

Ion Speciation: A Key for the Understanding of the Solution Properties of Ionic Liquid Mixtures

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Electronic Supplementary Information

Table S1. Experimental and predicted activity coefficient of water, γ_w , in aqueous solution of ionic liquids with different alkyl chain length, $[C_nC_1im]Cl$, $n = 1-10$, using COSMO-RS at 298.15 K. The COSMO-RS model uses 100% free cation and anion.

x_{H_2O}	$\gamma_{w,E}$	$\gamma_{w,COSMO-RS}$	ARD
$[C_1C_1im]Cl$			
0.985	0.984	0.991	0.007
0.967	0.969	0.961	0.008
0.946	0.947	0.905	0.042
0.914	0.907	0.806	0.101
$[C_1C_2im]Cl$			
0.988	0.989	0.994	0.005
0.964	0.964	0.956	0.008
0.940	0.931	0.893	0.038
0.909	0.875	0.801	0.074
0.880	0.808	0.713	0.095
0.836	0.707	0.587	0.120
0.774	0.571	0.448	0.123
0.721	0.455	0.362	0.093
0.635	0.349	0.270	0.079
0.582	0.273	0.231	0.042
$[C_1C_4im]Cl$			
0.998	1.002	1.000	0.002
0.989	1.005	0.996	0.009
0.982	0.990	0.988	0.002
0.968	0.976	0.968	0.008
0.954	0.961	0.942	0.019
0.940	0.941	0.912	0.029
0.919	0.913	0.857	0.056
0.904	0.890	0.816	0.074
0.887	0.858	0.769	0.089
0.866	0.808	0.709	0.099
0.821	0.713	0.590	0.123
0.792	0.653	0.525	0.128
0.830	0.738	0.613	0.125
0.761	0.585	0.462	0.123
0.691	0.443	0.358	0.085
0.650	0.376	0.313	0.063
$[C_1C_5im]Cl$			
0.989	0.998	0.996	0.002
0.976	0.986	0.982	0.004
0.962	0.976	0.962	0.014
0.940	0.944	0.919	0.025
0.908	0.897	0.840	0.057
0.879	0.848	0.760	0.088
0.816	0.725	0.595	0.130
0.706	0.517	0.393	0.124
$[C_1C_6im]Cl$			0.000

0.990	1.002	0.997	0.005
0.978	0.991	0.987	0.004
0.963	0.981	0.967	0.014
0.944	0.952	0.934	0.018
0.917	0.916	0.875	0.041
0.883	0.865	0.787	0.078
0.827	0.747	0.639	0.108
0.737	0.597	0.455	0.142
0.555	0.424	0.265	0.159
[C ₁ C ₇ im]Cl			
0.991	0.996	0.998	0.002
0.980	1.001	0.990	0.011
0.964	1.012	0.973	0.039
0.950	1.013	0.951	0.062
0.923	1.002	0.899	0.103
0.898	0.959	0.841	0.118
0.841	0.872	0.692	0.180
0.749	0.665	0.490	0.175
0.494	0.467	0.242	0.225
[C ₁ C ₈ im]Cl			
0.992	0.997	0.998	0.001
0.981	1.004	0.992	0.012
0.968	1.013	0.980	0.033
0.950	1.015	0.958	0.057
0.929	1.013	0.921	0.092
0.895	0.982	0.847	0.135
0.849	0.907	0.729	0.178
[C ₁ C ₁₀ im]Cl			
0.992	0.998	0.999	0.001
0.983	1.005	0.996	0.009
0.971	1.015	0.989	0.026
0.956	1.018	0.976	0.042
0.934	1.018	0.950	0.068

Table S2. Experimental and predicted activity coefficient of water, γ_w , in aqueous solution of ionic liquids with different head group, $[C_4C_1X]Cl$, using COSMO-RS at 298.15 K. The COSMO-RS model uses 100% free cation and anion.

x_{H_2O}	$\gamma_{w,E}$	$\gamma_{w,COSMO-RS}$	ARD
[C₁C₄im]Cl			
0.998	1.002	1.000	0.002
0.989	1.005	0.996	0.009
0.982	0.990	0.988	0.002
0.968	0.976	0.968	0.008
0.954	0.961	0.942	0.019
0.940	0.941	0.912	0.029
0.919	0.913	0.857	0.056
0.904	0.890	0.816	0.074
0.887	0.858	0.769	0.089
0.866	0.808	0.709	0.099
0.821	0.713	0.590	0.123
0.792	0.653	0.525	0.128
0.830	0.738	0.613	0.125
0.761	0.585	0.462	0.123
0.691	0.443	0.358	0.085
0.650	0.376	0.313	0.063
Ortho-[C₄C₁py]Cl			
0.990	0.999	0.996	0.003
0.977	0.991	0.980	0.011
0.961	0.965	0.955	0.010
0.941	0.935	0.910	0.025
0.913	0.867	0.826	0.041
0.877	0.784	0.715	0.069
0.819	0.616	0.553	0.063
0.734	0.405	0.378	0.027
meta[C₄C₁py]Cl			
0.989	0.999	0.996	0.003
0.977	0.992	0.981	0.011
0.961	0.967	0.954	0.013
0.943	0.939	0.915	0.024
0.917	0.892	0.847	0.045
0.883	0.811	0.748	0.063
0.825	0.656	0.588	0.068
0.751	0.456	0.424	0.032
0.621	0.224	0.269	0.045
para[C₄C₁py]Cl			
0.989	0.998	0.996	0.002
0.977	0.990	0.981	0.009
0.960	0.967	0.954	0.013
0.941	0.937	0.915	0.022
0.912	0.883	0.837	0.046

