34703	125.683	132.721	139.854	147.082	154.390	161.781	169.263	176.810	184.470
5.03886	124.654	131.638	138.707	145.870	153.102	160.425	167.849	175.312	182.891
5.85755	123.556	130.471	137.469	144.561	151.719	158.965	166.304	173.692	181.173
6.55531	122.718	129.579	136.525	143.557	150.515	157.845	165.116	172.443	179.845
[hmim][NTf_4], $b = 0.1593$									
0.28646	119.686	126.469	133.355	140.357	147.451	154.634	161.939	169.365	176.913
0.59543	118.049	124.732	131.507	138.404	145.392	152.473	159.662	166.953	174.391
0.93839	116.725	123.348	130.042	136.851	143.763	150.755	157.867	165.082	172.409
1.31468	115.608	122.145	128.791	135.530	142.371	149.283	156.316	163.472	170.717
1.72982	114.581	121.064	127.645	134.318	141.097	147.955	154.928	161.990	169.149
2.16023	113.691	120.124	126.650	133.288	139.970	146.781	153.685	160.686	167.796
2.60364	112.881	119.268	125.755	132.343	138.974	145.737	152.579	159.538	166.609
3.07180	112.139	118.481	124.921	131.438	138.037	144.743	151.544	158.439	165.451
3.60302	111.405	117.696	124.082	130.567	137.124	143.784	150.532	157.343	164.298
4.09629	110.788	117.056	123.413	129.852	136.362	142.978	149.703	156.465	163.365
4.86059	110.010	116.214	122.516	128.914	135.374	141.944	148.579	155.303	162.140
5.69740	109.220	115.395	121.653	127.993	134.400	140.922	147.518	154.204	160.987
6.35776	108.686	114.808	121.036	127.335	133.716	140.197	146.746	153.402	160.151

[a]Units: m in mol·kg^{-1}; T in K; Λ in Ω^{-1}cm^{2}mol^{-1}; b in kg^{2}L^{-1}mol^{-1}

Table S3: Data for Density, ρ, Viscosity, η, and Relative Permittivity, ε, of Acetonitrile[S1] as a Function of Temperature, T, used for Evaluating the Conductivity Measurements.[a]

T	ρ	$\eta \cdot 10^3$	ε	T	ρ	$\eta \cdot 10^3$	ε
273.15	0.803574	0.4439	40.11	298.15	0.776669	0.3413	35.96
278.15	0.798246	0.4196	39.24	303.15	0.771208	0.3253	35.19
283.15	0.792892	0.3975	38.39	308.15	0.765719	0.3105	34.43
288.15	0.787511	0.3772	37.56	313.15	0.760203	0.2967	33.96
293.15	0.782103	0.3585	36.76				

[a]Units: T in K; ρ in kg·L^{-1}; η in Pa·s.

Table S4: Density, ρ, Electrical Conductivity, κ, and Dielectric Parameters[a] (Amplitudes, S_1 & S_2, Relaxation Times, τ_1 & τ_2, Cole-Cole Width Parameter, α_1, Infinite-frequency Permittivity, ε_∞, and Value of the Reduced Error Function, χ^2_{r}) as a Function of IL Mole Fraction, x, for [hmim][NTf$_2$] + AN Mixtures at 298.15 K.[b]

