Association of Ionic Liquids in Solution: A Combined Dielectric and Conductivity Study of [bmim][Cl] in Water and Acetonitrile

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Supporting Information
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NB: Quoted equations and references refer to the main paper.

Table S1: Densities, d_s, viscosites, η, and relative permittivities, ε, of acetonitrile (AN) and of water as a function of temperature, T, interpolated from literature data.[a]

T	d_s	η	ε	d_s	η	ε
	AN[b]			water[c]		
273.15	0.803574	0.4439	40.11			
278.15	0.798246	0.4196	39.24	0.999967	1.5192	85.897
283.15	0.792892	0.3975	38.39	0.999702	1.3069	83.945
288.15	0.787511	0.3772	37.56	0.999102	1.1382	82.039
293.15	0.782103	0.3585	36.76	0.998206	1.0020	80.176
298.15	0.776669	0.3413	35.96	0.997048	0.8903	78.358
303.15	0.771208	0.3253	35.19	0.995651	0.7975	76.581
308.15	0.765719	0.3105	34.43	0.994036	0.7195	74.846
313.15	0.760203	0.2967	33.96	0.992219	0.6530	73.157

[a] Units: T in K; d_s in kg·dm^{-3}; η in mPa·s.; [b] ref 35; [c] ref 36.

Table S2: Molar conductivities, Λ, as a function of IL molality, m, and density gradients, b, for solutions of [bmim][Cl] in AN and in Water.[a]

T	273.15	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$10^3 \cdot m$					Λ				
AN ($b = 0.0513$)									
0.4619	125.642	133.255	140.924	148.664	156.542	164.507	172.628	180.838	189.155
0.6981	123.872	131.326	138.841	146.447	154.199	162.039	170.014	178.078	186.215
0.9858	121.926	129.228	136.614	144.105	151.701	159.377	167.204	175.107	183.081
1.2753	120.165	127.335	134.617	141.969	149.433	156.981	164.661	172.421	180.278
1.7295	117.717	124.736	131.851	139.039	146.330	153.710	161.212	168.790	176.440
2.2785	115.161	122.014	128.965	135.993	143.072	150.288	157.626	164.989	172.446
2.9664	112.343	119.027	125.776	132.635	139.575	146.577	153.659	160.874	168.123
3.7219	109.646	116.149	122.751	129.412	136.173	142.974	149.891	156.905	163.932
4.7048	106.560	112.887	119.294	125.774	132.312	138.940	145.647	152.426	159.248
5.7160	103.841	110.019	116.274	122.568	128.945	135.396	141.903	148.503	155.138
water ($b = 0.0125$)									
0.7462		65.084	74.724	84.829	95.320	106.180	117.410	128.951	140.696
1.0540		64.601	74.185	84.201	94.644	105.486	116.665	128.168	139.905
1.3953		64.264	73.794	83.767	94.162	104.940	116.081	127.523	139.141
1.7899		63.887	73.370	83.295	93.646	104.385	115.490	126.918	138.566
2.2107		63.577	73.026	82.899	93.208	103.887	114.941	126.330	137.972
2.6451		63.301	72.703	82.539	92.792	103.439	114.455	125.801	137.326
3.0889		63.105	72.477	82.292	92.518	103.076	114.107	125.421	136.987

[a] Units: m in mol·kg^{-1}; T in K; Λ in Ω^{-1}·cm^2·mol^{-1}; b in kg^2·dm^{-3}·mol^{-1} [see eqn (1)].

Table S3: Fit parameters of eqn (7) assuming the D+CC+D model for the DR spectra of [bmim][Cl] solutions in AN at 25 °C at mole fractions, x, and molar concentrations, c, of the solute. Also included are the experimental densities, ρ, and conductivities, κ.[a]

x	c	ρ	κ	ε	S_1	τ_1	S_2	τ_2	α_2	S_3	τ_3	ε_∞	$\chi^2_r/10^{-4}$
0[b]	0	776.67	0	35.84	-	-	-	-	-	32.4	3.33	3.47	-
0.002633	0.04959	779.97	0.382	36.55	-	-	1.50	50.0[c]	0.32	31.7	3.31	3.36	126
0.005508	0.1033	783.44	0.611	36.99	0.17	141	1.71	62.3	0.05[c]	31.2	3.5[c]	3.90	436
0.01261	0.2335	791.60	0.984	37.97	2.87	71.5	2.77	11.4	0.05[c]	28.7	3.39	3.58	243
0.02572	0.4658	805.63	1.403	39.12	4.19	77.1	4.43	15.7	0.05[c]	26.6	3.51	3.89	220
0.03837	0.6799	818.22	1.652	39.44	5.30	73.1	5.27	15.4	0.05[c]	24.6	3.76	4.31	380
0.05100	0.8843	829.99	1.818	39.45	6.01	76.0	7.60	13.6	0.05[c]	21.9	3.59	3.98	294
0.07585	1.261	850.93	1.981	38.81	6.75	81.2	9.16	14.1	0.05[c]	18.3	3.96	4.65	412

[a] Quantities: static permittivity, ε; relaxation times, τ_j, and amplitudes, S_j, of process j; Cole-Cole shape parameter, α_2, of the second (intermediate-frequency) process; infinite frequency permittivity, ε_∞, and reduced error function of the overall fit, χ^2_r. Units: c in M^{-1}; ρ in $kg \cdot dm^{-3}$; κ in $\Omega^{-1}m^{-1}$; τ_j in 10^{-12} s. [b] DRS parameters taken from ref 53. [c] Parameter fixed during fitting procedure.