0.876	0.793	0.731	0.062
0.817	0.631	0.565	0.066
0.739	0.426	0.408	0.018
0.678	0.327	0.323	0.004
[C ₄ C ₁ pyrr]Cl			
0.989	0.997	0.996	0.001
0.978	0.989	0.982	0.007
0.960	0.954	0.947	0.007
0.946	0.921	0.912	0.009
0.926	0.857	0.854	0.003
0.898	0.739	0.763	0.024
0.859	0.576	0.630	0.054
0.804	0.392	0.478	0.086
0.755	0.264	0.378	0.114
[C ₄ C ₁ pip]Cl			
0.990	0.999	0.996	0.003
0.978	0.991	0.982	0.009
0.962	0.969	0.954	0.015
0.943	0.932	0.911	0.021
0.920	0.874	0.842	0.032
0.884	0.781	0.724	0.057
0.823	0.573	0.535	0.038
0.747	0.404	0.365	0.039

Table S3. Experimental and predicted activity coefficient of water, γ_w , in aqueous solution of ionic liquids with different anion, $[C_4C_1X]A$, using COSMO-RS at 298.15 K. The COSMO-RS model uses 100% free cation and anion.

x_{H_2O}	$\gamma_{w,E}$	$\gamma_{w,COSMO-RS}$	ARD
$[C_4C_1im][CF_3SO_3]$			
0.993	0.987	1.000	0.013
0.984	0.992	0.998	0.006
0.974	1.000	0.996	0.004
0.960	1.012	0.994	0.018
0.941	1.031	0.993	0.038
0.916	1.051	0.993	0.058
0.871	1.092	1.003	0.089
0.799	1.139	1.033	0.106
0.650	1.181	1.133	0.048
0.406	1.121	1.373	0.252
0.339	1.115	1.457	0.342
0.180	1.098	1.706	0.608
$[C_4C_1im][SCN]$			
0.990	0.987	0.999	0.012
0.978	0.995	0.997	0.002
0.962	1.006	0.993	0.013
0.943	1.017	0.989	0.028
0.916	1.037	0.985	0.052
0.880	1.047	0.984	0.063
0.827	1.051	0.985	0.066
0.781	1.032	0.987	0.045
0.735	0.954	0.988	0.034
0.560	0.740	0.981	0.241
0.351	0.564	0.949	0.385
0.322	0.537	0.943	0.406
$[C_4C_1im][TFA]$			
0.992	0.987	0.999	0.012
0.982	0.989	0.997	0.008
0.970	0.989	0.994	0.005
0.954	0.988	0.987	0.001
0.934	0.992	0.978	0.014
0.905	0.979	0.960	0.019
0.861	0.945	0.924	0.021
0.781	0.837	0.843	0.006
0.778	0.830	0.840	0.010
0.614	0.579	0.670	0.091
0.606	0.566	0.663	0.097
0.553	0.526	0.617	0.091
$[C_4C_1im]Br$			
0.991	0.989	0.997	0.008
0.980	0.992	0.987	0.005

0.965	0.988	0.967	0.021
0.948	0.982	0.936	0.046
0.923	0.967	0.885	0.082
0.890	0.929	0.813	0.116
0.841	0.886	0.717	0.169
0.757	0.756	0.595	0.161
0.590	0.504	0.467	0.037
0.506	0.425	0.432	0.007
[C ₄ C ₁ im][TOS]			
0.994	0.991	0.999	0.008
0.986	0.995	0.996	0.001
0.976	1.000	0.991	0.009
0.963	0.998	0.982	0.016
0.945	1.004	0.964	0.040
0.919	0.983	0.934	0.049
0.875	0.965	0.871	0.094
0.816	0.879	0.789	0.090
0.666	0.660	0.636	0.024
0.589	0.567	0.586	0.019
[C ₁ C ₄ im]Cl			
0.998	1.002	1.000	0.002
0.989	1.005	0.996	0.009
0.982	0.990	0.988	0.002
0.968	0.976	0.968	0.008
0.954	0.961	0.942	0.019
0.940	0.941	0.912	0.029
0.919	0.913	0.857	0.056
0.904	0.890	0.816	0.074
0.887	0.858	0.769	0.089
0.866	0.808	0.709	0.099
0.821	0.713	0.590	0.123
0.792	0.653	0.525	0.128
0.830	0.738	0.613	0.125
0.761	0.585	0.462	0.123
0.691	0.443	0.358	0.085
0.650	0.376	0.313	0.063
[C ₄ C ₁ im][CH ₃ SO ₃]			
0.991	0.984	0.998	0.014
0.981	0.984	0.987	0.003
0.963	0.963	0.960	0.003
0.951	0.950	0.941	0.009
0.931	0.910	0.894	0.016
0.898	0.840	0.818	0.022
0.850	0.736	0.708	0.028
0.767	0.568	0.558	0.010
0.624	0.377	0.405	0.028
0.588	0.325	0.380	0.055
[C ₄ C ₁ im][DMP]			
0.9923	0.984	0.998	0.014

0.9832	0.981	0.993	0.012
0.9604	0.962	0.966	0.004
0.9479	0.938	0.947	0.009
0.91	0.877	0.870	0.007
0.8871	0.809	0.817	0.008
0.8704	0.748	0.773	0.025
0.8411	0.671	0.701	0.030
0.7891	0.578	0.578	0.000
0.7612	0.501	0.519	0.018
0.6926	0.407	0.398	0.009
0.6206	0.293	0.308	0.015
[C ₄ C ₁ im][Ac]			
0.9897	0.981	0.997	0.016
0.9778	0.978	0.989	0.011
0.9651	0.956	0.977	0.021
0.9425	0.915	0.941	0.026
0.9176	0.854	0.893	0.039
0.8813	0.74	0.800	0.060
0.8317	0.616	0.648	0.032
0.7428	0.416	0.391	0.025
0.722	0.339	0.345	0.006