x	ρ	κ	S_1	τ_1	α_1	S_2	τ_2	ε_∞	χ^2_{r}
0	0.77650	0				32.63	3.32	3.33	
0.00235	0.78545	0.490	2.36	269	0.46	31.15	3.35	3.51	0.019
0.00481	0.79568	0.891	2.32	278	0.18	30.85	3.40	3.44	0.135
0.00739	0.80363	1.247	3.48	65.0	0.30	29.44	3.38	3.39	0.036
0.01009	0.81384	1.573	4.22	63.4	0.32	28.66	3.42	3.28	0.039
0.01592	0.83232	2.130	4.62	46.4	0.20	26.80	3.55	3.82	0.029
0.02244	0.85383	2.620	5.94	47.3	0.23	25.14	3.65	3.75	0.023
0.03795	0.89825	3.340	8.34	32.5	0.25	20.82	3.91	3.88	0.043
0.05770	0.94604	3.730	9.00	46.6	0.22	18.30	4.56	4.49	0.048
0.08403	0.99912	3.800	12.83	40.5	0.30	13.53	4.85	4.12	0.037
0.1229	1.06081	3.510	13.70	55.9	0.30	10.70	5.91	4.25	0.034
0.1776	1.12519	2.920	14.48	73.6	0.30	7.71	7.02	4.19	0.027
0.2595	1.19200	2.100	13.94	72.5	0.30	4.17	8.06	4.11	0.020
0.3417	1.23760	1.506	14.53	81.7	0.35	1.89	7.15	3.66	0.015
0.4541	1.28051	0.985	13.49	76.0	0.40	0.57	1.41	2.97	0.007
0.5969	1.31740	0.613	11.35	108	0.43	0.94	0.74	2.52	0.003
0.8171	1.35332	0.330	9.91	207	0.50	0.69	0.80	2.53	0.005
1	1.37292	0.218	9.40	233	0.47	0.68	0.80	2.58	

[a] Data for AN from Ref. S2, for [hmim][NTf$_2$] from Ref. S3. [b]Units: ρ in kg·L^{-1}; κ in Ω^{-1}m^{-1}; τ_1 & τ_2 in 10^{-12} s.

Figures

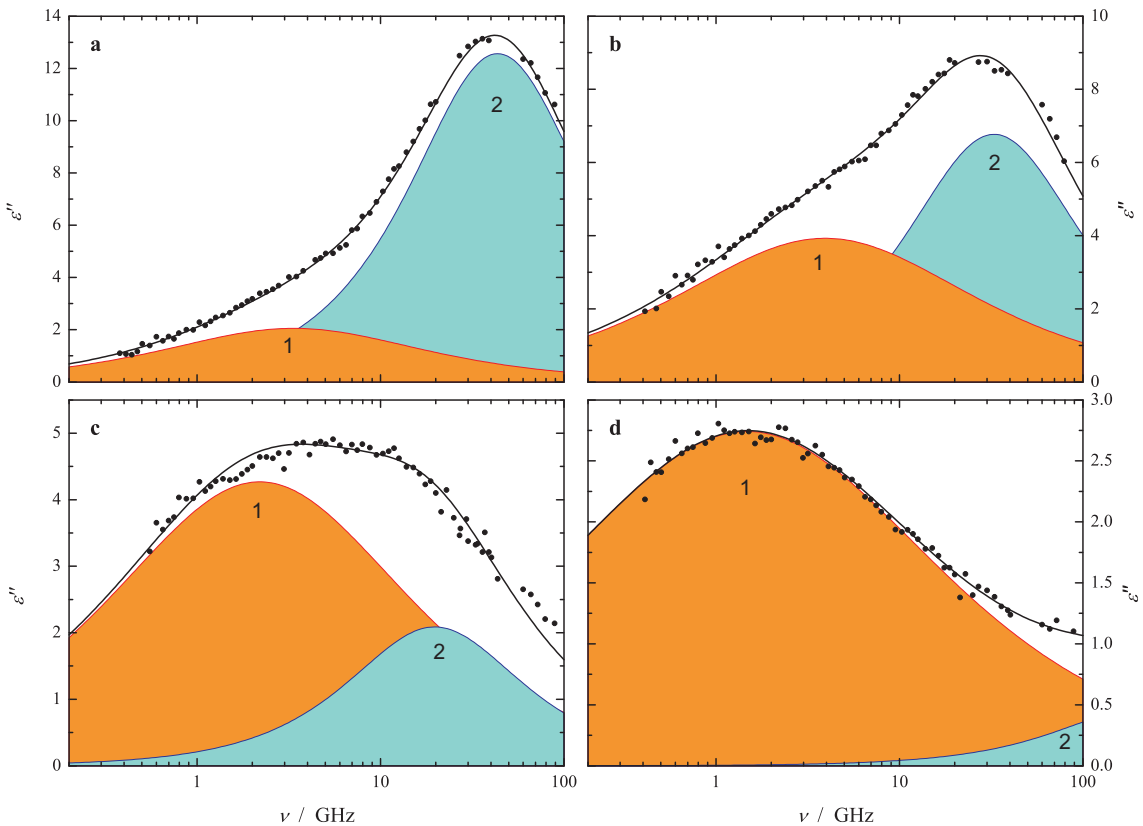

Figure S1: Dielectric loss, $\varepsilon''(\nu)$ (•), of [hmim][BF_4] + AN mixtures at 298.15 K and IL mole fractions, $x = 0.02244$ (a); 0.08403 (b); 0.2595 (c); and 0.5969 (d). Lines indicate the fit with the CC+D model, eq 3 & Table S4, shaded areas show the contributions of the lower-frequency CC mode (1) and the higher-frequency D mode (2).