Table S4: Fit parameters of eqn (7) assuming the D+CC model for the DR spectra of [bmim]Cl solutions in water at 25 °C at mole fractions, x, and molar concentrations, c, of the solute. Also included are the experimental densities, ρ, and conductivities, κ.[a]

x	c	ρ	κ	ε	S_1	τ_1	S_2	τ_2	α_2	ε_∞	$\chi^2_r/10^{-4}$
0[b]	0	997.05	-	78.33	-	-	72.45	8.32	0	5.87	-
0.0009005	0.0495	997.65	0.459	77.76	0.32	521	71.98	8.47	0.0036	5.46	885
0.001797	0.0980	998.28	0.849	77.36	0.70	328	71.38	8.51	0.0083	5.28	713
0.004466	0.2386	1000.15	1.816	75.45	1.49	166	68.58	8.92	0.0094	5.38	1079
0.008938	0.4618	1003.30	3.06	72.38	1.46	165	66.21	9.56	0.031	4.72	765
0.01311	0.6569	1006.20	3.93	69.61	1.68	155	63.15	10.25	0.038	4.78	941
0.01769	0.8587	1009.38	4.67	66.74	1.66	167	60.30	11.07	0.047	4.79	1181
0.02647	1.2124	1015.29	5.62	61.86	1.66	206	55.31	12.68	0.063	4.90	1148

[a] Quantities: static permittivity, ε; relaxation times, τ_j, and amplitudes, S_j, of process j; Cole-Cole shape parameter, α_2, of the second (higher-frequency) process; infinite frequency permittivity, ε_∞, and reduced error function of the overall fit, χ^2_r. Units: c in M^{-1}; ρ in $kg \cdot dm^{-3}$; κ in $\Omega^{-1}m^{-1}$; τ_j in 10^{-12} s. [b] DRS parameters taken from ref 55.

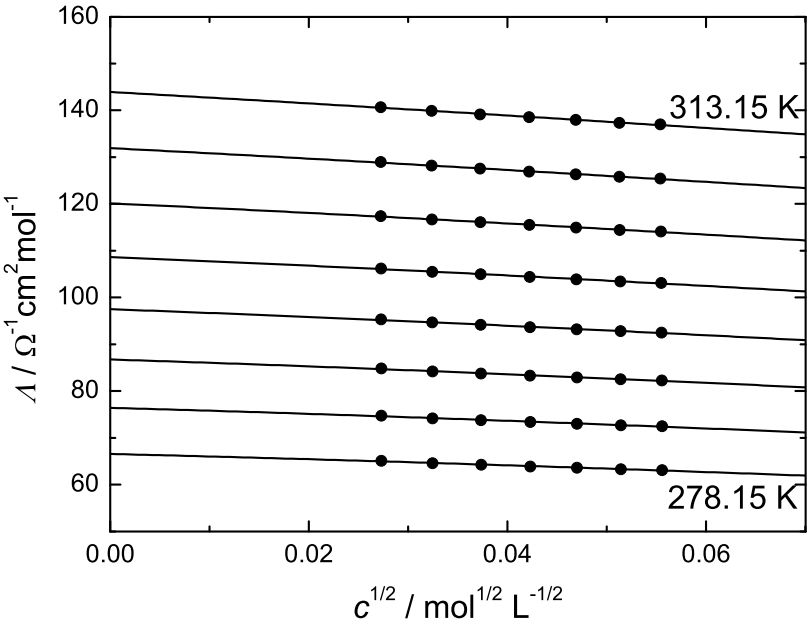

Figure S1: Molar conductivities, Λ (●), of [bmim][Cl] solutions in water from 278.15 K to 313.15 K (in steps of 5 °C) in the concentration range $0.0007 \lesssim c/\mathrm{M} \lesssim 0.003$. Lines show the results of the lcCM calculations.