Table S4. Experimental and predicted activity coefficient of water, γ_w , in aqueous solution of ionic liquids [C₄C₁im][CF₃SO₃] using COSMO-RS at 298.15 K with different amount of free ion and ion pair.

x_{H_2O}	$\gamma_{w,E}$	$\gamma_{w,COSMO-RS}$	ARD
Model 1 [C ₄ C ₁ im][CF ₃ SO ₃]: 100% of [C] and [A]; and 10% of [CA]			
0.993	0.987	1.000	0.013
0.984	0.992	0.998	0.006
0.974	1.000	0.996	0.004
0.960	1.012	0.994	0.018
0.941	1.031	0.993	0.038
0.916	1.051	0.993	0.058
0.871	1.092	1.003	0.089
0.799	1.139	1.033	0.106
0.650	1.181	1.133	0.048
0.406	1.121	1.373	0.252
0.339	1.115	1.457	0.342
0.180	1.098	1.706	0.608
Model 2[C ₄ C ₁ im][CF ₃ SO ₃]: 90% of [C] and [A]; and 10% of [CA]			
0.993	0.987	0.998	0.011
0.984	0.992	0.995	0.003
0.974	1.000	0.992	0.008
0.960	1.012	0.991	0.021
0.941	1.031	0.993	0.038
0.916	1.051	1.002	0.049
0.871	1.092	1.027	0.065
0.799	1.139	1.077	0.062
0.650	1.181	1.186	0.005
0.406	1.121	1.359	0.238
0.339	1.115	1.406	0.291
0.180	1.098	1.525	0.427
Model 3[C ₄ C ₁ im][CF ₃ SO ₃]: 50% of [C] and [A]; and 50% of [CA]			
0.993	0.987	0.999	0.012
0.984	0.992	0.997	0.005
0.974	1.000	0.994	0.006
0.960	1.012	0.992	0.020
0.941	1.031	0.992	0.039
0.916	1.051	0.996	0.055
0.871	1.092	1.015	0.077
0.799	1.139	1.058	0.081
0.650	1.181	1.169	0.012
0.406	1.121	1.280	0.159
0.339	1.115	1.244	0.129
0.180	1.098	1.216	0.118

Model 4[C ₄ C ₁ im][CF ₃ SO ₃]: 10% of [C] and [A]; and 90% of [CA]			
0.993	0.987	0.998	0.011
0.984	0.992	0.995	0.003
0.974	1.000	0.992	0.008
0.960	1.012	0.991	0.021
0.941	1.031	0.993	0.038
0.916	1.051	1.001	0.050
0.871	1.092	1.025	0.067
0.799	1.139	1.074	0.065
0.650	1.181	1.184	0.003
0.406	1.121	1.163	0.042
0.339	1.115	1.114	0.001
0.180	1.098	1.041	0.057
Model 4[C ₄ C ₁ im][CF ₃ SO ₃]: 0% of [C] and [A]; and 100% of [CA]			
0.993	0.987	0.989	0.002
0.984	0.992	0.987	0.005
0.974	1.000	0.984	0.016
0.960	1.012	0.982	0.030
0.941	1.031	0.982	0.049
0.916	1.051	0.996	0.055
0.871	1.092	1.005	0.087
0.799	1.139	1.078	0.061
0.650	1.181	1.179	0.002
0.406	1.121	1.180	0.059
0.339	1.115	1.154	0.039
0.180	1.098	1.056	0.042

Table S5. Experimental and predicted activity coefficient of water, γ_w , in aqueous solution of ionic liquids mixtures of ($[[C_4C_1im]Cl + [C_4C_1im][CF_3SO_3]$) using COSMO-RS at 298.15 K. The model assumes all cation and anion are 100% in the aqueous solution.

X_{H_2O}	$X_{[C_4C_1im]Cl}$	$X_{[C_4C_1im][CF_3SO_3]}$	$\gamma_{w,E}$	$\gamma_{w,COSMO-RS}$	ARD
H ₂ O + (0% of [C ₄ C ₁ im]Cl and 100% of [C ₄ mim][CF ₃ SO ₃])					
0.993	0	0.007	0.987	1.000	0.013
0.984	0	0.016	0.992	0.998	0.006
0.974	0	0.026	1.000	0.996	0.004
0.960	0	0.040	1.012	0.994	0.018
0.941	0	0.059	1.031	0.993	0.038
0.916	0	0.084	1.051	0.993	0.058
0.871	0	0.129	1.092	1.003	0.089
0.799	0	0.201	1.139	1.033	0.106
0.650	0	0.350	1.181	1.133	0.048
0.406	0	0.594	1.121	1.373	0.252
0.339	0	0.661	1.115	1.457	0.342
0.180	0	0.820	1.098	1.706	0.608
H ₂ O + (10% of [C ₄ C ₁ im]Cl and 90% of [C ₄ mim][CF ₃ SO ₃])					
0.4355	0.0795	0.4849	1.0378	0.989	0.049
0.5024	0.0701	0.4274	1.0727	0.983	0.089
0.6222	0.0532	0.3244	1.0895	0.973	0.116
0.7220	0.0391	0.2387	1.0704	0.966	0.104
0.8134	0.0262	0.1602	1.0424	0.965	0.077
0.8617	0.0194	0.1187	1.0188	0.968	0.051
0.9369	0.0088	0.0541	0.9968	0.983	0.014
H ₂ O + (25% of [C ₄ C ₁ im]Cl and 75% of [C ₄ mim][CF ₃ SO ₃])					
0.3551	0.2178	0.4270	0.6419	0.613	0.029
0.4264	0.0743	0.4992	0.7574	1.015	0.258
0.5480	0.0585	0.3933	0.8228	0.998	0.175
0.6566	0.0444	0.2988	0.8954	0.983	0.088
0.7624	0.0307	0.2067	0.9377	0.972	0.034
0.8210	0.0231	0.1557	0.9707	0.970	0.001
0.9162	0.0108	0.0728	0.9811	0.979	0.002
H ₂ O + (50% of [C ₄ C ₁ im]Cl and 50% of [C ₄ mim][CF ₃ SO ₃])					
0.4396	0.3390	0.2212	0.4480	0.381	0.067
0.5344	0.2817	0.1838	0.5632	0.438	0.125
0.6002	0.2418	0.1578	0.6646	0.490	0.175
0.6841	0.1911	0.1247	0.7791	0.573	0.207
0.8101	0.1148	0.0749	0.8825	0.744	0.138
0.8978	0.0617	0.0403	0.9522	0.886	0.066
0.9448	0.0333	0.0217	0.9980	0.955	0.043