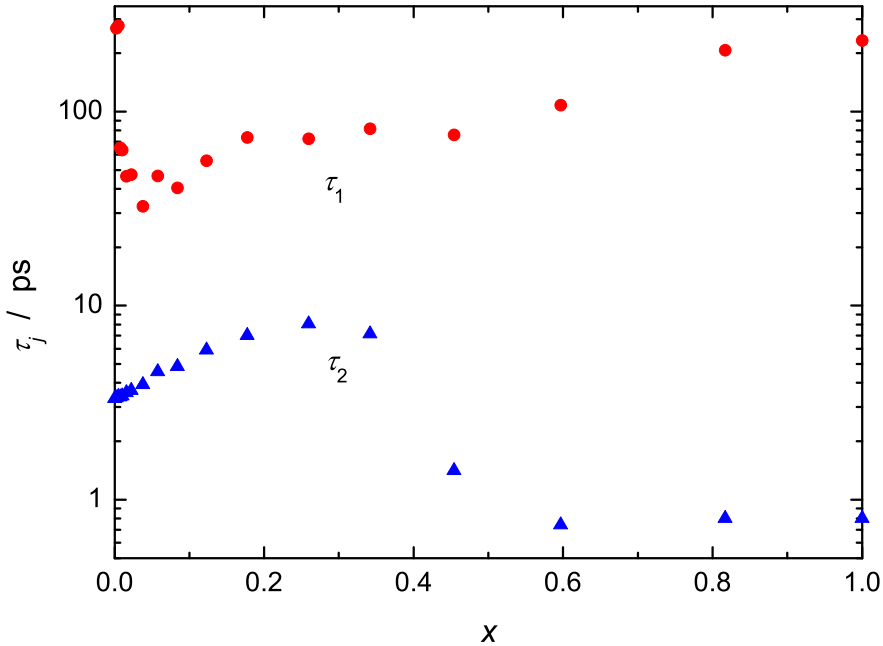

Figure S2: Relaxation times of the lower-frequency CC mode (τ_1) and the higher-frequency D mode (τ_2) as a function of RTIL mole fraction, x, of [hmim][BF_4] + AN mixtures at 298.15 K.