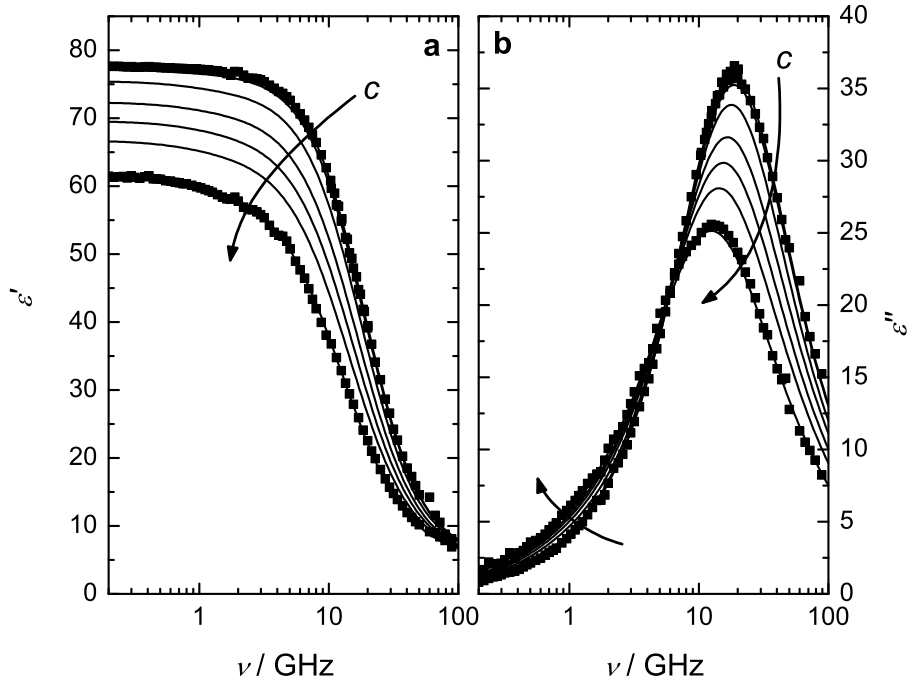

Figure S2: (**a**) Dielectric permittivity, $\varepsilon'(\nu)$, and (**b**) dielectric loss, $\varepsilon''(\nu)$, spectra of [bmim][Cl] + water mixtures at 25 °C. Arrows indicate increasing IL content ($c/\mathrm{M} = 0.0495$, 0.0980, 0.2368, 0.4618, 0.6569, 0.8587, 1.2124).

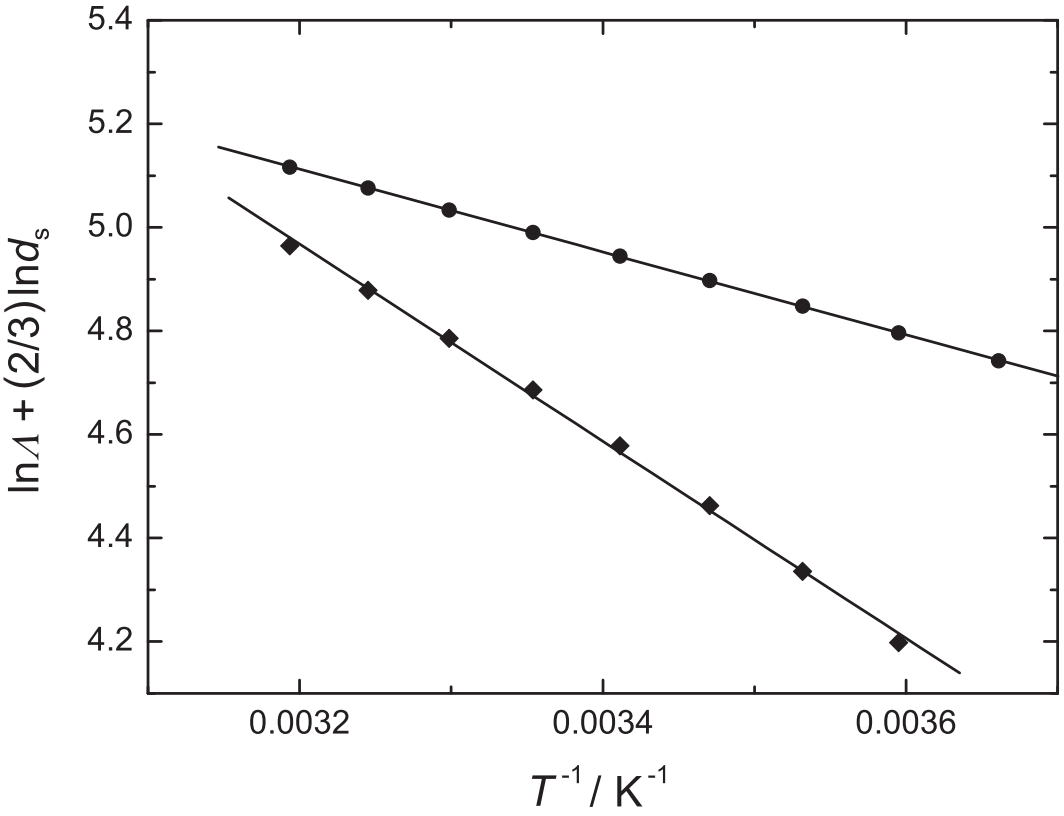

Figure S3: Plot of $\ln\Lambda^{\infty} + (2/3)\ln d_s$ as a function of $1/T$ for [bmim][Cl] in AN (●) and water (⧫).