H ₂ O + (75% of [C ₄ C ₁ im]Cl and 25% of [C ₄ mim][CF ₃ SO ₃])					
0.5025	0.4160	0.0814	0.4317	0.280	0.152
0.5693	0.3602	0.0704	0.4988	0.322	0.177
0.6559	0.2877	0.0563	0.6174	0.398	0.220
0.7897	0.1758	0.0344	0.8141	0.595	0.219
0.8855	0.0956	0.0187	0.9169	0.808	0.109
0.9377	0.0520	0.0101	1.0002	0.923	0.077
H ₂ O + (90% of [C ₄ C ₁ im]Cl and 10% of [C ₄ mim][CF ₃ SO ₃])					
0.6201	0.3553	0.0244	0.3812	0.314	0.067
0.7018	0.2789	0.0191	0.5325	0.402	0.131
0.8226	0.1658	0.0114	0.7539	0.621	0.132
0.9053	0.0885	0.0060	0.9053	0.833	0.072
0.9490	0.0476	0.0032	0.9708	0.937	0.034
H ₂ O + (100% of [C ₄ C ₁ im]Cl and 0% of [C ₄ mim][CF ₃ SO ₃])					
0.998	0.002	0	1.002	1.000	0.002
0.989	0.011	0	1.005	0.996	0.009
0.982	0.019	0	0.990	0.988	0.002
0.968	0.032	0	0.976	0.968	0.008
0.954	0.046	0	0.961	0.942	0.019
0.940	0.060	0	0.941	0.912	0.029
0.919	0.081	0	0.913	0.857	0.056
0.904	0.096	0	0.890	0.816	0.074
0.887	0.113	0	0.858	0.769	0.089
0.866	0.134	0	0.808	0.709	0.099
0.821	0.179	0	0.713	0.590	0.123
0.792	0.208	0	0.653	0.525	0.128
0.830	0.170	0	0.738	0.613	0.125
0.761	0.239	0	0.585	0.462	0.123
0.691	0.309	0	0.443	0.358	0.085
0.650	0.350	0	0.376	0.313	0.063

Table S6. Experimental and predicted activity coefficient of water, γ_w , in aqueous solution of ionic liquids mixtures of ($[[C_4C_1im]Cl + [C_4C_1im][CF_3SO_3]$) using COSMO-RS at 298.15 K with different concentration of ion speciations.

Experimental			COSMO-RS Ion Speciation						$\gamma_{w,E}$	$\gamma_{w,COSMO}$	ARD
X_{H_2O}	$X_{[C_4C_1im]Cl}$	$x_{[C_4C_1im][CF_3SO_3]}$	X_{H_2O}	X_{C-Cl-C}	$X_{[C_4C_1im]^+}$	$X_{[CF_3SO_3]^-}$	x_{CA}	X_{Cl^-}			
H ₂ O + (0% of [C ₄ C ₁ im]Cl and 100% of [C ₄ mim][CF ₃ SO ₃])											
0.993	0	0.007	0.99250	0.00000	0.00037	0.00037	0.00675	0.00000	0.987	0.998	0.011
0.984	0	0.016	0.98400	0.00000	0.00080	0.00080	0.01440	0.00000	0.992	0.995	0.003
0.974	0	0.026	0.97370	0.00000	0.00132	0.00132	0.02367	0.00000	1.000	0.992	0.008
0.960	0	0.040	0.96010	0.00000	0.00200	0.00200	0.03591	0.00000	1.012	0.991	0.021
0.941	0	0.059	0.94070	0.00000	0.00297	0.00297	0.05337	0.00000	1.031	0.993	0.038
0.916	0	0.084	0.91640	0.00000	0.00418	0.00418	0.07524	0.00000	1.051	1.001	0.050
0.871	0	0.129	0.87070	0.00000	0.00647	0.00647	0.11637	0.00000	1.092	1.025	0.067
0.799	0	0.201	0.79880	0.00000	0.01006	0.01006	0.18108	0.00000	1.139	1.074	0.065
0.650	0	0.350	0.65010	0.00000	0.01750	0.01750	0.31491	0.00000	1.181	1.184	0.003
0.406	0	0.594	0.40590	0.00000	0.02971	0.02971	0.53469	0.00000	1.121	1.163	0.042
0.339	0	0.661	0.33890	0.00000	0.03306	0.03306	0.59499	0.00000	1.115	1.114	0.001
0.180	0	0.820	0.18030	0.00000	0.04099	0.04099	0.73773	0.00000	1.098	1.041	0.057
H ₂ O + (10% of [C ₄ C ₁ im]Cl and 90% of [C ₄ mim][CF ₃ SO ₃])											
0.4355	0.0795	0.4849	0.43550	0.05645	0.02305	0.05645	0.42845	0.02305	1.0378	1.038	0.000
0.5024	0.0701	0.4274	0.50240	0.04976	0.02034	0.04976	0.37764	0.02034	1.0727	1.026	0.047
0.6222	0.0532	0.3244	0.62220	0.03778	0.01542	0.03778	0.28662	0.01542	1.0895	1.006	0.084
0.7220	0.0391	0.2387	0.72200	0.02780	0.01130	0.02780	0.21090	0.01130	1.0704	0.990	0.080
0.8134	0.0262	0.1602	0.81340	0.01866	0.00754	0.01866	0.14154	0.00754	1.0424	0.981	0.061
0.8617	0.0194	0.1187	0.86170	0.01383	0.00557	0.01383	0.10487	0.00557	1.0188	0.980	0.039
0.9369	0.0088	0.0541	0.93690	0.00631	0.00249	0.00631	0.04779	0.00249	0.9968	0.988	0.008