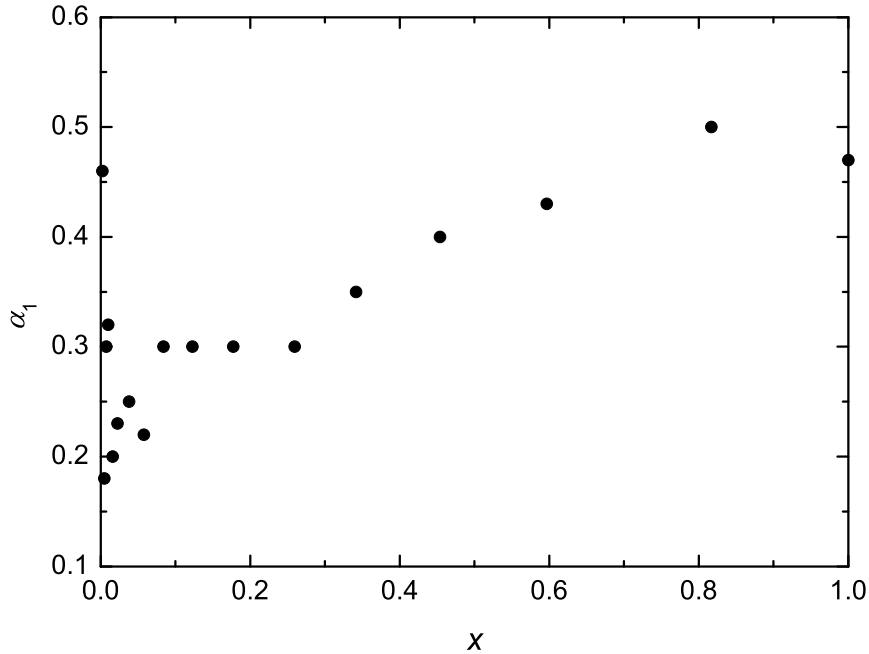

Figure S3: Width parameter, α_1, of the lower-frequency CC mode as a function of RTIL mole fraction, x, of [hmim][BF_4] + AN mixtures at 298.15 K.

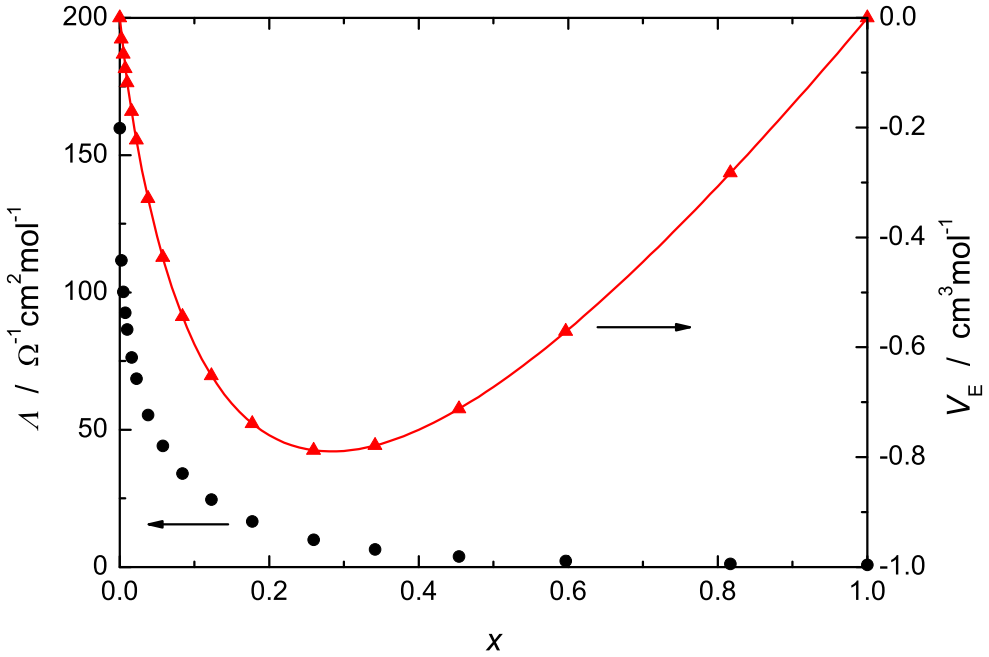

Figure S4: Molar conductivtity, Λ (•), and excess volume, V_{E} (▲), as a function of RTIL mole fraction, x, of [hmim][BF_4] + AN mixtures at 298.15 K.