H ₂ O + (25% of [C ₄ C ₁ im]Cl and 75% of [C ₄ mim][CF ₃ SO ₃])											
0.3551	0.2178	0.4270	0.35510	0.21780	0.00010	0.21780	0.20920	0.00000	0.6419	0.656	0.014
0.4264	0.0743	0.4992	0.42640	0.05736	0.01694	0.05736	0.44184	0.01694	0.7574	1.065	0.308
0.5480	0.0585	0.3933	0.54800	0.04520	0.01330	0.04520	0.34810	0.01330	0.8228	1.037	0.214
0.6566	0.0444	0.2988	0.65660	0.03434	0.01006	0.03434	0.26446	0.01006	0.8954	1.013	0.118
0.7624	0.0307	0.2067	0.76240	0.02376	0.00694	0.02376	0.18294	0.00694	0.9377	0.993	0.055
0.8210	0.0231	0.1557	0.82100	0.01790	0.00520	0.01790	0.13780	0.00520	0.9707	0.985	0.015
0.9162	0.0108	0.0728	0.91620	0.00838	0.00242	0.00838	0.06442	0.00242	0.9811	0.986	0.005
H ₂ O + (50% of [C ₄ C ₁ im]Cl and 50% of [C ₄ mim][CF ₃ SO ₃])											
0.4396	0.3390	0.2212	0.43960	0.05604	0.28296	0.05604	0.16516	0.28296	0.4480	0.403	0.045
0.5344	0.2817	0.1838	0.53440	0.04656	0.23514	0.04656	0.13724	0.23514	0.5632	0.457	0.107
0.6002	0.2418	0.1578	0.60020	0.03998	0.20182	0.03998	0.11782	0.20182	0.6646	0.505	0.159
0.6841	0.1911	0.1247	0.68410	0.03159	0.15951	0.03159	0.09311	0.15951	0.7791	0.585	0.194
0.8101	0.1148	0.0749	0.81010	0.01899	0.09581	0.01899	0.05591	0.09581	0.8825	0.752	0.131
0.8978	0.0617	0.0403	0.89780	0.01022	0.05148	0.01022	0.03008	0.05148	0.9522	0.891	0.062
0.9448	0.0333	0.0217	0.94480	0.00552	0.02778	0.00552	0.01618	0.02778	0.9980	0.957	0.041
H ₂ O + (75% of [C ₄ C ₁ im]Cl and 25% of [C ₄ mim][CF ₃ SO ₃])											
0.5025	0.4160	0.0814	0.50250	0.04975	0.36625	0.04975	0.03165	0.36625	0.4317	0.288	0.143
0.5693	0.3602	0.0704	0.56930	0.04307	0.31713	0.04307	0.02733	0.31713	0.4988	0.329	0.170
0.6559	0.2877	0.0563	0.65590	0.03441	0.25329	0.03441	0.02189	0.25329	0.6174	0.403	0.214
0.7897	0.1758	0.0344	0.78970	0.02103	0.15477	0.02103	0.01337	0.15477	0.8141	0.599	0.215
0.8855	0.0956	0.0187	0.88550	0.01145	0.08415	0.01145	0.00725	0.08415	0.9169	0.810	0.107
0.9377	0.0520	0.0101	0.93770	0.00623	0.04577	0.00623	0.00387	0.04577	1.0002	0.924	0.076
H ₂ O + (90% of [C ₄ C ₁ im]Cl and 10% of [C ₄ mim][CF ₃ SO ₃])											
0.6201	0.3553	0.0244	0.62010	0.03799	0.31731	0.02440	0.00000	0.33090	0.3812	0.317	0.064
0.7018	0.2789	0.0191	0.70180	0.02982	0.24908	0.01910	0.00000	0.25980	0.5325	0.403	0.129
0.8226	0.1658	0.0114	0.82260	0.01774	0.14806	0.01140	0.00000	0.15440	0.7539	0.623	0.131
0.9053	0.0885	0.0060	0.90530	0.00947	0.07903	0.00600	0.00000	0.08250	0.9053	0.834	0.071

0.9490	0.0476	0.0032	0.94900	0.00510	0.04250	0.00320	0.00000	0.04440	0.9708	0.937	0.034
H ₂ O + (100% of [C ₄ C ₁ im]Cl and 0% of [C ₄ mim][CF ₃ SO ₃])											
0.998	0.002	0	0.99800	0.00000	0.00100	0.00000	0.00000	0.00100	1.002	2.724	1.722
0.989	0.011	0	0.98940	0.00000	0.00530	0.00000	0.00000	0.00530	1.005	2.732	1.727
0.982	0.019	0	0.98150	0.00000	0.00925	0.00000	0.00000	0.00925	0.990	2.691	1.701
0.968	0.032	0	0.96770	0.00000	0.01615	0.00000	0.00000	0.01615	0.976	2.654	1.678
0.954	0.046	0	0.95370	0.00000	0.02315	0.00000	0.00000	0.02315	0.961	2.614	1.653
0.940	0.060	0	0.94030	0.00000	0.02985	0.00000	0.00000	0.02985	0.941	2.563	1.622
0.919	0.081	0	0.91900	0.00000	0.04050	0.00000	0.00000	0.04050	0.913	2.492	1.579
0.904	0.096	0	0.90370	0.00000	0.04815	0.00000	0.00000	0.04815	0.890	2.435	1.545
0.887	0.113	0	0.88720	0.00000	0.05640	0.00000	0.00000	0.05640	0.858	2.358	1.500
0.866	0.134	0	0.86610	0.00000	0.06695	0.00000	0.00000	0.06695	0.808	2.243	1.435
0.821	0.179	0	0.82070	0.00000	0.08965	0.00000	0.00000	0.08965	0.713	2.040	1.327
0.792	0.208	0	0.79230	0.00000	0.10385	0.00000	0.00000	0.10385	0.653	1.921	1.268
0.830	0.170	0	0.83010	0.00000	0.08495	0.00000	0.00000	0.08495	0.738	2.092	1.354
0.761	0.239	0	0.76070	0.00000	0.11965	0.00000	0.00000	0.11965	0.585	1.795	1.210
0.691	0.309	0	0.69080	0.00000	0.15460	0.00000	0.00000	0.15460	0.443	1.557	1.114
0.650	0.350	0	0.64980	0.00000	0.17510	0.00000	0.00000	0.17510	0.376	1.456	1.080

Table S7. Interaction energy of pure water, cation and anion of ionic liquids determined using COSMO-RS at 298.15

Compound	H _{int}	H _{MF}	H _{HB}	H _{vdW}
	kJ·mol ⁻¹			
H ₂ O	-23.77	1.22	-25.91	-3.86
Ionic liquid as cation and anion				
1-butyl-3-methylimidazolium chloride, [C ₄ C ₁ im]Cl				
[C ₄ C ₁ im] cation	-17.61	40.90	-14.75	-44.87
Cl anion	-11.80	15.49	-14.73	-12.56
1-butyl-2-methylpyridinium chloride, o-[C ₄ C ₁ py]Cl				
o-[C ₄ C ₁ py] cation	-12.20	44.22	-9.86	-46.87
Cl anion	-5.08	17.36	-9.86	-12.57
1-butyl-3-methylpyridinium chloride, m-[C ₄ C ₁ py]Cl				
m-[C ₄ C ₁ py] cation	-16.81	42.35	-11.94	-47.51
Cl anion	-7.52	16.96	-11.92	-12.57
1-butyl-4-methylpyridinium chloride, p-[C ₄ C ₁ py]Cl				
p-[C ₄ C ₁ py] cation	-17.34	42.06	-11.82	-47.81
Cl anion	-7.38	17.01	-11.82	-12.57
1-butyl-1-methylpiperidinium chloride, p-[C ₄ C ₁ py]Cl				
[C ₄ C ₁ pip] cation	-7.06	47.50	-6.85	-47.66
Cl anion	-0.35	19.03	-6.85	-12.52
1-butyl-1-methylpyrrolidinium chloride, p-[C ₄ C ₁ py]Cl				
[C ₄ C ₁ pyrr] cation	-2.83	48.06	-6.94	-45.18
Cl anion	-1.01	18.44	-6.92	-12.52
1,3-dimethylimidazolium chloride, [C ₁ C ₁ im]Cl				
[C ₁ C ₁ im] cation	-0.81	47.05	-15.82	-32.79
Cl anion	-14.54	13.83	-15.82	-12.56
1-ethyl-3-methylimidazolium chloride, [C ₂ C ₁ im]Cl				
[C ₂ C ₁ im] cation	-6.00	44.60	-15.18	-36.51
Cl anion	-13.00	14.69	-15.14	-12.55
1-butyl-3-methylimidazolium chloride, [C ₄ C ₁ im]Cl				
[C ₄ C ₁ im] cation	-17.61	40.90	-14.75	-44.87
Cl anion	-11.80	15.49	-14.73	-12.56
1-pentyl-3-methylimidazolium chloride, [C ₅ C ₁ im]Cl				
[C ₅ C ₁ im] cation	-22.28	39.78	-14.60	-48.93
Cl anion	-11.47	15.69	-14.61	-12.56
1-hexyl-3-methylimidazolium chloride, [C ₆ C ₁ im]Cl				
[C ₆ C ₁ im] cation	-26.95	39.15	-14.43	-53.01
Cl anion	-11.04	15.95	-14.44	-12.56
1-heptyl-3-methylimidazolium chloride, [C ₇ C ₁ im]Cl				
[C ₇ C ₁ im] cation	-31.65	38.54	-14.37	-57.22
Cl anion	-10.77	16.16	-14.38	-12.56
1-octyl-3-methylimidazolium chloride, [C ₈ C ₁ im]Cl				
[C ₈ C ₁ im] cation	-36.64	38.10	-14.40	-61.62
Cl anion	-10.57	16.38	-14.40	-12.56