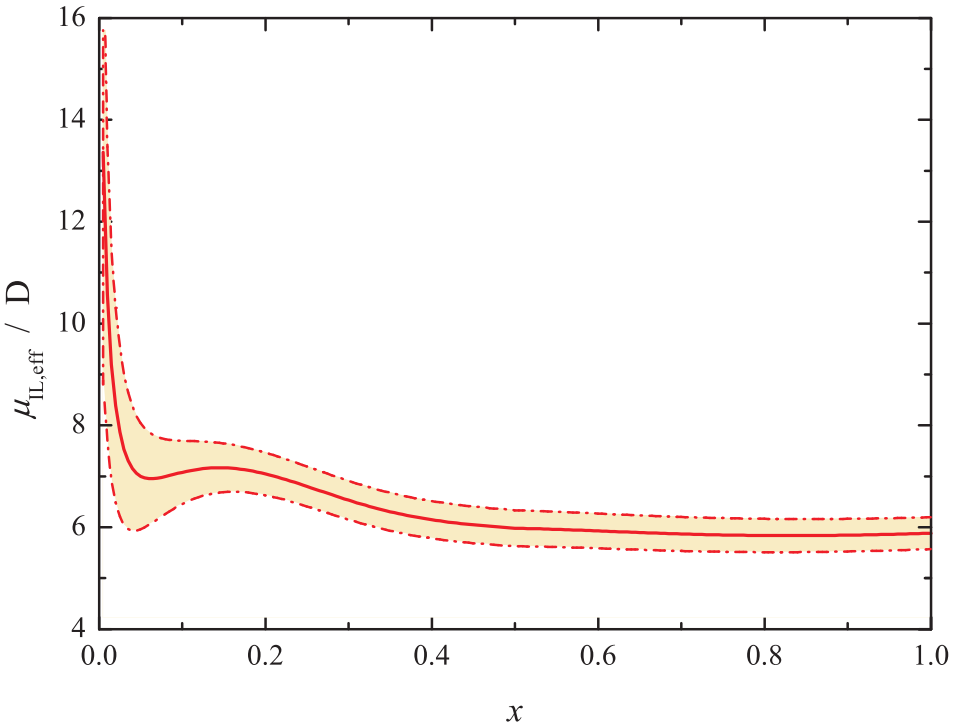

Figure S5: Effective dipole moment of [hmim][BF_4] in mixtures with AN at 298.15 K calculated from the amplitude, S_1, of the CC mode corrected for bound AN (curve 3 of Fig. 3a). Its estimated uncertainty (shaded area) corresponds to the combined standard deviations of the fits to S_1 and S_2.

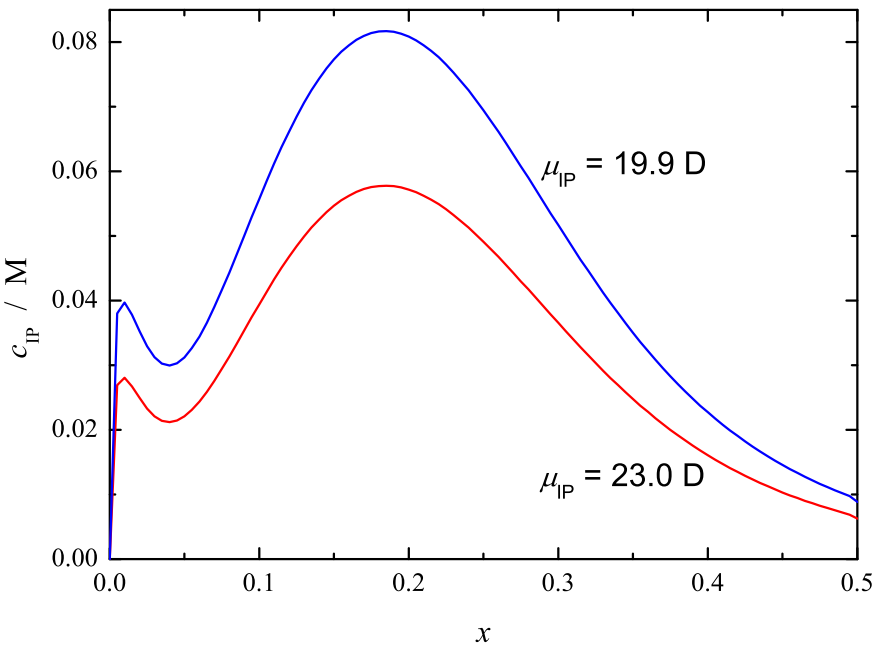

Figure S6: Ion-pair concentrations in [hmim][BF_4] + AN mixtures at 298.15 K calculated with (μ_{IP} = 19.9 and 23.0) D from the amplitude, S_1, of the CC mode corrected for bound AN (curve 3 of Fig. 3a).

References

(S1) Barthel, J.; Neueder, R. In *Chemistry Data Series*; Eckermann, R., Kreysa, G., Eds.; DECHEMA Monographien; DECHEMA: Frankfurt, Germany, 1996; Vol. XII.

(S2) Hunger, J.; Stoppa, A.; Schrödle, S.; Hefter, G.; Buchner, R. *ChemPhysChem* **2009**, *10*, 723–733.

(S3) Stoppa, A.; Hunger, J.; Hefter, G.; Buchner, R. *J. Phys. Chem. B* **2012**, *116*, 7509–7521.