1-decyl-3-methylimidazolium chloride, [C ₁₀ C ₁ im]Cl				
[C ₁₀ C ₁ im] cation	-45.70	37.79	-14.16	-70.46
Cl anion	-9.83	16.88	-14.16	-12.56
1-butyl-3-methylimidazolium trifloromethanesulfonate, [C ₄ C ₁ im][CF ₃ SO ₃]				
[C ₄ C ₁ im] cation	-23.03	20.57	-6.87	-38.20
[CF ₃ SO ₃] anion	-13.36	9.95	-6.86	-21.22
1-butyl-3-methylimidazolium thiocyanate, [C ₄ C ₁ im][SCN]				
[C ₄ C ₁ im] cation	-25.27	25.52	-8.28	-43.91
[SCN] anion	-19.67	7.64	-8.27	-19.04
1-butyl-3-methylimidazolium trifluoroacetate, [C ₄ C ₁ im][TFA]				
[C ₄ C ₁ im] cation	-24.60	23.85	-11.38	-38.40
[TFA] anion	-14.06	10.36	-11.37	-17.83
1-butyl-3-methylimidazolium bromide, [C ₄ C ₁ im]Br				
[C ₄ C ₁ im] cation	-19.18	37.03	-11.79	-45.61
Br anion	-13.42	12.95	-11.78	-14.60
1-butyl-3-methylimidazolium toluene-p-sulfonate, [C ₄ C ₁ im][TOS]				
[C ₄ C ₁ im] cation	-26.82	24.94	-11.48	-41.57
[TOS] anion	-28.01	21.03	-11.48	-37.52
1-butyl-3-methylimidazolium chloride, [C ₄ C ₁ im]Cl				
[C ₄ C ₁ im] cation	-17.61	40.90	-14.75	-44.87
Cl anion	-11.80	15.49	-14.73	-12.56
1-butyl-3-methylimidazolium methanesulfonate, [C ₄ C ₁ im][CH ₃ SO ₃]				
[C ₄ C ₁ im] cation	-22.21	31.18	-13.30	-41.29
[CH ₃ SO ₃] anion	-12.11	16.99	-13.40	-20.47
1-butyl-3-methylimidazolium dimethylphosphate, [C ₄ C ₁ im][DMP]				
[C ₄ C ₁ im] cation	-26.21	29.73	-15.69	-41.43
[DMP] anion	-17.71	19.88	-15.69	-27.77
1-butyl-3-methylimidazolium acetate, [C ₄ C ₁ im][OAc]				
[C ₄ C ₁ im] cation	-25.27	35.48	-20.10	-41.75
[OAc] anion	-15.67	17.13	-20.08	-17.49

Table S8. Excess energy at equimolar of water and ionic liquids of each component determined using COSMO-RS at 298.15

Compound	H _{int}	H _{MF}	H _{HB}	H _{vdW}
	kJ·mol ⁻¹			
1-butyl-3-methylimidazolium chloride, [C ₄ C ₁ im]Cl				
[C ₄ C ₁ im] cation	-0.40	-1.07	0.27	0.38
Cl anion	-7.38	-0.81	-6.59	0.02
H ₂ O	2.47	0.73	2.37	-0.63
1-butyl-2-methylpyridinium chloride, o-[C ₄ C ₁ py]Cl				
o-[C ₄ C ₁ py] cation	-0.50	-1.13	0.24	0.39
Cl anion	-7.78	-0.92	-6.88	0.02
H ₂ O	2.68	0.78	2.52	-0.63
1-butyl-3-methylpyridinium chloride, m-[C ₄ C ₁ py]Cl				
m-[C ₄ C ₁ py] cation	-0.46	-1.10	0.24	0.39
Cl anion	-7.70	-0.93	-6.79	0.02
H ₂ O	2.59	0.76	2.45	-0.63
1-butyl-4-methylpyridinium chloride, p-[C ₄ C ₁ py]Cl				
p-[C ₄ C ₁ py] cation	-0.46	-1.09	0.24	0.39
Cl anion	-7.73	-0.94	-6.80	0.02
H ₂ O	2.59	0.77	2.45	-0.63
1-butyl-1-methylpiperidinium chloride, p-[C ₄ C ₁ py]Cl				
[C ₄ C ₁ pip] cation	-0.68	-1.26	0.19	0.38
Cl anion	-8.12	-1.03	-7.10	0.01
H ₂ O	2.84	0.82	2.64	-0.62
1-butyl-1-methylpyrrolidinium chloride, p-[C ₄ C ₁ py]Cl				
[C ₄ C ₁ pyrr] cation	-0.69	-1.28	0.20	0.38
Cl anion	-8.02	-0.97	-7.07	0.01
H ₂ O	2.83	0.81	2.64	-0.62
1,3-dimethylimidazolium chloride, [C ₁ C ₁ im]Cl				
[C ₁ C ₁ im] cation	-0.78	-1.48	0.31	0.40
Cl anion	-7.06	-0.64	-6.44	0.02
H ₂ O	2.47	0.81	2.29	-0.62
1-ethyl-3-methylimidazolium chloride, [C ₂ C ₁ im]Cl				
[C ₂ C ₁ im] cation	-0.59	-1.29	0.29	0.39
Cl anion	-7.25	-0.73	-6.54	0.02
H ₂ O	2.46	0.77	2.31	-0.62
1-butyl-3-methylimidazolium chloride, [C ₄ C ₁ im]Cl				
[C ₄ C ₁ im] cation	-0.40	-1.07	0.27	0.38
Cl anion	-7.38	-0.81	-6.59	0.02
H ₂ O	2.47	0.73	2.37	-0.63
1-pentyl-3-methylimidazolium chloride, [C ₅ C ₁ im]Cl				
[C ₅ C ₁ im] cation	-0.33	-1.00	0.27	0.38
Cl anion	-7.41	-0.83	-6.60	0.02
H ₂ O	2.48	0.72	2.39	-0.63
1-hexyl-3-methylimidazolium chloride, [C ₆ C ₁ im]Cl				
[C ₆ C ₁ im] cation	-0.30	-0.95	0.27	0.38
Cl anion	-7.45	-0.86	-6.61	0.02
H ₂ O	2.51	0.71	2.42	-0.63

1-heptyl-3-methylimidazolium chloride, [C ₇ C ₁ im]Cl				
[C ₇ C ₁ im] cation	-0.25	-0.91	0.26	0.38
Cl anion	-7.47	-0.88	-6.61	0.02
H ₂ O	2.53	0.72	2.44	-0.63
1-octyl-3-methylimidazolium chloride, [C ₈ C ₁ im]Cl				
[C ₈ C ₁ im] cation	-0.22	-0.87	0.26	0.38
Cl anion	-7.50	-0.90	-6.61	0.02
H ₂ O	2.55	0.72	2.46	-0.63
1-decyl-3-methylimidazolium chloride, [C ₁₀ C ₁ im]Cl				
[C ₁₀ C ₁ im] cation	-0.17	-0.82	0.26	0.38
Cl anion	-7.57	-0.95	-6.63	0.02
H ₂ O	2.60	0.74	2.50	-0.63
1-butyl-3-methylimidazolium trifloromethanesulfonate, [C ₄ C ₁ im][CF ₃ SO ₃]				
[C ₄ C ₁ im] cation	-0.19	-0.11	-0.11	0.03
[CF ₃ SO ₃] anion	-2.94	-0.30	-2.68	0.05
H ₂ O	3.30	0.10	3.48	-0.28
1-butyl-3-methylimidazolium thiocyanate, [C ₄ C ₁ im][SCN]				
[C ₄ C ₁ im] cation	-0.05	-0.33	0.15	0.13
[SCN] anion	-4.14	-0.36	-3.92	0.14
H ₂ O	2.53	0.20	2.60	-0.27
1-butyl-3-methylimidazolium trifluoroacetate, [C ₄ C ₁ im][TFA]				
[C ₄ C ₁ im] cation	0.00	-0.41	0.36	0.03
[TFA] anion	-6.01	-0.50	-5.54	0.03
H ₂ O	2.07	0.33	2.04	-0.30
1-butyl-3-methylimidazolium bromide, [C ₄ C ₁ im]Br				
[C ₄ C ₁ im] cation	-0.24	-0.74	0.08	0.41
Br anion	-5.39	-0.63	-4.89	0.13
H ₂ O	3.06	0.44	3.16	-0.55
1-butyl-3-methylimidazolium toluene-p-sulfonate, [C ₄ C ₁ im][TOS]				
[C ₄ C ₁ im] cation	-0.10	-0.32	0.15	0.06
[TOS] anion	-6.02	-0.70	-5.41	0.09
H ₂ O	2.85	0.34	2.84	-0.33
1-butyl-3-methylimidazolium chloride, [C ₄ C ₁ im]Cl				
[C ₄ C ₁ im] cation	-0.40	-1.07	0.27	0.38
Cl anion	-7.38	-0.81	-6.59	0.02
H ₂ O	2.47	0.73	2.37	-0.63
1-butyl-3-methylimidazolium methanesulfonate, [C ₄ C ₁ im][CH ₃ SO ₃]				
[C ₄ C ₁ im] cation	-0.22	-0.52	0.21	0.08
[CH ₃ SO ₃] anion	-6.82	-0.72	-6.16	0.06
H ₂ O	2.58	0.40	2.50	-0.32
1-butyl-3-methylimidazolium dimethylphosphate, [C ₄ C ₁ im][DMP]				
[C ₄ C ₁ im] cation	-0.11	-0.70	0.51	0.07
[DMP] anion	-8.71	-0.88	-7.90	0.08
H ₂ O	1.49	0.62	1.19	-0.33
1-butyl-3-methylimidazolium acetate, [C ₄ C ₁ im][OAc]				
[C ₄ C ₁ im] cation	-0.09	-1.34	1.13	0.09
[OAc] anion	-11.15	-0.89	-10.31	0.05
H ₂ O	-0.53	1.10	-1.30	-0.34

Table S9. Activity coefficient of ion speciation in aqueous solution at infinite dilution determined using COSMO-RS at 298.15

Ion speciation	$\ln y_{w,\text{COSMO-RS}}$	$y_{w,\text{COSMO-RS}}$
$[(\text{C}_4\text{C}_1\text{im})_2\text{Cl}]^{+\text{a}}$	-0.152	0.858988
$[(\text{C}_4\text{C}_1\text{im})_2\text{Cl}]^{+\text{b}}$	0.098	1.102963
$[(\text{C}_4\text{C}_1\text{im})_2\text{CF}_3\text{SO}_3]^{+\text{b}}$	0.000278	1.000278
$[(\text{C}_4\text{C}_1\text{im})_3(\text{CF}_3\text{SO}_3)_2]^{+\text{b}}$	0.00000138	1.000001
$[(\text{C}_4\text{C}_1\text{im})_4(\text{CF}_3\text{SO}_3)_3]^{+\text{b}}$	2.6E-8	1

^aDetermined as $[\text{CF}_3\text{SO}_3]$ -based salt.

^bDetermined as Cl-based salt